CHEMICAL ENGINEERING TRANSACTIONS

VOL. 70, 2018

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Timothy G. Walmsley, Petar S. Varbanov, Rongxin Su, Jiří J. Klemeš

ISBN 978-88-95608-67-9; **ISSN** 2283-9216

DOI: 10.3303/CET1870335

Environmental Evaluation of Agar Production from Macroalgae *Gracilaria* sp.

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Agar is a polysaccharide that is extracted from algae of the Rhodophyta class, better known as red algae. Since the discovery of agar extraction, an attempt has been made to optimize this process in order to obtain a high-quality product that produces less negative environmental impacts and is economically profitable. In the present study, the environmental analysis of the agar production process was carried out from red macroalgae of the genus *Gracilaria* sp. For which, the WAR algorithm or Waste Reduction algorithm was used by the implementation of the WARGUI software and Microsoft Excel. Initially, the environmental impact assessment was carried out in which different categories were evaluated to determine the total environmental impact potential generated by the process. Subsequently, we analyzed both the flow of toxicological and atmospheric environmental impacts generated by the limits of the system, as well as those generated by the total process chemistry. Finally, we compared the variation of the total environmental impacts generated after the change of the energy source. Results shows that the highest environmental impacts are generated when the energy consumed by the process is included in the evaluation. The highest atmospheric impacts value obtained was 107 PEI/hr, as well as the toxicological impacts, the highest value of PEI generated was 118 PEI/hr, which is low compared to other processes. In addition, in the analysis of the effect of energy source, the highest impact was 17.7 PEI/hr and when the gas is used as an energy source, the total environmental impacts were reduced by 16%.

1. Introduction

The study of marine algae is becoming increasingly important in chemical-industrial research, because these plants constitute one of the largest reserves of products of very varied use, both in human consumption and in various aspects of modern industry, this is why the demand for algae has increased in recent years, reaching world production in 2010 of 15.8 Mt. (Gómez, 2012). Adding to this its ecological diversity and economic value that have allowed this type of algae to become raw material for many industries. Macroalgae are a particular type of algae that are characterized by being rich in carbohydrates (Suutari et al., 2015), these also have great ecological importance as primary producers of coastal environments and participate in ecological processes as niches of recruitment, re-production and breeding of different species of fish and invertebrates, being responsible for a large part of the planet's primary production, as well as excellent CO_2 fixers (Mansilla and Alveal, 2013). The macroalgae form a large family and can be of different genus, being the best known *Gracilaria* sp because it is the most important genus as a raw material worldwide in the agar industry, contributing 60 % of the raw material (Vergara-Rodarte et al., 2010).
The macroalgae of the genus *Gracilaria* sp. is mainly used in the industry as raw material for the production of agar. Agar is defined as a hydrophilic colloid extracted from certain macroalgae, such as the one mentioned, *Gracilaria* sp. It is a mixture of polysaccharides whose main monomer is galactose, so it's also defined as a non-toxic and non-reactive biopolymer with proteins (Karim et al., 2014). It also can reach 31 % in dry weight in the *Gracilaria* species. The agar extracted from these algae is also called agar-agar and is used mainly as a gelling agent in processed foods, cosmetics and pharmaceuticals, also has applications in medicine and biotechnology

since 1880, thanks to its antioxidant and anticancer properties (Gómez et al., 2012) and is also one of the most promising biopolymers for the development of biodegradable packaging films (Kanmani and Rhim, 2014).
Currently, several processes have been studied for the extraction of agar from macroalga, where it is evaluated how the different process variables are affected; as performance and quality, after the variation of the industrial process used or the treatment given to the algae, for which various studies have been carried out, in different places such as the Philippines, Costa Rica, Cartagena, among others. All this with the ultimate goal of finding the best route for the optimization of these processes. However, there are no studies that allow the evaluation of the environmental performance of a process of agar production at pilot scale, nor that quantify the impacts generated and output of the process.
On the other hand, the War algorithm quantifies the total and generated environmental impacts of a process taking into account the waste and the energy source which it evaluates under eight impact categories (Herrera et al., 2017). In this work, the computer - assisted environmental analysis of the agar production process is carried out from the red macroalga of the genus *Gracilaria* sp, using the waste reduction algorithm. Since this analysis allows the evaluation of the possible environmental impacts of the process, which allow to detect points of improvement from the environmental point of view, helping to quantify the environmental effects and make decisions to improve the process under this criterion of sustainability.

2. Materials and methods

2.1 Environmental evaluation with WAR algorithm

An environmental analysis is done in order to ensure that a process, project or activities developed are environmentally sustainable and adequate based on a multidisciplinary analysis. The environmental analysis identifies different methods for environmentally improving the projects and minimizing the adverse impacts in a timely and practical manner. The waste reduction algorithm or WAR algorithm is one of the tools to carry out an analysis of the environmental impacts of processes where it calculates the generation of potential environmental impacts (PEI) resulting from the activities of the chemical industry. The WAR algorithm considers two points of view; PEI output, which measures the PEI impact emitted by the process to the environment, and the PEI generated which measures the generation of PEI within the limits of the process.
The WAR algorithm calculates four environmental impact indicators:

Total rate of impact output

$$i_{out}^{(t)} = i_{out}^{(cp)} + i_{out}^{ep} + i_{we}^{(cp)} + i_{we}^{(ep)} = \sum_{j}^{cp} \dot{M}_j^{(out)} \sum_k X_{kj}\psi_k + \sum_{j}^{ep-g} \dot{M}_j^{(out)} \sum_k X_{kj}\psi_k \tag{1}$$

Total impact output per mass of products

$$i_{out}^{(t)} = i_{out}^{(cp)} + i_{out}^{ep} + i_{we}^{(cp)} + i_{we}^{(ep)} = \sum_{j}^{cp} \dot{M}_j^{(out)} \sum_k X_{kj}\psi_k + \sum_{j}^{ep-g} \dot{M}_j^{(out)} \sum_k X_{kj}\psi_k \tag{2}$$

Total rate of impact generation

$$i_{gen}^{(t)} = i_{out}^{(cp)} - i_{in}^{(cp)} + i_{out}^{(ep)} - i_{in}^{(ep)} + i_{we}^{(cp)} + i_{we}^{ep} = \sum_{j}^{cp} \dot{M}_j^{(out)} \sum_k X_{kj}\psi_k - \sum_{j}^{cp} \dot{M}_j^{(in)} \sum_k X_{kj}\psi_k + \sum_{j}^{ep-g} \dot{M}_j^{(out)} \sum_k X_{kj}\psi_k \tag{3}$$

Total impact generated per mass of products

$$\hat{i}_{out}^{(t)} = \frac{i_{out}^{(cp)} + i_{out}^{ep} + i_{we}^{(cp)} + i_{we}^{(ep)}}{\sum_P P_P} = \frac{\sum_j^{cp} \dot{M}_j^{(out)} \sum_k X_{kj}\psi_k + \sum_j^{ep-g} \dot{M}_j^{(out)} \sum_k X_{kj}\psi_k}{\sum_P P_P} \tag{4}$$

The WAR algorithm also calculates eight categories where the PEI of chemicals and process are evaluated. These categories are classified in two groups: the toxicological impacts: Human Toxicity Potential by Ingestion or HTPI (5), Human Toxicity Potencial by Exposure or HTPE (6), Aquatic Toxicity Potential or ATP (7), Terrestrial Toxicity Potential or TTP (8); and the atmospheric impacts: Global Warning Potential or GWP (9), Ozone Depletion Potential or ODP (10), Smog Formation Potential or PCOP (11) and Acidification Potential or AP (12).

$$\mathrm{HTPI} = \frac{1}{LD_{50}} \tag{5}$$

$$\mathrm{HTPE} = \frac{1}{TLV} \tag{6}$$

$$\text{ATP} = \frac{1}{LC_{50}} \quad (7)$$

$$\text{TTP} = \frac{1}{LD_{50}} \quad (8)$$

$$\text{GWP} = \frac{\int_0^t a_i c_i(t)\,dt}{\int_0^t a_{CO_2} c_{CO_2}(t)\,dt} m_i \quad (9)$$

$$\text{ODP} = \frac{\delta[O_3]}{\delta[O_3]FCKW-11} m_i \quad (10)$$

$$\text{PCOP} = \frac{\frac{a_i}{b_i(t)}}{\frac{a_{C_2H_4}}{b_{C_2H_4(t)}}} m_i \quad (11)$$

$$\text{AP} = \frac{\frac{V_i}{M_i}}{\frac{V_{SO_2}}{M_{SO_2}}} m_i \quad (12)$$

2.2 Process description

The process of agar production begins with the washing stage in which the raw material (stream 1), the red algae, is washed with water (stream 3) in order to eliminate all the solid impurities (stream 4) adhered to these from the habitat (sand, salt, moss, etc.), mainly because the product to obtain is aim to the food industry. Continuously, it passes to a filtration stage (stream 2) to separate the water and the remaining impurities (stream 6) from the previous washing process in order to be taken to the next drying step. In this stage, the filtered algae (stream 5) is fed to an oven at 354.15 K of efficiency of approximately 100 %, in order to be able to completely remove the water impregnated in the algae (stream 8) and obtain the raw material.
After several purification processes, the stream 7 is subjected to an alkaline treatment step in order to release the agar contained in the algae, where they are mixed with a 5 % by weight NaOH solution to 353.15 K (stream 10). In this stage, alternate reactions take place, such as the hydrolysis of cellulose and hemicellulose, which are reduced to sugars. Then, the alkaline biomass (stream 9) is taken to a filtration process to separate the residual alkaline solution (stream 12) so that the treated biomass (stream 11) is neutralized with a 1.5% by weight H_2SO_4 solution at 353.15 K (stream 14) converting the excess NaOH into Na_2SO_4 (Cabarcas et al., 2014).
After the chemical treatment, the neutralized biomass (stream 13) is boiled with water at a temperature of 353.15 K (stream 16), to be taken to a pressure filtration process where the agar is separated from the components obtained from the alternate reactions in the alkaline treatment stage (stream 18) and finally, the flow is taken to the final stage of evaporation where energy supplied in the form of heat, evaporates the water contained in the mixture (stream 19) and thus purify the product (stream 20).

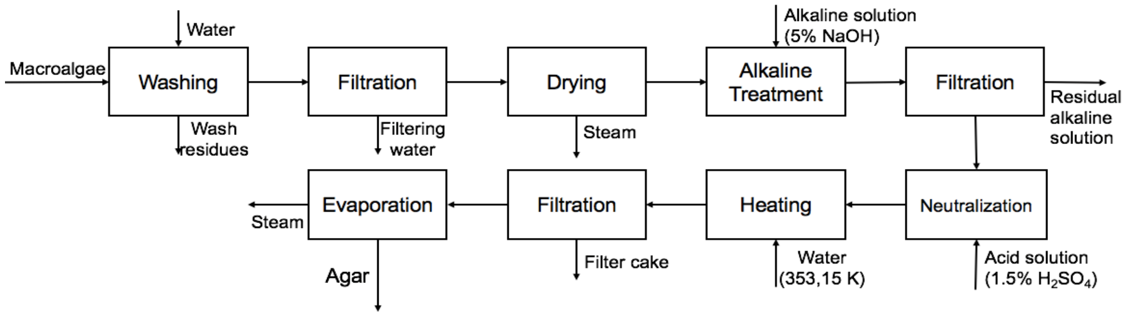

Figure 1: Block diagram of agar production from macroalgae.

Table 1: Mass fraction of the raw material (stream 1).

Component	Mass fraction
Water	0.06
NaCl	0.10
$CaCO_3$	0.10
CaO	0.06
Cellulose	0.15
Xilan	0.07
Triolein	0.01
Lysine	0.00
Palmitic Acid	0.01
Oleic Acid	0.01
Tripalmitin	0.01
Galactose	0.39
Alanine	0.01
Glycine	0.02

3. Results and discussion

3.1 Total Potential Environmental Impact (PEI): generated and output

As it is observed, in the Figure 1 presents the results obtained from the generation and output rate of environmental impacts (PEI) in the agar production, where it is observed that the greatest environmental impacts of output are generated when the analysis includes the energy consumed by the process, increasing by 25 % with respect to the case in which only the product is included. It is observed that this rate doesn't generate considerable environmental impacts, since they are small compare to other processes such as the palm oil production from African palm (Herrera et al., 2017), biodiesel production from sunflower (De marco et al., 2016), and second-generation ethanol from sugar cane (Bonomi et al., 2016). The negative values in some categories represent a decrease in the impact potentials, by transforming contaminating substances into other less polluting substances within the process.

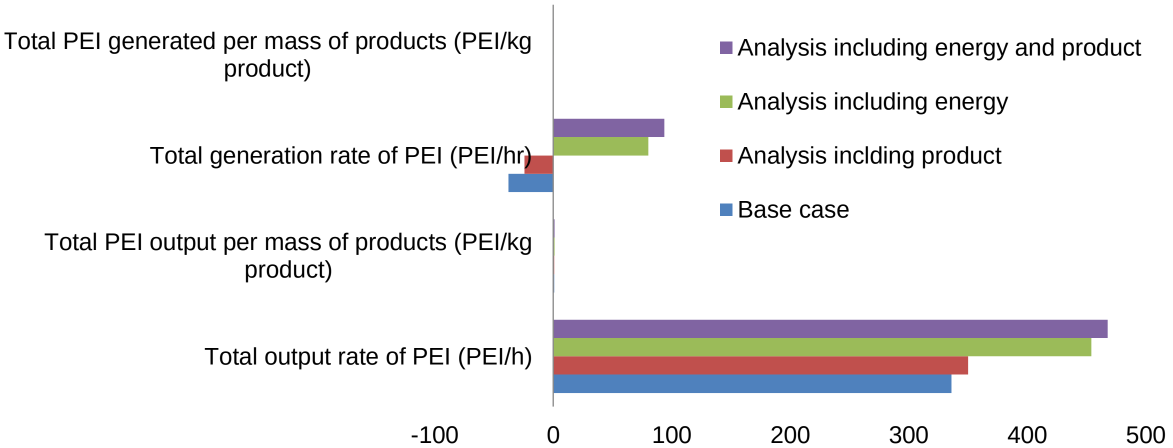

Figure 2: Total PEI generated and output of the system for the agar production from macroalgae

3.2 Local toxicological impacts of the process: generated and output

Figure 2 shows the local toxicological impacts generated output of the process, where there are no positive generated impacts in any category. Starting from the toxicological impacts in humans, it is observed that the HTPI and the HTPE are one of the highest bars of the graph (118 PEI/h, 103 PEI/h), but these have low values compared with those of the production process of second generation ethanol from sugarcane, which means a high dose is needed to be lethal, due to the contaminants generated in this process are mostly of organic origin. For the ecological impacts, it is observed that environmental impacts are also low, with the ATP category being the lowest for all cases (11 PEI/h). This means that this process is much less likely to affect aquatic systems, mainly because the agar comes from the marine habitat.

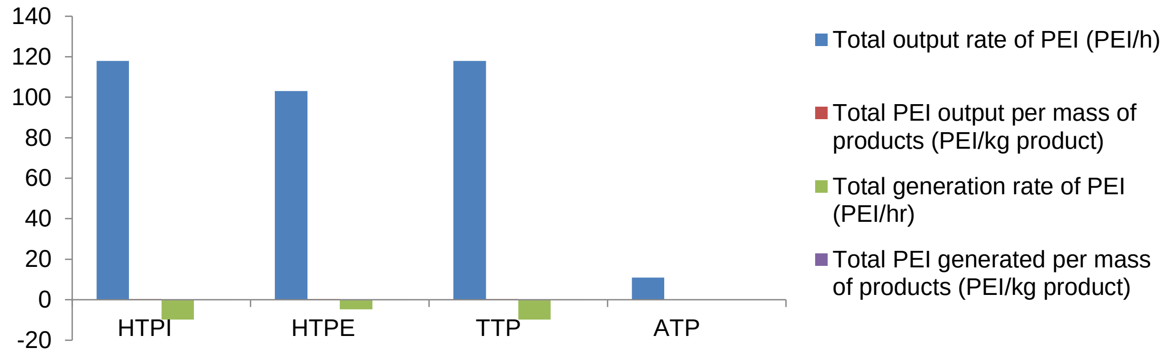

Figure 3: Local output and generated toxicological impacts of the agar production from macroalgae

3.3 Atmospheric impacts of the process: generated and output

The analysis of the generated atmospheric impacts was based on Figure 3, where it can be observed that for some of the impact categories, the generated and output PEI are null. Except for the AP, given that in this analysis, the energy source used is coal, it implies the release of combustion gases, mainly SO, which comes directly from the coal because neither the agar, the filter cake nor the water vapor contain sulphur compounds. This compound contributes to a large proportion of the potential environmental impact due to the formation of SO_2. This is the reason why the AP is large compared to the other atmospheric categories (107 PEI/h), although, it is still a small value compared to other processes.

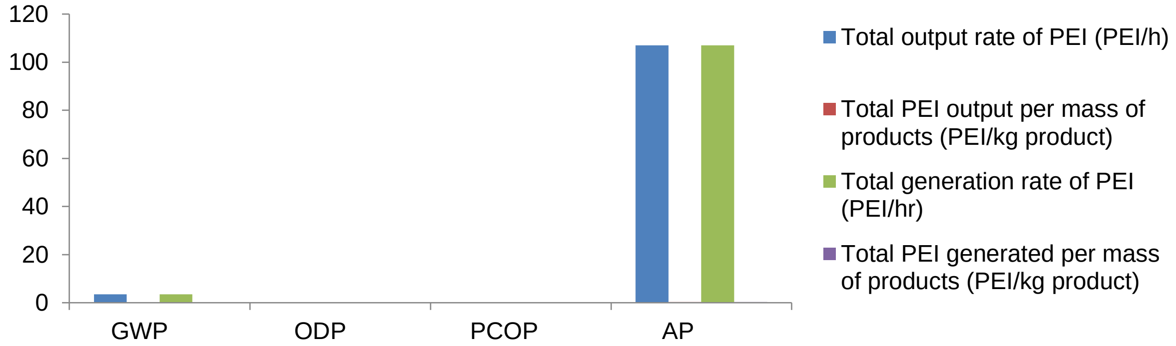

Figure 4: Output and generated atmospheric impacts of the agar production from macroalgae

3.4 Effect of energy source

Finally, Figure 4 is taken for the analysis on the effect of the energy source on the output rate by changing the source of energy, and the amount of impacts generated by the process also varies. It is observed environmental impact categories with coal usage are higher than those obtained with other fuels, especially for the AP. By changing the source of energy from coal to gas, impacts are reduced by 16 %.

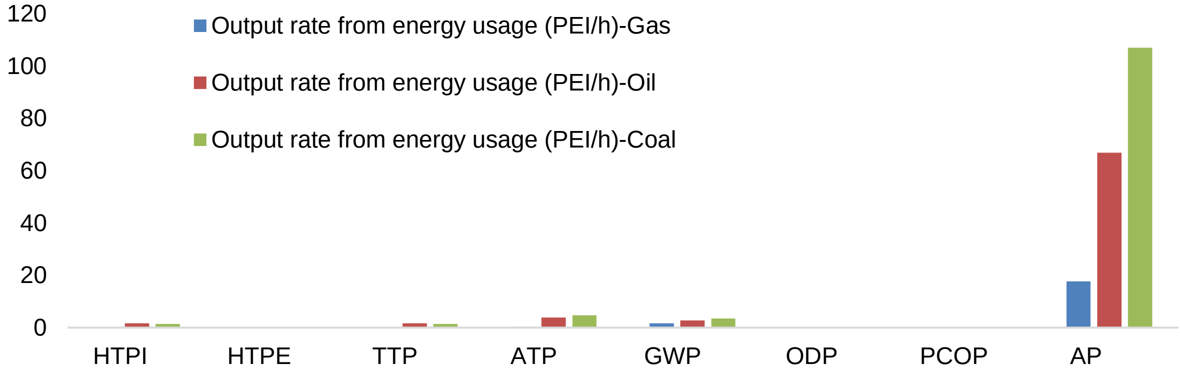

Figure 5: Effect of energy source on output rate from energy usage for the agar production from macroalgae

4. Conclusions

Based on the environmental evaluation carried out on the agar extraction process from red macroalgae of the genus *Gracilaria* sp., it's concluded that the product obtained doesn't generate toxicological or atmospheric environmental impacts that could affect the environment or the human population.
Regarding the ecological impacts, it is concluded that the total output rate of the process, in such case will come into contact with the environment, won't have a significant effect on terrestrial and aquatic systems. On the contrary, it will generate some positive impacts on the environment.
The process is atmospherically friendly, due to its low production of trichlorofluoromethane, CO_2, among other compounds that contribute to the generation of these impact categories, this is mainly due to the composition of the raw material used in the process is in its totality of organic composition.
It is possible to reduce the PEI for each category and obtain better environmental conditions for the production of agar by changing the energy source from coal to gas, due to the gas combustion doesn't leave consistent residues, while the coal produces sulphur dioxides that react with water vapor from the atmosphere causing acid rain.
Due to the total PEI output per mass of products rate of the process is low, it's concluded that this's an environmentally friendly process, indeed, it's because the raw material is algae. In general, when comparing this process with the palm oil from African palm production and second-generation ethanol from sugar cane production, it is clear that it has better and lower environmental impacts in all categories.

Acknowledgments

Authors thank to University of Cartagena for supplying the equipment necessary to conclude successfully this work.

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