Sustainable solution for alien algae management to reduce the environmental consequences of sea and river transport

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Abstract. The accelerated development of sea and river transport over the past few decades has led to a negative phenomenon regarding the invasion and development of alien algal species, threatening to modify the ecosystem functions. Algae are an attractive feedstock for biofuels production due to many advantages such as rapid growth, chemical composition rich in lipids, carbohydrates and proteins, but also because algae do not require farmland and do not create controversy in using arable land for energy purpose to the detriment of food-intended crops. Indigenous or alien algal biomass has been excessively developed in the Black Sea basin and areas affected by eutrophication, causing environmental problems. This paper presents a sustainable management solution for mitigating the negative impact of alien algae by exploiting their energy potential for producing biogas. An innovative concept of tubular bioreactor for biogas production was developed within INCDIE ICPE-CA and could be successfully applied to harness algal biomass and produce biogas for domestic and industrial use, while simultaneously ensuring sanitation of sea shore and fresh water streams.

1. Introduction
Accounting for more than 90% (by weight) of global trade, marine transportation activities are associated with many environmental concerns, generated by factors including air polluting emissions, hazardous spills, wastes generated on board and discarded into the sea, discharge of ballast water containing aquatic invasive species, harbours expansion etc. [1]. Although several mitigation actions addressing the negative environmental effects of marine transportation have been implemented (e.g. regulations and enforcement measures, technological solutions, regional and international initiatives, incentive and awarding, awareness campaigns), many efforts still have to be done in finding complementary strategies for managing pollution from naval ship traffic [2].

Harvesting algae from areas affected by algal invasions could be an efficient solution for the remediation of aquatic areas. Algae are an attractive feedstock for various industries since they can be converted in a wide varieties of useful and valuable products. The use of algal biomass has many benefits, both for the economic sector (food industry, chemical-pharmaceutical industry, energy industry), but also in terms of preservation of local ecosystems and environment protection.

In the past decades, some of the features related to algae growth have been exploited for energetic purposes. At laboratory scale, algal biomass has proven to be a suitable feedstock for the production of biofuels and it has emerged as a renewable and sustainable alternative for fossil fuels, especially when related to the transportation sector [3]. Algae have a high growth rate while their chemical composition allows conversion into various types of fuels simply by selecting a specific technology, the strain and the part of the used cells. Moreover, algae-derived biofuels, unlike those produced from crops, have no impact
on the food supply due to the fact that they do not require agricultural land, for which reason their cultivation and exploitation is not the subject of controversies regarding the land intended for food production. This aspect is significant because ethical policies regarding the use of finite bioresources from arable land for energy production (around 0.2 ha of arable land per inhabitant worldwide) play an increasingly important role when promoting and implementing bioresource recovery technologies.

On the other hand, the economic feasibility of technologies for industrial algae conversion to biofuels has been questioned over time due to the high biofuel production costs. The technological process for producing algal-based biofuels includes three major stages: cultivation, harvesting and conversion into biofuels (mainly biodiesel and biogas). If algal biomass is harvested directly from the natural habitats where it grows excessively, the cultivation stage is eliminated from the technological chain, thus reducing the production costs of the biofuel.

The present paper presents a technological solution for energy recovery of algal biomass from the Black Sea basin, including Danube Delta, particularly addressed to invasive algae which exhibit multiple negative effects on the local biodiversity. A concept design of an algal-based biogas generator is briefly presented in terms of technological features, advantages brought for the energy and environmental sectors and manufacturing possibilities in isolated communities.

2. Alien algae environmental impact

In the Black Sea basin, problems related to invasive algal species emerged more heavily at the end of the 20th century along with the increasing effects of eutrophication, a phenomenon that generated multiple effects on the local ecosystems. For instance, the aquatic life modified conditions made that some large populations of phyto- and zooplankton expanded excessively, thus leading to oxygen depletion in water and creating anoxic aquatic environments. These environments which became unsuitable for indigenous species are adequate for invasive species growth which are more resistant to lack of oxygen dissolved in water and will arrive to gradually replace native species.

Also, the intensification of the naval traffic in the Romanian ports has fostered the emergence of alien plant species that are brought with the water ballast which is transported along the way and usually discarded in the shore proximity [4]. In the coastal and delta areas of the Black Sea basin, a total of 27 aquatic and semi-aquatic invasive plants species were identified. Among these, the western waterweed (Elodea nuttallii) is a highly invasive species which grows in dense layers on the bottom of lakes and rivers or in the aquatic channels of narrow streams, making river navigation difficult [5]. Spirulina is another highly invasive microalgae species entered into Romanian aquatic ecosystem; this belongs to the cyanobacteria group of photosynthetic bacteria and reached the Romanian ecosystem around 1970, finding adequate growth conditions in eutrophication-affected lakes and forming freshwater phytoplankton [6]. Eutrophication has also caused abnormal abundance of phytoplankton in numerous lakes in the Danube Delta where the algal bloom occasionally exceeds the threshold level.

The invasion of alien species is a negative phenomenon affecting the biodiversity of the Black Sea basin. This phenomenon cannot be controlled under the current conditions of continuous intensification of the goods volume transported on aquatic route, respectively the intensification of the naval traffic. The main mechanisms by which alien species negatively influence the biodiversity are shortly presented in figure 1. Nevertheless, it should be noted that the role of alien species in marine ecosystems is rather complex and each case should be carefully examined individually.
On the other hand, the negative impact of alien species expansion can be reduced or controlled by identifying and developing technological solutions to harness their energy and material potential; hence, the excessively developed algal biomass could become a valuable bioresource to be exploited in various industries like pharmaceuticals, cosmetics, food, as well as for the production of biofuels.

3. Anaerobic digestion of algae for energy production
Both macroalgae and microalgae are considered raw materials for the third generation biofuels, which are thought to be the biofuels of the future [7]. Generally, the use of algae for the production of third generation biofuels has showed a continuously ascendant trend, with the main advantage that they do not require agricultural land compared to those of the first and second generation.

However, production of algae-based biofuels at the commercial scale is currently still very poor. Synthesis, methods and technologies for producing biofuels using algal biomass are not enough documented, nor in consensus in different scientific publications, although many authors claim that biogas production from seaweed is industrially feasible, as even complex carbohydrates can be converted to biogas [8]. On the other hand, when treating algae, the energy balance of biogas systems has proven superior to that of biodiesel production units, primarily because biogas systems use wet resources and energy-consuming drying is not required. Moreover, in the case of anaerobic digestion, the preliminary extraction of oils is not needed compared to biodiesel production technologies.

The biomethane potential (BMP) of algae, i.e. the ratio of the cumulative methane volume obtained by anaerobic digestion and the total mass of volatile solids (VS) subjected to fermentation, varies greatly depending on many factors, as shown in figure 2. The literature data shows a biogas potential for marine algae in the range of 150 - 350 litres of CH$_4$/kg volatile solids.

Figure 1. Impact of alien species on natural biodiversity.

Figure 2. Some of the factors affecting the biomethane potential (BMP) of algae.
Among the algal species, microalgae have gained the special attention of researchers and are largely considered an appropriate fermentation substrate, mostly due to their high growth rate, low carbon content and lack of competition for agricultural land. The biomethane potential of microalgae commonly varies between 100 and 450 litres CH₄/kg VS. The wide interval for the biomethane potential values could be explained by differences in the performances of the anaerobic digestion process from one species to another, but also by the large variation in specific productivities in case of using substrates composed of microalgal species mixtures.

Another advantage of microalgae when used for biogas production is the high lipid content, given that the theoretical yield of biogas from lipids is higher (1390 L CH₄/g VS) than from protein (800 L CH₄/g VS) or carbohydrates (746 L CH₄/g VS). [9] Compared to terrestrial plants, the oil content of microalgae is considerably higher, usually in range of 20-50% (in dry weight), while some strains can reach a fat content of up to 80% [10].

In table 1, the biomethane potential of some indigenous and alien aquatic plant species used in some lab-scale experiments is presented.

### Table 1. Biomethane potential of several algae and aquatic plants BMP (in L CH₄/g VS).

<table>
<thead>
<tr>
<th>Plant specie</th>
<th>BMP</th>
<th>Ref.</th>
<th>Plant specie</th>
<th>BMP</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Brown seaweeds</strong></td>
<td></td>
<td></td>
<td><strong>Microalgae</strong></td>
<td></td>
<td></td>
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<tr>
<td>Saccorhiza polyschides</td>
<td>255</td>
<td>[12]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sargassum muticum</td>
<td>130</td>
<td>[8]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Red seaweeds</strong></td>
<td></td>
<td></td>
<td><strong>Nanochloropsis spp.</strong></td>
<td>312</td>
<td>[17]</td>
</tr>
<tr>
<td>Palmaria palmata</td>
<td>279</td>
<td>[8]</td>
<td>Scenedesmus obliquus</td>
<td>178</td>
<td>[14]</td>
</tr>
<tr>
<td>Gracilaria verrucosa</td>
<td>144</td>
<td>[8]</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td><strong>Fresh waters plants</strong></td>
<td></td>
<td></td>
<td><strong>Chlorella maxima</strong></td>
<td>190-340</td>
<td>[18]</td>
</tr>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Green microalgae</td>
<td>310</td>
<td>[17]</td>
</tr>
</tbody>
</table>

In order to achieve an increased performance of methods converting the algal biomass into biogas, it is essential to consider and evaluate some essential issues that are known to influence the biogas yield, such as: the type of algal biomass used as main substrate and/or co-digestion substrate, the cultivation techniques, algae pre-treatment methods, biogas plant configuration, the gas planned to be obtained (methane or hydrogen), co-substrate materials, integration of the biogas technology with other technologies (e.g. aquaculture, preliminary extraction of components by biorefining, etc.).

### 4. Innovative technological solution for algae conversion to biogas

A variety of anaerobic bioreactor concepts are available for the energy recovery of organic biomass, sludge and wastewater of different origins. The constructive and functional particularities of biogas reactors are multiple and decided by several aspects, amongst which the feedstock type, space availability, financial resources, etc. Developing a unique bioreactor design is unrealistic; the constructive differences between the existing bioreactors concepts may refer to substrate feeding method into the bioreactor, geometric shape of the bioreactor, number of digestion units, layout of the biogas plant components, operation regime, etc. [20]. New improved concepts of bioreactors are aimed to serve the particular purposes of each biogas facility.

In order to capitalize the biogas potential of algal biomass and other wet organic materials, an innovative concept of tubular bioreactor for biogas production was developed within INCIDE ICPE-CA research institute. The bioreactor is of tubular construction, consisted of a glass fibre fermenter placed underground, thermally insulated, divided by a longitudinal separating wall fitted with an overflow that allows partial recirculation of the liquid effluent. The fermenter is connected to an organic slurry tank through an inlet
pipe, and to a digested sludge tank with expansion chamber through an outlet pipe, both tanks being made of concrete and covered with a lid provided with two openings with flexible valves for supplying the organic slurry, respectively discharging the digested sludge. The bioreactor is equipped with a gas pipe for evacuating biogas and with an appropriate device for measuring the liquid level in the fermenter, as shown in figure 3.

![Figure 3. Tubular bioreactor concept - 3D view](image)

Given the rich potential of algal biomass in the Danube Delta and coastal areas, as well as the negative impact that this resource creates locally, the bioreactor concept can be developed to harness algal biomass, with biogas production for domestic or industrial needs, simultaneously with the sanitation of the sea shores and water streams.

The tubular bioreactor, which is claimed by the patent application A 2016-00324 [21], presents a high level of novelty and originality, both regarding the constructing elements, as well as due to the economic, energy and environmental advantages that it can bring to the beneficiaries. The anaerobic digestion chamber is tubular, semi-compartmentalized to ensure an extended double path for the fermentation mass inside the bioreactor, which renders an improved decomposition of the organic compounds, by extending the retention time of the organic mass in contact with the fermentation microbiota. Among the main advantages of this bioreactor design the followings can be highlighted:

- Higher efficiency in organic waste, algal biomass and wastewater treatment compared to any conventional horizontal tubular bioreactors without compartmentalization and liquid effluent return;
- Enhancement of biochemical processes by intake of active bacterial mass discharged into the feeding chamber, thus improving the decomposition effectiveness of the organic compounds;
- Simple and natural hydrodynamics made naturally by mass movement along the longitudinal wall;
- Extended decomposition time to ensure advanced or complete degradation of organic compounds to biogas with a high methane content;
- Ensuring a mesophilic temperature fermentation medium due to the underground bioreactor location without the need for any additional heating sources;
- Feeding the bioreactor directly from the inlet tank by free flowing without the need for a pumping system;
- Biogas capture in the tubular bioreactor with a direct use to the consumer;
- Protecting the environment from unpleasant odors by covering mud tanks with a lid fitted with flexible flaps at the inlet / outlet holes;
- Possibility of manufacturing for different sizes and modular construction in accordance with the available materials to be treated; Thus it does not require a minimum guaranteed biomass feedstock;
• It can be implemented with relatively low costs in small and isolated communities from delta and coastal areas or around organic waste generating farms;
• It allows periodic drainage and washing of the bioreactor body by conventional vacuuming methods, with access through the inlet tank;
• The bioreactor is completely autonomous energetically, requiring no energy-consuming operations such as homogenization and heating of the organic mass, neither mechanized extraction of the fermented sludge from the exhaust tank.
• Can be easily manufactured, with existing technology and at affordable costs for series production, scaled to various dimensions; it allows modular construction.

The location of the auxiliary components on the ground and on the same side of the bioreactor (feeding and drainage tanks) ensures a minimal space requirement. The round corners of the tubular profile secure a smooth organic mass flow, avoiding accumulation of unfermented material if edges or other dead spaces where the organic material would be improperly exposed to the active microbial mass. The expansion chamber allows the regulation of pressure created inside the fermenter, while the level device controls and regulates the volume of organic mass subjected to fermentation.

The main advantages of the presented innovative concept are summarized below:
• It ensures a high degree of organic material decomposition due to the existence of the partition wall that imposes a double extended circuit of organic mass between the feeding and outlet ports;
• It allows the partial recirculation of the liquid effluent to the feeding area, so that the freshly fed material is right from the start enriched with active fermentative bacteria that increase the efficiency of the fermentation processes and improves the energetic value of generated biogas;

Taking into account the biomethane potential of algae as presented in table 1, which ranges between 100 and 450 litres of methane per kilogram of volatile substances, for a tubular digester of 10 m³, a biomethane production of 7,000 – 31,000 litres/day could be obtained in optimal operating conditions; this production corresponds to a daily biogas volume of 11,500 - 52,500 litres (if 60% methane content in biogas). Thereby, if burnt to produce electricity, the biogas produced in this tubular 10 m³ bioreactor could ensure about 60 to 300 kWh electrical energy.

5. Conclusions
Human activities such as the development of naval transports or the construction of navigation channels have amplified in the last decades the phenomenon of the local flora extension, any introduction of new species into an ecosystem leading to irreversible ecological changes. The Black Sea basin proved to be particularly sensitive to the invasion of alien algal species since the sea shore and wetlands ecosystems were severely disrupted by human activities. This led to an intensification of the eutrophication phenomenon, the biggest problems related to invasive species occurring at the end of the 20th century when the effects of eutrophication become obviously visible.

The invasion of alien algal species has some undeniable negative effects on the indigenous algal species and local ecosystems, but also on the transport sector. On the other side, due to the rich content of organic compounds suited for anaerobic fermentation, algal biomass can be considered a very beneficial substrate for biogas production. Numerous research papers indicate the fairly high biogas potential of different species of macro and microalgae, which varies between 100 and 450 litres CH₄ per kilogram of algal volatile solids.

The attempts to mitigate the disadvantages of the anaerobic treatment systems of the different types of organic materials have led to the development of anaerobic systems with different constructive designs. The innovative tubular bioreactor concept created by INCDIE ICPE-CA is intended for the treatment of biodegradable materials and wastewaters from different economic sectors, as well as for processing algal biomass generated abundantly in the delta-coastal areas in the Black Sea basin. This concept offers an advantageous solution for energy recovery of the algal potential at local or regional level, with the production of biogas and organic fertilizers.
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