

INTEGRATED SYSTEM FOR SIMULTANEOUS REMOVAL OF NITROGEN AND PHOSPHORUS BY *ULVA LACTUCA* AND ITS SUBSEQUENT UTILIZATION FOR BIOGAS PRODUCTION

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ABSTRACT: *Biogas is a combustible mixture of gases produced by microorganisms when livestock manure and other biological wastes are allowed to ferment in the absence of air in closed containers or reactor. This process design proposes an integrated biogas production system that aims to remove nitrogen and phosphorus from polluted seawater using U. lactuca and consequently utilize this as a feedstock for biogas production. Anaerobic digestion is done in the process which accomplished in three stages: (1) hydrolysis of insoluble polymers, (2) fermentation of monomeric breakdown products and (3) fermentation of acetate and hydrogen from volatile fatty acids and (4) generation of methane. The basis of the design is 1,000 metric tons of purified biogas per year which is intended for kitchen stove application. It can promote utilization of endemic U. lactuca for seawater treatment and at the same time provide livelihood to communities and save the aquatic environment from pollution. In addition, utilizing purified biogas as an additional source of fuel can save the dwindling natural gas and oil reserves in the world. This purified biogas can be an alternative to the conventional LPG (liquefied petroleum gas) used for kitchen stoves since their energy value and price are comparable.*

KEYWORDS: Anaerobic Digestion, Biogas, Microalgae, *U. Lactuca*, Philippines

INTRODUCTION

It has been the usual practice for fish farmers, and local residents to discharge their wastewaters without treatment. They just neglect the possible effect of such practice in the environment specifically to the marine life living in the adjacent waterways or body of water. Polluted fishpond effluent and human wastes generally result in elevated concentrations of nutrients (nitrogen and phosphorus), suspended solids, bacteria, and phytoplankton compared with the influent water. One potential and cost-effective method of effluent treatment is the use of ponds or raceways stocked with macroalgae that act as natural bio-filters by removing nitrogen and phosphorus. In addition to improving effluent water quality prior to discharge, the use of biological filters provides a method for capturing otherwise wasted nutrients [Jones, *et al.*, 2002].

Macroalgae ('seaweeds') are an ancient class of large multi-cellular plants that resemble vascular plants but lack the complex array of tissues used for reproduction and water transport. They belong to the lower plants, meaning that they do not have roots, stems, and leaves. Instead, they are composed of a *thallus* (leaf-like), sometimes a stem, and a foot. They are important elements of shallow coastal waterways and are found in red (*Rhodophyta*), green (*Chlorophyta*) and brown (*Phaeophyta*) divisions [Trono, 1997].

Ulva spp. is common in the intertidal zones of the Philippines. In Mactan Island (Cebu), central Philippines, at least two species constitute the *Ulva* population, either as free-living or attached form. *Ulva lactuca* mainly consists of free-living population while *Ulva reticulata* consists mainly of attached population. 'Green tide' caused by *U. lactuca* occur almost regularly in the northern part of Mactan Island. *Ulva reticulata*, although was less abundant in the rocky tidal zone at most times had caused green tide located near the Mactan Bridge around February-March [Largo, *et al.*, 2004].

Aside from using this macroalgae in nutrient removal, this can also be utilized subsequently for biogas production by anaerobic digestion. Biogas is a combustible mixture of gases produced by microorganisms when livestock manure and other biological wastes are allowed to ferment in the absence of air in closed containers or reactor. The major constituents of biogas are methane (CH₄, 60% - 70% by volume) and carbon dioxide (CO₂, about 30 - 40% by volume); but small amounts of water vapor, hydrogen sulfide (H₂S) are also present [Droste, 1997].

The primary domestic uses of biogas are cooking and lighting. Biogas can also be used as a fuel in stationary and mobile engines, to supply motive power, pump water, drive machinery, or generate electricity. When upgraded to natural gas quality, biogas can be used in the same vehicles that use natural gas (NGVs) [Vijay *et al.*, 2006].

Objectives

This project aims to design an integrated system for the simultaneous removal of nutrients by macroalgae and subsequent utilization for biogas production in polluted seawater. This includes a design process that has high efficiency or yield, economical, environmentally safe, and could provide a renewable and greenhouse emission-free fuel.

Design Scope

This is limited only to a pilot-scale production of biogas from macroalgae (e.g. *Ulva lactuca*). Although, plenty of biogas plants have been put up worldwide, a pilot-scale is desirable considering that new feedstock is utilized for the process. The use of macroalgae instead of cattle dung and other animal waste also makes this process unique from recent and previous processes. Upstream and downstream stages are described in detail including design specifications of the pieces of process and auxiliary equipment. Downstream processes are based on the production of biogas limited only for kitchen stove use. Economic evaluation determines the feasibility of the proposed process.

Conceptual Framework

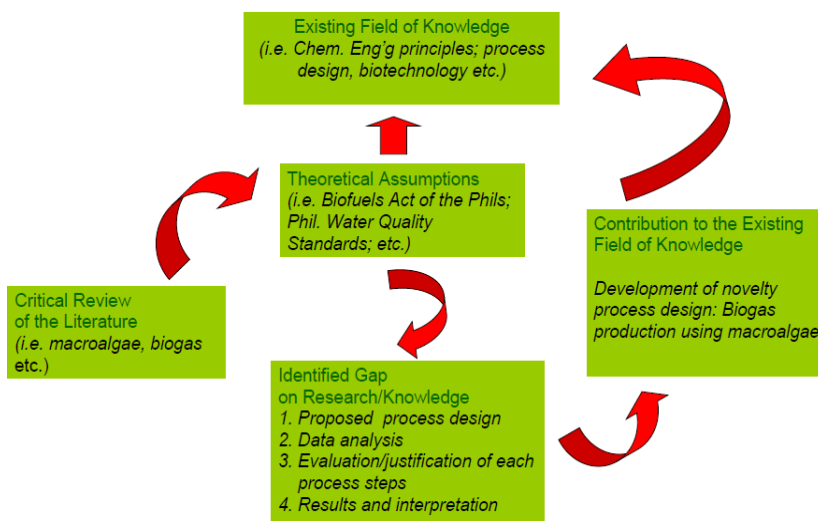


Fig. 1.1 The conceptual design process for biogas production in polluted seawater using macroalgae, *Ulva Lactuca*.

Significance of the study

Producing biogas by cultivation of *U. lactuca* which can remove nitrogen and phosphorus from polluted seawater has great beneficial to aquatic systems and to people who depends their living on it. This technique could then promote *U. lactuca* and biogas utilization saved our environment from water and air pollution.

Biogas when purified, is a good alternative to LPG (liquefied petroleum gas) typically used by households since this has low greenhouse gas emission level, and is renewable. Likewise, the price of purified biogas is cheaper than LPG.

METHODOLOGY

In order to attain the objectives of the study, the following shall be utilized as strategies in which necessary data and relevant information will be obtained.

- a. Prepare a preliminary process design based on the proposed process steps. The process steps are to be evaluated based on mode of operation, types of macroalgae, size reduction, types of digestion, purification process, dewatering of sludge and drying process. Fig. 1.2 depicts the basic process steps involved in biogas production.

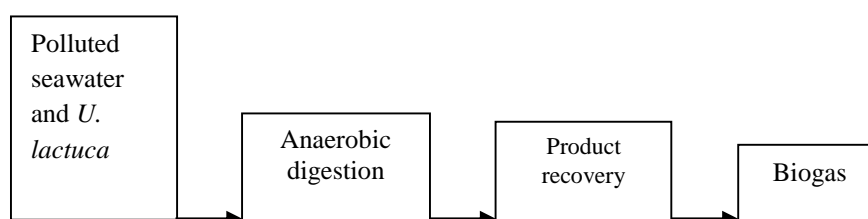


Fig. 1.1 The basic process steps in biogas production.

- b. Evaluate and justify each process steps using different process options criteria in terms of suitability, economy, process safety, and environmental safety. These criteria are used in evaluation since these covers the whole aspect of an ideal process. Table 1.1 shows the guidelines for process selection and process option with the highest average rating are selected for the process.

Table 1.1 Process Option Criteria

Criteria	General Description	Rating
Suitability	High satisfaction to met its own purpose to one's own needs	5 to 1
Economy	Less production cost and has viable products	5 to 1
Environmental Safety	Have minimal the outputs of wastes	5 to 1
Process Safety	Must not be hazardous and operate within safe conditions	5 to 1

Rating: 1-poor; 2-slightly satisfactory; 3- satisfactory; 4- very satisfactory; 5- excellent

- c. Present technical and financial studies for the completion of the pilot-scale biogas production.
- d. Submit a technical paper to the review committee and apply to the different funding institutions for the realization of this project

Process Concepts: The upstream dictates the productivity of the process. The upstream process involves the cultivation of *U. lactuca* and then its digestion to produce biogas. This process are dictated or affected by the concentration of the nutrient coming into the reactor and the operating conditions.

Culture Preparation: *U. lactuca* occurs almost regularly in the Mactan Channel of Cebu which causes “green tide” in the area [Largo *et al.*, 2004]. It is practically important to select this species to control their population on the sea since they could cause detrimental effect to other beneficial marine lives [Jones, 2007]. Moreover, its rapid growth and high nutrient uptake leads me to choose this type of macroalgae for biofiltration [Taboada *et al.*, 2007; Neori *et al.*, 1991].

There is no need to worry about culturing *U. lactuca* since this could survive even on high light and strong water flow [Parker, 1981]. *U. lactuca* needs only moderate temperature of 26 to 30°C, and pH range of 7 to 8 [Taboada *et al.*, 2007].

After harvesting *U. lactuca*, this is acclimatized for four days in a tank with the required conditions aforementioned. This is done to optimize the activity of the *U. lactuca* inside the reactor; it is common for living organisms such as in fermentation to acclimatize it first. A sufficient amount of inoculums is used in order to produce sufficient amount of *U. lactuca* [Taboada *et al.*, 2007].

Biofiltration: Growth requirements must be sustained in order to achieve high uptake rate. The light, flow, temperature and pH requirement of *U. lactuca* is just the same as it is acclimatized.

However, in bio-filtration process, nutrient from fishpond effluent is introduced in order for it to survive. With required conditions and enough substrate, *U. lactuca* could grow optimally to an average rate of 0.5-kilogram dry weight per square meter [Largo *et al.*, 2004]. Nutrient concentration may be equal to 77 μM (ammonium as nitrogen, maximum) to produce 0.02 gram (dry weight) algal biomass per liter [Neori *et al.*, 1991].

Anaerobic Digestion: This process allows to convert sludge to end products of liquid and gases while producing as little biomass as possible. The process is much more economical than aerobic digestion. Anaerobic digestion is accomplished in three stages: (1) hydrolysis of insoluble polymers, (2) fermentation of monomeric breakdown products and (3) fermentation of acetate and hydrogen from volatile fatty acids and (4) generation of methane [Droste, 1997].

The optimum pH and temperature of acid-forming bacteria and methane bacteria are 6.5 to 7.5, and 35°C, respectively. Detention time is 3 to 30 days depending on the required capacity of the digester tank [Droste, 1997; Tchobanoglous and Burten, 1991]. A practical minimum limit of 1,000 mg/L on the influent COD (chemical oxygen demand) concentration is needed to obtain successful anaerobic treatment. A conservative value for methane yield is 0.20 m³ of methane per kg of COD (chemical oxygen demand) removed [Droste, 1997].

The normal composition of biogas from anaerobic processes ranges from 60 to 70% methane (CH₄), and a balance of 30 to 40% of carbon dioxide (CO₂). Small amounts of hydrogen sulfide (H₂S), water vapor and other gases are also present. [Droste, 1997].

Product Recovery. The product that is the biogas is naturally separated from the slurry and is collected by a gas collector on top of the digester [Tchobanoglous and Burten, 1991].

Biogas Purification. The raw biogas is purified in order to have a kitchen stove fuel that has high energy value, corrosion-free (for hydrogen sulfide), and low emission of greenhouse gas (carbon dioxide, hydrogen sulfide when converted to sulfur dioxide in the atmosphere). In addition, the purified biogas produced would be able to compete the natural gas that the household is commonly using for kitchen stove.

In order to reduce the energy consumption for gas compression, a series of vessels are typically linked together. The gas pressure released from one vessel is subsequently used by the others. Usually four vessels in a row are used filled with molecular sieve which removes at the same time hydrogen sulfide, carbon dioxide, and water vapor. During adsorption, pure biogas with a concentration of greater than 95% (by volume) is recovered. After adsorption, desorption is conducted in order to regenerate the adsorbents and recover significant amounts of carbon dioxide. Recovered gas is filled in high-pressure steel cylinders [Geankoplis, 2005; Peters *et al.*, 2003].

RESULTS AND DISCUSSION

Fig 1.2 shows the input and output diagram integrated biofiltration and biogas production process utilizing *U. lactuca*; Basis: 1,000 metric tons of purified biogas per annum (MT/a)

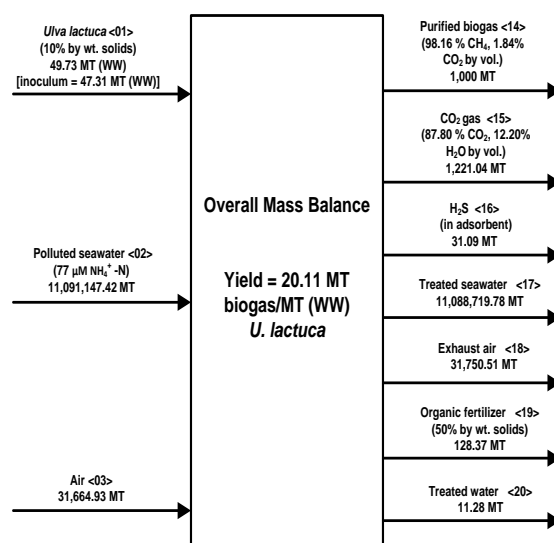


Fig. 1.2 Overall Input-Output Diagram of the Integrated Bio-filtration and Biogas Production Process Utilizing *U. lactuca*

Block Scheme Diagram

The composition and the amounts of the components, process conditions, phases, yields and conversions are incorporated in all major streams of the process.

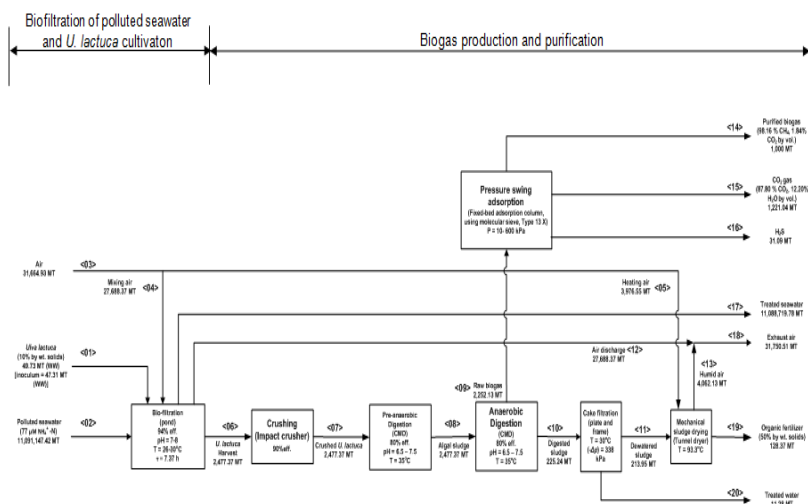


Fig. 1.3 Block scheme diagram of the integrated bio-filtration and biogas production process utilizing *U. lactuca*

Cash Flow Diagram

The behavior of the cash flow of the plant is depicted in fig.1.4. It is shown in the figure the milestones of the plant which include the pay-out time for debts (point A to B), the time wherein all the capital investments are paid or break-even point (point B), and the profitable years that is enjoyed up to the end life of the plant (point B to C).

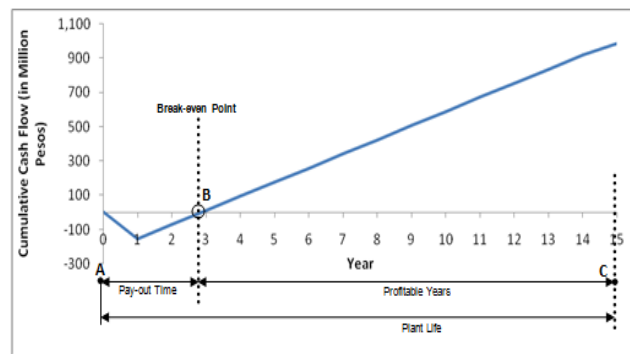


Fig. 1.4 The cash flow analysis of the proposed biogas production.

Sensitivities

Sensitivity to economic criteria with respect to investment, operating costs, and product prices is determined. This anticipates variability of these factors and is taken into consideration. Variance of $\pm 10\%$ is used. Table 1.2 shows the sensitivities of applied variance to economic criteria.

Table 1.2 Sensitivities of economic criteria

Economic Criteria/Values		Total Capital Investment		Operating Cost		Product Price	
		-10%	+10%	-10%	+10%	-10%	+10%
ROR (%)	34.80	37.93	32.25	37.91	31.70	28.88	40.73
POT (yrs)	2.87	2.64	3.10	2.64	3.15	3.46	2.46
Ave. Cash Flow (in Php, M)	80.36	78.82	81.90	87.53	73.18	66.69	94.03
DCFR (%)	5.25	6.50	4.19	9.72	-0.06	-1.53	10.71

Based on the sensitivity analysis, a variance of $\pm 10\%$ in total capital investment would give no detrimental effect to the economic criteria of the plant. However, as to what typically happens to a plant, product price and operating cost plays the major role in giving life to the operation of the plant. As observed, variance of $+10\%$ to operating cost gives a negative value of DCFR. Though the value is almost negligible, it is also necessary to impose strict regulations in the company in case of utilizing resources and utilities of the plant such as manpower, water, and electricity. Research and development of the company can also help minimizing operating cost by adapting new technologies that is more efficient and cost-effective. On the other hand, product price also gave a negative effect to the economic criteria of the plant when decreased by 10% . However, the possibility is just less since the trend for product price of commodities frequently goes up especially for the gas fuels such as biogas. A 10% product price increase maybe achieved and would give the highest ROR based on the sensitivity analysis. Hence, annual net cash flow or the earning power may even go higher than what was estimated and would eventually boost the economy of the plant.

CONCLUSION AND RECOMMENDATION

U. lactuca is a potential feedstock for biogas production. Aside from producing biogas, cultivation of *U. lactuca* can remove nitrogen and phosphorus from polluted seawater. This technique is beneficial to aquatic systems and to people who depends their living on it. Laboratory studies which have proved the feasibility of *U. lactuca* as biofilter served as a basis for the pilot plant design. This design could then promote *U. lactuca* and biogas utilization which could save the environment from water and air pollution.

U. lactuca is cheap and is indigenous. This costs only 0.04% of the raw materials cost. Hence, this feedstock would give sure profit from the product revenues. However, expansion can be limited by the land area available since bio-filtration requires large space and could give high production cost due to high land cost.

Biogas when purified, is a good alternative to LPG (liquefied petroleum gas) typically used by households since this has low greenhouse gas emission level, and is renewable. Aside from that, the price of purified biogas is cheaper than LPG. The price of biogas is marked at Php 53.14 per kilogram compare to LPG which is Php 55.36 per kilogram. This means that in every 11-kg tank of biogas used, Php 24.42 or about 4% is saved from the budget of consumers.

Economic analysis of the pilot plant showed that the design is economically viable with a rate of return of 34.80% and payback period of 2.87 years. Economic analysis also showed that the product price is the most sensitive among other criteria justified. However, there is nothing to worry about when product price decreases by 10% since the trend of gas price nowadays is often ascending.

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REFERENCES

- [1] Arceivala SJ, Asolekar SR. 2007. Wastewater Treatment for Pollution Control and Reuse, 3rd edition, Tata McGraw-Hill Publishing Company, Limited, New Delhi, pp 377-378.
- [2] ASEAN Secretariat. 2004. Marine Water Quality Criteria for the ASEAN Region, 6th Meeting of the ASEAN Working Group on Coastal and Marine Environment, 22 – 23 June 2004, Jakarta, Indonesia.
- [3] Bergeron PW, Corder RE, Hill AM, Lindsey H, Lowenstein MZ. 1983. SERI (Solar Energy Research Institute) Biomass Program, Annual Technical Report, US Department of Energy, USA.
- [4] Carayo CC, Culango KC, Estrera D, Largo DB, Dy DT. 2005. Correlation of Inorganic Nutrients to the Standing Crop of “Green Tide” Algae During the Peak Growth Season in Mactan Island, Central Philippines, Philipp. Scient. 42:1-14.

- [5] Cheremisinoff NP, Cheremisinoff PN. 1993. Water Treatment and Waste Recovery (Advanced Technology and Applications), PTR Prentice-Hall, Inc., NJ, pp103-105.
- [6] Corbo RY, Obedoza MP, Panaligan NK, Taboada EB. 2007. Ammonium (nitrogen) uptake of *Ulva reticulata* species in polluted seawaters, USC Chemical Engineering Research 1: 67-73.
- [7] Droste R.1997. Theory and Practice of Water and Wastewater Treatment, USA, p 630.
- [8] Fogler H.1999. Elements of Chemical Reaction Engineering, 3rd edition, Prentice Hall, New Jersey, pp 871-830.
- [9] Geankoplis CJ. 2005. Principles of Transport Processes and Separation processes, 1st ed., Philippine edition, Pearson Education South Asia PTE.
- [10] Gerardi MH. 2003. The Microbiology of Anaerobic Digesters, John-Wiley and Sons, Inc., NJ, pp 51-76.
- [11] Geertz-Hansen O, Sand-Jensen K. 1992. Growth rates and photon yield of growth in natural populations of a marine macroalga *U. lactuca*, Marine Ecology Progress Series 81: 179-183.
- [12] Ilyas SZ. 2006. A Case Study to Bottle the Biogas in Cylinders as Source of Power for Rural Industries Development in Pakistan, World Applied Sciences Journal 1 (2): 127-130.
- [13] Jones AB, Presto NP, Dennison WC. 2007. The efficiency and condition of oysters and macroalgae used as biological filters of shrimp pond effluent, Aquaculture Research 33 (1), pp. 1–19.
- [14] Kargi F, Shuler M. 2002. Bioprocess Engineering: Basic Concepts, 2nd ed., Prentice –Hall Inc., New Jersey, pp 57
- [15] Kohl A, Neilsen R. 1997. Gas Purification, Golf Publishing Company, Texas, p1395.
- [16] Largo D, Sembrano J, Hiraoka M, Ohno M. 2004. Taxonomic and ecological profile of 'green tide' species of *Ulva* (*Ulvales*, *Chlorophyta*) in central Philippines, Hydrobiologia 512:247-253.
- [17] Neori A, Cohen I, Gordin H.1991. *Ulva lactuca* Biofilters for Marine Fishpond Effluents:Growth Rate, Yield, and C:N Ratio. Botanica Marina 34:483-489.
- [18] Neori A, Msuya FE, Shauli L, Schuenhoff A, Kopel F, Shpigel M. 2003. A novel three-stage seaweed (*Ulva lactuca*) biofilter design for integrated mariculture. Journal of Applied Phycology 15(6):543-553.
- [19] Parker HS. 1981. Influence of Relative Water Motion on the Growth, Ammonium Uptake and Carbon and Nitrogen Composition of *U. lactuca* (Chlorophyta). Mar. Biol. 63: 309-318.
- [20] Perry RH, Green DW, Maloney JO.1998. Perry's Chemical Engineer's Handbook, 7th ed., McGraw-Hill Co., International edition, Singapore.
- [21] Persson M, Jonsson O, Wellinger A. 2006. Biogas Upgrading to Vehicle Fuel Standards and Grid Injection, Task 37-Energy from Biogas and Landfill Gas, IEA Bioenergy, Sweden.
- [22] Taboada EB, Maglente VM, Tan PU. 2007. Modeling the Nutrient Uptake by the Green Macroalgae (*Ulva Lactuca*) species, Department of Chemical Engineering, University of San Carlos, Cebu City, Philippines.
- [23] Tchobanoglous G, Burten FL.1991. Wastewater Engineering: Treatment, Disposal, and Reuse, 3rd ed., Mc Graw Hill, New York,
- [24] Torreliel IC, Mislos KJ, Apalisok AR, Dy DT. 2004. Comparative NH_4^+ uptake of *Caulerpa lentillifera* (Chlorophyta, *Caulerpales*) and *Gracilariopsis Heteroclada* (Rhodophyta, *Gracilariiales*): competition between a cultured alga versus an unwanted species, The Phillippine Scientist 41:36-46.

- [25] Trono GC, Jr.. 1997. Field Guide and Atlas of the Seaweed Resources of the Philippines, Bookmark Inc., Makati City, Philippines, pp 23-27.
- [26] Turovskiy IS, Mathai PK. 2006. Wastewater Sludge Processing, John-Wiley and Sons, Inc., NJ, p 107.
- [27] Vermaat JE, Sand-Jensen K. 1987. Survival, metabolism, and growth of *U. lactuca* under winter conditions: a laboratory study of bottlenecks in the life cycle, Marine Biology 95:55-61.
- [28] Vijay, VK, Chandra R, Subbarao PMV, Kapdi S. 2006. Biogas Purification and Bottling into CNG Cylinders: Producing Bio-CNG from Biomass for Rural Automotive Applications, The 2nd Joint International Conference on "Sustainable Energy and Environment, Bangkok, Thailand.
- [29] Wellinger A, Linberg A. 2000. Biogas Upgrading Utilization – IEA Bioenergy Task 24. International Energy Association, Paris, France, p 20.
- [30] Woodside G, Kocurek D. 1997. Environmental Safety, and Health Engineering, John Wiley and Sons, Inc., NY.