Inherent Safety Analysis and Sustainability Evaluation of Chitosan Production from Shrimp Exoskeleton in Colombia

Antonio Zuorro¹*, Kariana Andrea Moreno-Sader² and Ángel Dario González-Delgado²

Abstract: Waste valorization strategies are key to achieve more sustainable production within the shrimp industry. The crustacean exoskeletons can be potentially used to obtain value-added products such as chitosan. A comprehensive analysis including both safety and sustainability aspects of chitosan production from shrimp shells is presented in this study. The inherent safety analysis and sustainability evaluation was performed using the Inherent Safety Index (ISI) methodology and the Sustainable Weighted Return on Investment Metric (SWROIM), respectively. The process was designed for a processing capacity of 57,000 t/year. The return on investment (%ROI), potential environmental impact (PEI output), exergy efficiency, and the total inherent safety index ($I_T$) were used as indicators to evaluate process sustainability. The total inherent safety index was estimated at 25 indicating that the process is inherently unsafe. The main process risks were given by handling of flammable substances, reactivity, and inventory subindices. The overall sustainability evaluation showed a SWROIM of 36.33% indicating that the case study showed higher weighted performance compared to the return on investment metric of 18.08%.

Keywords: inherent safety analysis; sustainability evaluation; SWROIM; shrimp exoskeleton; chitosan

1. Introduction

Chitosan is a natural bioactive polymer that supports the structural components of living organism such as insects, crustaceans, fungi, and some algae [1]. The chitosan market is driven by its attractive properties such as biocompatibility, biodegradability, absorption capacity, and antimicrobial activity [2]. This biopolymer is also known as a bioactive compound with biological anti-tumor, immune-enhancing, antifungal, antioxidant, and wound healing properties [3]. Natural sources for chitosan production at industrial scale have been explored, particularly chitin from the shells of the crustacean processing industries (shrimp, prawn, crab, and lobster) [4]. The main components of the crustacean exoskeletons are chitin, proteins, minerals, and carotenoids [5].

The shrimp farming and processing industry is a major fishing industry in the world since shrimp represent approximately 45% of the total seafood consumed worldwide [6]. The current production of shrimp is estimated to reach 5.03 million tons per year [7], and the demand is expected to continue growing in the coming years. In Colombia, shrimp farming and processing processes are located in coastal areas of the Pacific and Atlantic Ocean with an estimated rate of 2400 t/year. This production has led to huge amounts of wastes that represent around 65% of the initial weight of the shrimp including heads and shells [8]. The accumulation of these wastes causes several environmental and health issues; the latter because of their disagreeable odor and insect proliferations.
Chitosan from shrimp exoskeleton is produced through a chitin deacetylation process [9] that includes the following five stages: shells pretreatment, depigmentation, demineralization, deproteinization, and alkaline deacetylation [10]. The physicochemical characteristics of chitosan depend mainly on the deacetylation degree, solution viscosity, drying temperature, and percentage of acid solution [11]. In this context, the design and implementation of a chitosan production system from shrimp exoskeleton at large scale would improve the profits of crustacean processing companies and reduce impacts associated with shrimp waste generation [12]. Therefore, several works have been addressed to evaluate the economic, energetic, and environmental aspects of this process on a large scale. Meramo-Hurtado et al. [13] simulated a plant for chitosan production from shrimp exoskeleton in Colombia and carried out both environmental and exergy assessments, while Cogollo-Herrera et al. [14] performed the techno-economic sensitivity evaluation of the same process.

In this work, it is proposed the inherent safety analysis and sustainability evaluation for the chitosan production process from shrimp exoskeleton. The Inherent Safety Index (ISI) Methodology developed by Heikkilä [15] is used to identify the intrinsic risks of the process and to propose improvements that enable hazards mitigation. The process sustainability is evaluated under economic, environmental, energy, and safety criteria. The SWROIM approach presented by El-Halwagi is implemented to interpret the sustainable performance of the process in economic terms [16]. The Sustainable Weighted Return on Investment Metric (SWROIM) has been used by other authors to evaluate and compare processes; Meramo-Hurtado et al. compared biobutanol production pathways via acetone–butanol–ethanol fermentation [17] and evaluated the sustainability of a lignocellulosic multi feedstock biorefinery [18].

The novelty of this work lies on an integrated analysis of sustainability aspects, and the benefits of implementing this valorization strategy in economic terms. These results will provide useful information for bio-based companies to invest in the chitosan production from shrimp wastes for industrial-scale applications.

2. Materials and Methods

Figure 1 shows a schematic representation of methodology section. The inherent safety analysis and the sustainability evaluation are carried out using the ISI methodology and the SWROIM, respectively. The criteria considered to assess sustainability are economic, environmental, energy, and safety. The information required to perform the safety analysis and the sustainability indicators (return on investment (%ROI), potential environmental impact (PEI) output, and exergy efficiency) were obtained from process simulation, techno-economic evaluation [14], environmental analysis, and exergy analysis [13] previously developed by the authors.

2.1. Process Description

The chitosan production process from shrimp exoskeleton was modeled based on information reported in literature and data obtained by the authors during the process synthesis at laboratory scale [19]. The processing capacity (57,000 t/year) was established assuming the availability of 10% of the shrimp production capacity in Colombia (and other countries near the Pacific) [13]. As shown in Figure 2, the chitosan production from shrimp shells includes five basic operations: pretreatment, depigmentation, demineralization, deproteinization, and deacetylation [10].

The shrimp exoskeleton is first subjected to physical pretreatment by washing, drying, and grinding to remove impurities and reduce its size to a powder of 0.5 mm [5]. In the depigmentation stage, the astaxanthin content is removed from the treated exoskeleton using ethanol 85% vol [19]. Then, the shell powder is sent to the demineralization unit for calcium carbonate and other minerals removal using a 1.5 M hydrochloric acid solution to prevent chitin hydrolysis [20].
Figure 1. Schematic representation of the methodology.

Figure 2. Process diagram for chitosan production from shrimp exoskeleton.
The mainstream goes a deproteinization process where sodium hydroxide solution at 1M is added to remove the proteins while extracting chitin [21]. The extracted chitin is sent to the deacetylation stage to obtain chitosan through the removal of acetyl groups [22]. The deacetylation reaction is carried out at 110 °C, employing sodium hydroxide solution at 50% w/v with ratio chitin to solution of 1:10 w/v. After the reaction stages (demineralization, deproteinization, and deacetylation), the mainstreams are neutralized with HCl or NaOH and washed to adjust pH conditions to 7 [23]. Finally, the chitosan is dried in an oven at 100 °C [24] and isolated for further commercialization.

Figure 3 shows the Fourier transform infrared (FTIR) spectrum of chitosan from shrimp shells. The peaks around 1470–1629 cm⁻¹ corresponded to amide bands I-II. The deacetylation degree obtained at laboratory scale reached 81.81, similar to that reported by commercial chitosan [19].

\[ I_{TI} = I_{CI} + I_{PI} \]  

\[ I_{CI} = I_{RM, \ max} + I_{RS, \ max} + I_{INT, \ max} + (I_{FL} + I_{EX} + I_{TOX})_{\ max} + I_{COR, \ max} \]  

2.2. Inherent Safety Analysis

Early hazard prevention during the chemical process design stage enables the development of processes inherently safer and more resistant to operation deviations without affecting the productivity or plant efficiency [26]. Hence, both hazard elimination and risk reduction are recommended during the early design of process systems [27]. The Inherent Safety Index (ISI) methodology is a useful tool to identify intrinsic risks considering the worst-case scenario of conceptual designs.

The Total Inherent Safety Index \((I_{TI})\) is defined as the sum of the Chemical Inherent Safety Index \((I_{CI})\) and the Process Inherent Safety Index \((I_{PI})\) by Equation (1) [15].

\[ I_{TI} = I_{CI} + I_{PI} \]  

The chemical inherent safety index and the process inherent safety index are calculated as shown in Equations (2) and (3), respectively. The first contains chemical factors such as reactivity, flammability, explosiveness, toxicity, and corrosiveness of chemical substances involved in the process; while the second contains subindices of inventory, process temperature, and pressure, equipment safety, and safe process structure. Table 1 lists the symbols and scores for the safety subindices [15].
$$I_{PI} = I_1 + I_{T, \text{max}} + I_{P, \text{max}} + I_{EQ, \text{max}} + I_{ST, \text{max}}$$  \quad (3)

**Table 1. Symbols and scores for inherent safety subindices.**

<table>
<thead>
<tr>
<th>Inherent Safety Subindices</th>
<th>Symbol</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat of main reaction</td>
<td>$I_{RM}$</td>
<td>0–4</td>
</tr>
<tr>
<td>Heat of side reaction</td>
<td>$I_{RS}$</td>
<td>0–4</td>
</tr>
<tr>
<td>Chemical interaction</td>
<td>$I_{INT}$</td>
<td>0–4</td>
</tr>
<tr>
<td>Flammability</td>
<td>$I_{FL}$</td>
<td>0–4</td>
</tr>
<tr>
<td>Explosiveness</td>
<td>$I_{EX}$</td>
<td>0–4</td>
</tr>
<tr>
<td>Toxic exposure</td>
<td>$I_{TOX}$</td>
<td>0–6</td>
</tr>
<tr>
<td>Corrosiveness</td>
<td>$I_{COR}$</td>
<td>0–2</td>
</tr>
<tr>
<td>Inventory</td>
<td>$I_{I}$</td>
<td>0–5</td>
</tr>
<tr>
<td>Process temperature</td>
<td>$I_{T}$</td>
<td>0–4</td>
</tr>
<tr>
<td>Process pressure</td>
<td>$I_{P}$</td>
<td>0–4</td>
</tr>
<tr>
<td>Equipment safety</td>
<td>$I_{EQ}$</td>
<td>0–3</td>
</tr>
<tr>
<td>Inside battery limits</td>
<td>$I_{sbl}$</td>
<td>0–4</td>
</tr>
<tr>
<td>Outside battery limits</td>
<td>$O_{sbl}$</td>
<td>0–3</td>
</tr>
<tr>
<td>Safe process structure</td>
<td>$I_{ST}$</td>
<td>0–5</td>
</tr>
</tbody>
</table>

2.3. Economic Indicators

Techno-economic evaluation is used to determine the economic viability of engineering projects. Two types of primary costs are evaluated: Total Capital Investment (TCI) and Operating Costs (OC) [28]. The total capital investment refers to the money needed for the purchase and installation of the plant; while the operations costs refer to the money needed to maintain the plant in operation once the production starts [29]. Return on investment is an economic indicator to evaluate the profitability of the processes, which is calculated by Equation (4).

$$\%\text{ROI} = \frac{\text{Annual profit after taxes}}{\text{TCI}} \times 100$$  \quad (4)

2.4. Exergy Indicators

Exergy is defined as the maximum work that can be performed from a system towards the equilibrium with the environment [30]. During a chemical transformation, exergy is destroyed by irreversibilities. These irreversibilities are quantified via exergy analysis, which also provides key indicators to improve process designs [31].

Exergy efficiency ($\eta_{\text{exergy}}$) indicates the process performance in terms of exergy flow. This indicator is calculated by Equation (5), where $\dot{E}_x_{\text{total, in}}$ is the total inlet exergy flow and $\dot{E}_x_{\text{destroyed}}$ is the total exergy destroyed (the difference between the total inlet and total outlet product exergy flow).

$$\eta_{\text{exergy}} = 1 - \left( \frac{\dot{E}_x_{\text{destroyed}}}{\dot{E}_x_{\text{total, in}}} \right)$$  \quad (5)

2.5. Environmental Indicators

Potential environmental impacts can be calculated via computer-aided tools such as WARGUI software, SIMAPro and TRACI 2.1 tool [32]. The Waste Reduction Algorithm (WAR) is a tool used to perform environmental analysis. It introduces the concept of Potential Environmental Impact (PEI) calculated by product mass unit (kilograms) or time (hours) [33]. The PEI is considered from two points of view output and generated; the PEI output can be calculated by Equations (6) and measures the environmental effects that the process emits [34].

$$I_{out}^{(t)} = I_{out}^{(cp)} + I_{out}^{(ep)} + I_{we}^{(cp)} + I_{we}^{(ep)} = \sum_j C_{p_j} I_{j, \text{out}} \sum_k X_{k_j} \Psi_k + \sum_j C_{p_j}^g I_{j, \text{out}} \sum_k X_{k_j} \Psi_k$$  \quad (6)
where \( I_{\text{out}}^{(cp)} \) and \( I_{\text{out}}^{(ep)} \) are the PEI output rates for the chemical process and the power generation process, respectively. \( I_{\text{in}}^{(cp)} \) and \( I_{\text{in}}^{(ep)} \) are the PEI associated with residual energy; \( M_j \) is the mass flow of the stream \( j \); \( X_a \) is the mass fraction of a component \( a \) in the stream \( j \); \( \Psi_k \) is the overall potential environmental impact of substance \( a \).

In addition, the WAR uses eight impact categories to evaluate a chemical process: Human Toxicity Potential by Ingestion (HTPI), Human Toxicity Potential by Inhalation Dermal Exposure (HTPE), Aquatic Toxicity Potential (ATP), Terrestrial Toxicity Potential (TTP), Global Warming Potential (GWP), Ozone Depletion Potential (ODP), Photochemical Oxidation Potential (PCOP) and Acidification Potential (AP) [35].

2.6. Sustainability Evaluation

The SWROIM metric is used to determine a single value that shows the overall sustainable performance of the chitosan production process from shrimp exoskeleton. The approach proposed in this study involves economic, energy, environmental, and safety parameters. The SWROIM calculation is given by Equation (7) [36].

\[
\text{SWROIM} = \frac{\text{AEP} \left[ 1 + \sum_{i=1}^{\text{Nindicators}} w_i \left( \frac{\text{Indicator}_i}{\text{Indicator}_{i, \text{Target}}} \right) \right]}{\text{TCI}}
\]

where AEP is the annual net profit of the project, \( w_i \) is the weighting factors of sustainability indicator \( i \), \( \text{Indicator}_i \) and \( \text{Indicator}_{i, \text{Target}} \) are the current and target values of sustainability indicator \( i \), respectively. The weighting factor \( w_i \) depends on the priority of the decision-makers [36].

3. Results and Discussion

3.1. Inherent Safety Analysis

The results are presented for the Chemical Inherent Safety Index (\( I_{\text{CI}} \)) and Process Inherent Safety index (\( I_{\text{PI}} \)).

The reactivity subindices are estimated by the exothermic grade of the main and side reactions. In the chitosan production system, main reactions take place in the demineralization, deproteinization, and deacetylation units, while the side reactions occur in the neutralization stages. Table 2 shows the chemical reactivity subindices assigned for deacetylation and neutralization stages.

| Main reaction | \( \text{C}_8\text{H}_{15}\text{NO}_6 + \text{NaOH} \rightarrow \text{C}_6\text{H}_{13}\text{NO}_5 + \text{C}_2\text{H}_3\text{NaO}_2 \) | \( \Delta H^0 = -4616.98 \text{ J/g}^a \) |
| Side reaction | \( \text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O} \) | \( \Delta H^0 = 7689.86 \text{ J/g}^a \) |
| \( I_{\text{RM, max}} \) | 4 | Exothermic |
| \( I_{\text{RS, max}} \) | 0 | Endothermic |

\(^a\) Value estimated by the author.

The chemical interaction subindex \( I_{\text{INT,max}} \) refers to the chemical reactivity between substances in the plant including air or water. In this case, the worst chemical interaction involves the formation of flammable gases. Calcium chloride is present in the process, and upon contact with water, flammable vapors are released. Based on these possible scenarios, a score of 3 was assigned to this factor. The subindex of dangerous chemical substances is calculated for each component with information related to flammability, toxicity, and explosiveness properties. The flashpoint, TLV (8-h Threshold Limit Value), and explosive limits were gathered from safety data sheets. Among all the substances present in the chitosan production from shrimp exoskeleton, ethanol employed in the depigmentation stage achieves the highest value in the general danger subindex; therefore, it is the most dangerous substance within the process. Other substances within the process showed to be safe due to their non-flammability, non-toxicity, and non-explosiveness nature. Table 3 shows the results obtained for the dangerous substance safety subindex.
Table 3. Safety parameters for dangerous substances.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Ethanol (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flash point (°C)</td>
<td>13.9</td>
</tr>
<tr>
<td>TLV (ppm)</td>
<td>530.71</td>
</tr>
<tr>
<td>(UEL − LEL)(_{\text{VOL}}%)</td>
<td>11.5</td>
</tr>
<tr>
<td>(I(<em>{\text{TOX}}) + I(</em>{\text{FL}}) + I(<em>{\text{EX}}))(</em>{\text{max}})</td>
<td>6</td>
</tr>
</tbody>
</table>

\(^a\) Data reproduced from [37].

On the other hand, the corrosivity subindex evaluates the type of equipment construction material according to the substances handled; this parameter is defined considering the requirements for processing units. Table 4 lists a description of the equipment used for chitosan production. Stainless steel was considered as the main construction material due to the presence of corrosive substances in different stages (e.g., chlorides and sodium hydroxide). Therefore, a score of 1 is assigned to this subindex. The inherent chemical inherent safety index was estimated at 14 as depicted in Figure 4.

Table 4. Description of the main equipment used for chitosan production from shrimp exoskeleton.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Type of Unit</th>
<th>Temperature (°C)</th>
<th>Pressure (kPa)</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Washing 1</td>
<td>Tank</td>
<td>25</td>
<td>101.32</td>
<td>Carbon steel</td>
</tr>
<tr>
<td>Drying 1</td>
<td>Dryer</td>
<td>107</td>
<td>101.32</td>
<td>Carbon steel</td>
</tr>
<tr>
<td>Crushing</td>
<td>Crusher</td>
<td>25</td>
<td>101.32</td>
<td>Carbon steel</td>
</tr>
<tr>
<td>Depigmentation</td>
<td>Mixer</td>
<td>25</td>
<td>101.32</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>Demineralization</td>
<td>Reactor</td>
<td>25</td>
<td>101.32</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>Neutralization 1</td>
<td>Reactor</td>
<td>25</td>
<td>101.32</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>Washing 2</td>
<td>Tank</td>
<td>25</td>
<td>101.32</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>Deproteinization</td>
<td>Reactor</td>
<td>90</td>
<td>101.32</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>Neutralization 2</td>
<td>Reactor</td>
<td>25</td>
<td>101.32</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>Washing 3</td>
<td>Tank</td>
<td>25</td>
<td>101.32</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>Deacetylation</td>
<td>Reactor</td>
<td>110</td>
<td>101.32</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>Neutralization 3</td>
<td>Reactor</td>
<td>25</td>
<td>101.32</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>Washing 4</td>
<td>Tank</td>
<td>25</td>
<td>101.32</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>Drying 2</td>
<td>Dryer</td>
<td>100</td>
<td>101.32</td>
<td>Stainless steel</td>
</tr>
</tbody>
</table>

The process inherent safety index requires information associated with operating conditions, inventory, equipment type, and process structure. The temperature and pressure subindices were determined according to the maximum temperature and pressure conditions for each stage. For instance, the highest temperature reached in the deacetylation stage is 110 °C, and the pressure is kept at atmospheric conditions (101.32 kPa). Therefore, a score of 4 is assigned to the temperature subindex and 1 to the pressure subindex. The inventory subindex calculates the mass contained in any process equipment (tanks, reactors, mixers, and others) for a hydraulic retention time of 1 h [38]. A total inventory of 1500 tones was calculated for the inside battery limits; the outside battery limits were not considered in the inventory calculation due to the main processing units belonging to Isbl. A score equal to five was assigned to the inventory subindex.

Another important parameter for calculating the inherent safety of the process is the equipment safety subindex. Based on the features of the equipment reported in Table 4, I\(_{\text{EX}}\) is assigned according to the most dangerous operational equipment. In this process, the reactors and dryers are the equipment with the highest potential risks; therefore, a value of two is assigned for this subindex. Finally, the safe structure subindex is determined by considering historical data and reports from heuristics and engineering experience of well-known processes [38]. However, there is no historical information related to the safety of a chitosan production process from shrimp exoskeleton, hence a neutral position is assumed. A score of two is assigned for this subindex which refers to novel or emerging large-scale processes. The process safety index was calculated at 11 as shown in Figure 5.

![Figure 4. Subindices and total score for chemical inherent safety index.](image-url)
achieved by the system. The maximum temperature is reached in the deacetylation stage, where the reactor operates at 110 °C, and consequently, a score of 1 was assigned. Further, the operational pressure was kept at atmospheric (101.32 kPa), which represents a no risky condition. The inventory subindex measures the mass contained in any process equipment (tanks, reactors, mixers, and others) for a hydraulic retention time of 1 h [38]. A total inventory of 1500 tones was calculated for the inside battery limits; the outside battery limits were not considered in the inventory calculation due to the main processing units belongs to Isbl. A score equal to five was assigned to the inventory subindex.

Another important parameter for calculating the inherent safety of the process is the equipment safety subindex. Based on the features of the equipment reported in Table 4, $I_{EQ}$ is assigned according to the most dangerous operational equipment. In this process, the reactors and dryers are the equipment with the highest potential risks; therefore, a value of two is assigned for this subindex. Finally, the safe structure subindex is determined by considering historical data and reports from heuristics and engineering experience of well-known processes [38]. However, there is no historical information related to the safety of a chitosan production process from shrimp exoskeleton, hence a neutral position is assumed. A score of two is assigned for this subindex which refers to novel or emerging large-scale processes. The process safety index was calculated at 11 as shown in Figure 5.

![Figure 5. Subindices and total score for chemical inherent safety index.](image)

As shown in Table 5, the total inherent safety index was 25. According to Heikkilä [15], processes with $I_T$ higher than 24 are considered unsafe. These results reveal that the chitosan production from shrimp exoskeleton is inherently unsafe. The main process chemical risks were found in the depigmentation stage during ethanol storage, transport, and handling because of its high flammability, and in the deacetylation stage, given the exothermic reaction that takes place. Besides, the process handles large amounts of materials representing a stressed factor for the safety of the plant; inventory is a major critical and risky operational variable.

### Table 5. Total inherent safety index.

<table>
<thead>
<tr>
<th>Index</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_C$</td>
<td>14</td>
</tr>
<tr>
<td>$I_P$</td>
<td>11</td>
</tr>
<tr>
<td>$I_T$</td>
<td>25</td>
</tr>
</tbody>
</table>

Comparing these results with those obtained for a levulinic acid production process via acid-catalyzed ($I_T = 24$) [38] and a bioethanol production process ($I_T = 23$) [39], it was found that the process under study has a lower safety performance. Although
substances of equal risk potential such as ethanol are involved and exothermic reactions are performed, these two processes handle lower inventories. For the chitosan production from shrimp exoskeleton, it is recommended to evaluate the use of less dangerous solvents in the depigmentation stage or to establish strategies for its safe handling. Both depigmentation and deacetylation stages require design modifications that minimize the risk associated with explosions or fires [40].

3.2. Sustainability Evaluation

Sustainability is evaluated considering the following sustainability indicators: return on investment, the total inherent safety index, the exergy efficiency, and the total PEI output. The %ROI for chitosan production was gathered from the techno-economic sensitivity analysis developed by Cogollo-Herrera et al. [14]. The techno-economic sensitivity evaluation was carried out considering the United States dollar (USD) as the official currency, the useful life of the plant equal to 15 years, salvage value of 10%, construction time of three years, 20 USD/h for the salary per operator, a discount rate of 8.7%, and a percentage of the contingency of 20%. The key results are shown in Figure 6. According to the results, the %ROI of 18.08% reveals that the process is economically attractive. However, this process reported lower %ROI compared to those achieved for a shrimp-based biorefinery (65.88%) [25] and a process for crude palm and kernel oil production (41.16%) [41]. Gómez-Ríos et al. [42] also performed the techno-economic analysis of chitosan production from shrimp wastes. The authors obtained an internal rate of return of 25.5% for a batch processing of 1 t/cycle of fresh shrimp waste. From the techno-economic sensitivity analysis, it is possible to implement improvements that include increasing the selling price of chitosan and reducing operating costs.

Figure 6. Summary of Economic Evaluation Results for the chitosan production from shrimp exoskeleton. Adapted from: [14].

The potential environmental impact output was gathered from the environmental analysis performed by Meramo-Hurtado et al [13]. The key data and assumptions used in the environmental assessment include the use of oil and the evaluation of energy and product stream contributions. As shown in Figure 7, the process is friendly to the
environment due to the negative rates of total PEI generation. The potential environmental impact output reached around 22,466.46 PEI/h.

![Graph](image.png)

**Figure 7.** Total generated and output rates of potential environmental impact (PEI) for chitosan production from shrimp exoskeleton. Adapted from: [13].

Figure 8 depicts the output rate of PEI per impact category. Human toxicity potential by ingestion (HTPI), terrestrial toxicity potential (TTP), and photochemical oxidation potential (PCOP) were the impact categories that most contributed to the total PEI output due to the use of toxic chemicals such as ethanol, HCl, and NaOH in output streams. The global warming potential (GWP) was the second lowest value with 4.46 PEI/h.

![Graph](image.png)

**Figure 8.** Categories environmental impacts for chitosan production from shrimp exoskeleton (* 10^2). Adapted from: [13].

The exergy analysis revealed that the process leads to large amount of irreversibilities due to the high exergy of wastes (1,008,733.92 MJ/h). As shown in Figure 9, the overall exergy efficiency (4.58%) revealed inefficiencies in the system. From the energy viewpoint, it is recommended to implement technical improvements in the most critical stages (de-pigmentation and deacetylation). Improvements include the recovery of astaxanthin and residual ethanol, along with the heat released in the deacetylation reaction.

![Graph](image.png)
The SWROIM is applied to evaluate the sustainability of the chitosan production process from shrimp exoskeletons. The target value for the inherent safety index was considered as 24 because it describes processes with neutral performance in terms of inherent risks. An ITI equal to or lower than 24 is achieved by eliminating the most hazardous chemicals and the riskiest operations within the process.

For exergy efficiency, a target value was set at 90%. In a chemical process, the destruction of exergy could be avoided through the recovery of wastes and energy released in the different stages. These strategies increase the efficiency towards desired outcomes. Environmental impact reduction enables the development of sustainable processes; for chitosan production, a reduction of 50% of the PEI output is considered as a targeting. Through the recovery of the output streams which contain environmentally harmful substances, the potential environmental impact emitted to the media can be reduced. The weights $w_{\text{safety}}$, $w_{\text{PEI Output}}$, and $w_{\text{exergy}}$ are considered equal to one, assuming same importance of environmental conservation, reduction in energy consumption, and risk mitigation in the development of sustainable processes. Table 6 shows the indicators, target indicators, and weighting factors associated with each technical parameter.

Table 6. Targeting and weighting factor for each technical parameter.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Index</th>
<th>Indicator$^i$</th>
<th>Indicator$^\text{target}$</th>
<th>$W_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Safety</td>
<td>Total inherent safety index (ITI)</td>
<td>25</td>
<td>24</td>
<td>1</td>
</tr>
<tr>
<td>Energy</td>
<td>Exergy efficiency (%)</td>
<td>4.58</td>
<td>90</td>
<td>1</td>
</tr>
<tr>
<td>Environmental</td>
<td>PEI output rate (PEI/h)</td>
<td>22,466.46</td>
<td>11,233.23</td>
<td>1</td>
</tr>
</tbody>
</table>

The results for the sustainability evaluation of this case study are depicted in Figure 10. The project achieved a sustainable performance of 36.33% which is higher than the value obtained for the return on investment (18.08%). This result suggests that the evaluated technical parameter had positive effects that yield the economic performance of the plant. Notably, there is a positive contribution associated with the reduction of total PEI output, an increase in exergy efficiency, and a reduction of inherent process risks. The chitosan production has a higher sustainable performance compared to the SWROIM (27.29%) of a lignocellulosic multi feedstock biorefinery, where economic, safety, energy, and environmental parameters were evaluated [18].
To evaluate the effect of each technical parameter on the SWROIM, a sensibility analysis was performed by modifying the weighting factors. Three case studies were considered:

Case 1: $w_{\text{safety}} = 0.5; w_{\text{PEI Output}} = 0.5; \text{and } w_{\text{exergy}} = 1.0$

Case 2: $w_{\text{safety}} = 0.5; w_{\text{PEI Output}} = 1.0; \text{and } w_{\text{exergy}} = 0.5$

Case 3: $w_{\text{safety}} = 1.0; w_{\text{PEI Output}} = 0.5; \text{and } w_{\text{exergy}} = 0.5$

As shown in Figure 11, environmental parameter most contributed to SWROIM metric, considering the economic and environmental factor of equal relevance. The highest value is obtained (45.28%) given that the environmental conditions of the process are favorable. On the other hand, the safety indicator showed to lower contribution to the SWROIM. For future studies, other technical parameters can be included depending on process nature such as green solvent consumption to broaden the sustainability analysis.

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**Figure 10.** ROI and SWROIM for chitosan production from shrimp exoskeleton.

**Figure 11.** SWROIM sensibility analysis.
4. Conclusions

In this study, the inherent safety analysis and sustainability evaluation for the chitosan production process was performed using the inherent safety index methodology and the sustainable weighted return on investment metric, respectively. Economic, safety, energy, and environmental technical parameter were considered to evaluate the sustainability of the process. The economic, energy, and environmental indicators were obtained from the previous works performed by the authors. The total inherent safety index was estimated at 25, which indicates that the process is inherently unsafe. The main chemical risks were identified in the depigmentation stage due to the use of ethanol which is a flammable substance and in the deacetylation reaction because it is extremely exothermic. The inventory indicator was the most critical variable within the process in terms of safety. The SWROIM showed a yield of 36.33% which reveals that the technical parameters evaluated have a positive effect on the return on investment of the process. The environmental parameter was the most determinant in this result given the good environmental performance described by the process. However, future studies need to be carried and other essential parameters can be considered concerning process characteristics and model objectives to allow a broader sustainability analysis. Furthermore, the application of process intensification techniques might positively contribute to the ongoing development of this sector.


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References


12. Dalei, J.; Sahoo, D. Extraction and characterization of astaxanthin from the crustacean shell waste from shrimp processing industries. Int. J. Pharm. Sci. Res. 2015, 6, 2532–2537. [CrossRef]

13. Meramo-Hurtado, S.I.; Alarcón-Suesca, C.; González-Delgado, Á.D. Exergetic sensibility analysis and environmental evaluation of chitosan production from shrimp exoskeletons in Colombia. [CrossRef]


32. Zuorro, A.; Lavecchia, R.; Gonzalez-Delgado, A.D.; Garcia-Martinez, J.B.; L’Abbate, P. Optimization of enzyme-assisted extraction of flavonoids from corn husks. Processes 2019, 7, 804. [CrossRef]

