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Inherent safety assessment of a valorization alternative for shrimp wastes under the concept of biorefinery

Evaluación de la seguridad inherente de una alternativa de valorización de residuos de camarón bajo el concepto de biorefinería

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ABSTRACT

This research is focused on the safety analysis of a preliminary design for a pilot-scale shrimp biorefinery through the Inherent Safety Index (ISI) method. This approach analyzes hazards associated with chemicals and process conditions covering several safety aspects. The chemical approach encompasses the heat released by the reactions, the chemical interaction between substances, their toxicity, explosiveness, flammability, and corrosivity while the process approach covers the amount of inventory handled, maximum working temperature and pressure, equipment safety, and the process structure. In all cases, subindexes were determined considering the worst possible scenario. The results show that the biorefinery is inherently safe by obtaining an ISI of 21 points, with chemical and process safety indices of 15 and 6, respectively. The indicators that stood out were the heat of reaction associated with the deacetylation of chitin as it is highly exothermic, and the flammability of acetone as the most dangerous substance in the process.

Keywords*:* Biorefinery; Shrimp shells; Process Safety; Inherent Safety Index.

RESUMEN

Esta investigación se enfocó en la evaluación de seguridad de un diseño preliminar de una biorefinería de camarón a escala piloto a través del método de Índice de Seguridad Inherente (ISI). Este enfoque analiza riesgos asociados a variables de las sustancias químicas utilizadas y a condiciones operativas del proceso, abarcando muchos aspectos de la seguridad. El enfoque químico abarca el calor liberado por las reacciones, la interacción química entre sustancias, y la toxicidad, explosividad, inflamabilidad y corrosividad de ellas mientras que el enfoque de proceso cubre la cantidad de inventario manejado, temperatura y presión máximas trabajadas, la seguridad de equipos utilizados y la estructura del proceso. En todos los casos se determinan los subíndices considerando el peor escenario posible. Los resultados muestran que la biorefinería es inherentemente segura al obtener un ISI de 21 puntos, con índices de seguridad químico y de procesos de 15 y 6, respectivamente. Los indicadores que sobresalieron fueron el calor de reacción asociado a la desacetilación de la quitina al ser altamente exotérmica, y la inflamabilidad de la acetona como la sustancia más peligrosa en el proceso.

Palabras clave: Biorefinería, Cáscara de camarón, Seguridad de Procesos, Índice de Seguridad Inherente.

1. INTRODUCTION

The use and recovery of aquaculture waste is a topic that has acquired great interest in recent decades due to the economic, social and environmental benefits associated with this practice [1]. In particular, the shrimp sector has shown a constant increase in world production of farmed shrimp, with almost 4 million tons reported in 2018 [2] and, considering that shrimp for consumption is generally sold headless without shell, around 45-48% by weight of shrimp is discarded as waste from this industry [3]. However, the adequate processing of shrimp waste allows the recovery of value-added biomaterials, such as chitin, astaxanthin, proteins, lipids, among others, which have a wide spectrum of applications in industries as varied as agriculture, food, medical, pharmaceutical, textile and sanitary [4]. In this way, environmental contamination related to shrimp waste could be minimized and at the same time maximize profits [5].

The foregoing allows establishing the pertinence of a biorefinery based on shrimp, where the meat of the mollusk is obtained as the main product, and its shell is used to obtain other products. Biorefineries are distinguished as an alternative to transform biomass into marketable food, products (chemicals, materials) and energy [6], where sustainability has become a central topic for the development of the bioeconomy and future biorefinery systems [7]. This encompasses the integral balance of three dimensions: economic, environmental and social, where the low performance of one could affect the performance of the others [8].

In the chemical industry, the social dimension of sustainability is mainly referred to the process safety analysis, covering aspects such as chemical safety, potential process toxicity, process equipment safety, among others. The aim of safety analysis is to identify potential accident conditions, assess the risk and identify measures to mitigate or eliminate the risk [9]. There are a variety of safety analysis methods. Among the most important to identify hazards are the Dow Fire and Explosion Index, F&E; the Prototype Index of Inherent Safety, PIIS; the Inherent Safety Index, ISI; the Integrated Inherent Safety Index, I2SI; and the Hazard and Operability (HAZOP) analysis. Each of these tools can be differentiated according to its goal, focus, structure and/or the safety aspects considered [9, 10].

Several studies have been conducted to assess existing and emerging technologies based on safety analysis. Rathnayaka et al. [11] proposed the Risk-based Inherent Safety Index, RISI, a risk-based design decision-making tool considering inherent safety. Song et al. [12] formulated a framework and method for the assessment of inherent safety to enhance sustainability in conceptual chemical process design. Meramo et al. in 2019 [13] carried out the environmental and safety assessments of industrial production of levulinic acid via acid-catalyzed dehydration; in 2020 [14] carried out the synthesis and sustainability evaluation of a lignocellulosic multifeedstock biorefinery considering environmental, economic and safety indicators.

The inherent safety index, ISI, proposed by Heikkilä [15], stands out for requiring little information for its calculation compared to other safety analysis methods, which makes it suitable to be applied in the preliminary stages of process design. [16]. Considering the importance of evaluating the processes from their conceptual design under sustainability indicators, this research focused on the safety assessment of a pilot-scale shrimp-based biorefinery using the ISI method to determine its inherent safety and potential risks.

2. METHODS

2.1. Process description

A preliminary design of a shrimp biorefinery was performed to process 4,534 tons of fresh shrimp, equivalent to the farmed shrimp rate in north Colombia in 2018 [17]. It consists of a section shrimp meat production and another for shrimp shells processing to obtain by-products. *Figure 1* shows the block diagram of the process. In principle, the fresh shrimp is washed with a mixture of water and ice, with a concentration of sodium metabisulfite of 8% to avoid crustacean melanosis [18]. Once the shrimp are cleaned, broken or stained ones are removed from the stream, the shrimp in good condition are beheaded and peeled to obtain the shrimp meat for consumption.

The exoskeleton removed during peeling, goes through a process of washing, drying and crushing. The crushed shell, which is about 0.5 mm [19] is then subjected to a depigmentation stage, where ethanol 85% serves as a solvent to extract the astaxanthin present in the stream, the residual ethanol-pigment mixture passes through another stage of depigmentation, using acetone this time. Next, the astaxanthin is purified by centrifugation and evaporation as a value-added product.

Furthermore, the crushed exoskeleton stream leaving the first stage of depigmentation passes through stages of demineralization and deproteinization, each followed by washing and neutralized units where it is washed until the pH is about 7. In the demineralization stage, the carbonates present in the exoskeleton are transformed into chlorides, while in the deproteinization the proteins are removed from the stream by NaOH adding [20]; the waste stream obtained has a high nitrogen content so it can be sold as a nitrogenous extract, useful in agriculture as a base for fertilizers.

At this point, the process stream leaving the deproteinization reactor consists mostly of chitin, so half of the stream is sent to purification steps to be traded. The other half goes to the deacetylation reactor, where chitin at high temperatures and a basic environment, achieved by the addition of NaOH, is transformed into chitosan by acetyl groups removing [21]. Finally, this biopolymer is washed and dried to be sold as a value-added product, which due to its properties stands out for being very versatile in its applications [22].

2.2. Safety analysis of the Shrimp-based biorefinery

The safety analysis of the biorefinery was performed based on the calculation of the Inherent Safety Index which constitutes a correct methodology to establish the level of risk associated with the safety of an industrial chemical process, ideal to apply in the conceptual design stage. This methodology requires calculations based on the worst-case scenario that may arise, so the dangers intrinsic to the process can be identified and an adequate level of safety can be achieved with minimum layers of protection. The higher the value of the index obtained (up to 24), the more insecure the process is [23].

Eq. (1) states the two components that make up the Total Inherent Safety Index ($\mathrm{I_{TI}}$) these are, the Chemical Inherent Safety Index ($\mathrm{I_{CI}}$) and the Process Inherent Safety Index ($\mathrm{I_{PI}}$).

$$I_{TI} = I_{CI} + I_{PI} \tag{1}$$

The I_{CI} and I_{PI} are subdivided in different categories receiving a score. *Table 1* shows score ranges established by eight experts in different fields considering aspects inherent safety for each index, assigning their score by their relative importance [15].

Figure 1. Simplified process diagram of Shrimp-based biorefinery.

Figura 1. Diagrama de proceso simplificado de una biorefinería de camarón.

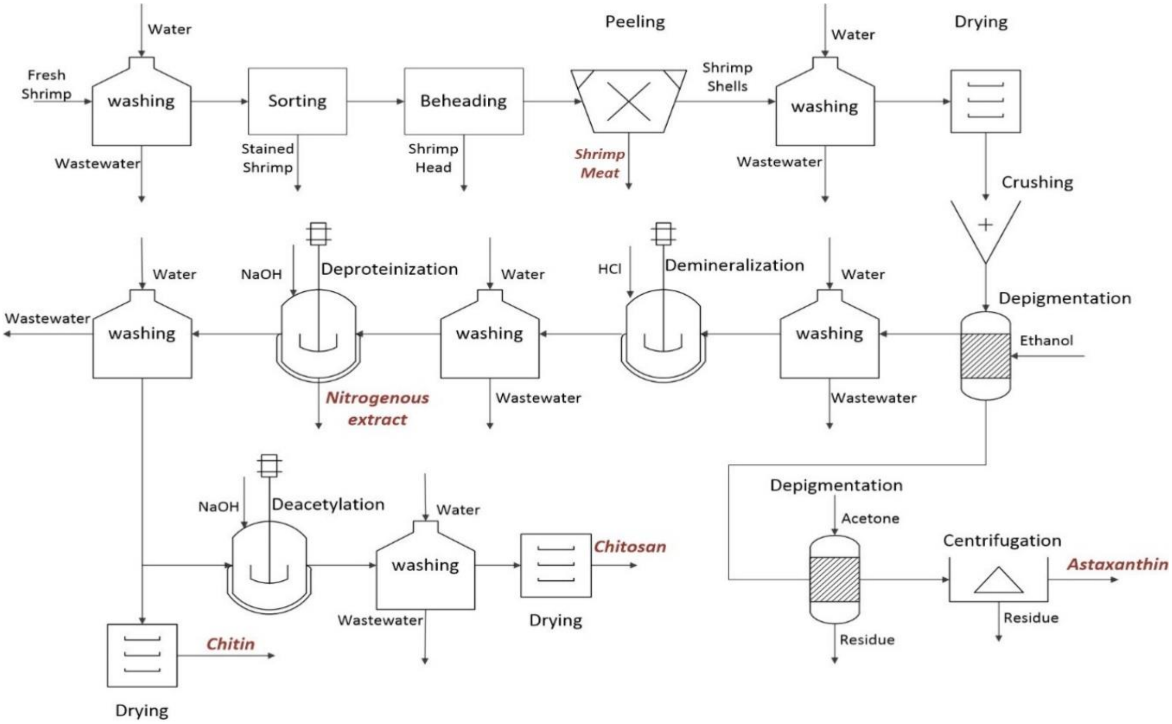


Table 1. Scores for Inherent safety sub-indexes.

Tabla 1. Puntuaciones para los subindices de seguridad inherente.

Chemical inherent safety index (I_{CI})	**Symbol**	**Score**
Heat of main reaction	I_{RM}	0-4
Heat of side reaction	I_{RS}	0-4
Chemical interaction	I_{INT}	0-4
Flammability	I_{FL}	0-4
Explosiveness	I_{EX}	0-4
Toxic exposure	I_{TOX}	0-6
Corrosiveness	I_{COR}	0-2
Process inherent safety index (I_{PI})		
Inventory	I_{I}	0-5
Process temperature	I_{T}	0-4
Process pressure	I_{P}	0-4
Equipment safety	I_{EQ}	
Inside battery limits (Isbl)		0-4

Outside battery limits (Osbl)		0-3
Safe process structure	I_{ST}	0-5

3. Results and discussion

The safety assessment of the shrimp-based biorefinery was carried out using the ISI method, where the worst possible scenario was assumed for indicator calculation. The total inherent safety index was calculated as the sum of the chemical inherent safety index and the process inherent safety index.

3.1. Chemical inherent safety index

This index is associated with the chemical factors of the substances involved in the process that could represent a risk, such as flammability, explosiveness, toxicity, corrosivity and chemical reactivity [15]. It is calculated by Eq. (2)

$$I_{CI} = I_{RM,max} + I_{INT,\text{máx}} + (I_{TOX} + I_{FL} + I_{EX})_{max} + I_{COR,\text{máx}} \qquad (2)$$

The first term of Eq. (2) refers to the chemical reaction safety subindex, $I_{RM,max}$, that takes into account the enthalpy of formation of the substances involved which is directly associated with the exothermic degree of the reactive system. It was found that the most exothermic main reaction in the biorefinery corresponds to the deacetylation reaction, where chitin is transformed into chitosan by removing the acetyl groups present in it [21]. Table 2 shows the reaction that occurs in this stage and the heat of reaction associated with it, this value indicates that the reaction is extremely exothermic, therefore a value of 4 was assigned to the $I_{RM,max}$.

Table 2. Heat of reaction in deacetylation unit.

Tabla 2. Calor de reacción de la reacción principal de la unidad de desacetilación.

Main reaction	Heat of reaction
$C_8H_{15}NO_6 + NaOH \rightarrow C_6H_{13}NO_5 + C_2H_3NaO_2$	$\Delta H_{\circ} = -4{,}617\ J/g$

The chemical interaction index of the species takes into account unwanted reactions that could develop due to the interaction of the substances among themselves or with plant materials. For this case, it was established that riskiest interaction was the formation of flammable gases due to the presence of calcium chloride in the process which releases flammable vapors in contact with water, setting an interaction subindex as $I_{INT,\text{máx}} = 3$.

Additionally, a global safety subindex was developed to measure dangerous chemical substances, $(I_{TOX} + I_{FL} + I_{EX})_{max}$, which allows establishing the potential inherent risk to toxicity, I_{TOX}, flammability, I_{FL}, and explosiveness, I_{EX}, of chemical substances. They are calculated for each compound involved in the process, added individually and the maximum sum is used as the global dangerous substances index value [15]. The values of the flashpoint, TLV and explosive limits were consulted in the safety data sheets of each substance. The TLV refers to the threshold limit value, an indicator commonly used in the evaluation of chemical substances toxicity, it is defined as the maximum concentration of a compound in the air that can be breathed during five consecutive working days of 8 hours without harmful effects [15]. Among all the compounds present in the biorefinery, acetone and ethanol were identified with the highest value in the general danger subindex. As shown in *Table 3*, both substances have equal value in the toxicity and explosiveness subindexes, however, when considering for the flammability index, acetone has a much lower flashpoint than ethanol, it is rated highly flammable with a flash point less than zero °C. Thus, acetone is considered the most dangerous substance in the process, therefore, the general safety index for dangerous substances will take a value of 7 [15].

Table 3. Safety parameters for dangerous substances.

Tabla 3. Parámetros de seguridad para las sustancias peligrosas.

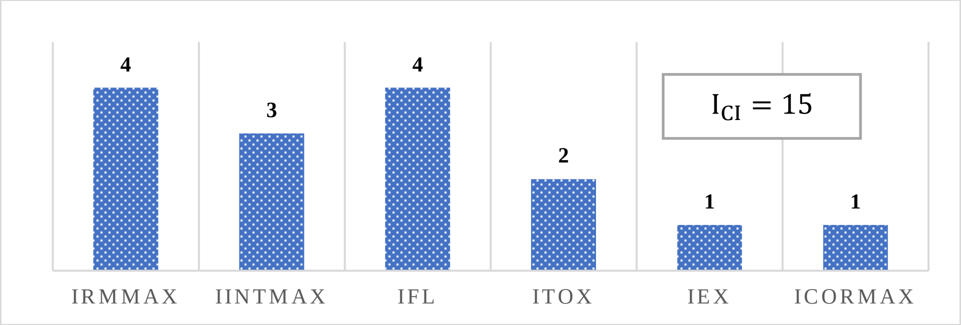
Substance	Acetone	Ethanol
TLV (ppm)	500	1,000
I_{TOX}	2	2
Flash point (°C)	-10	12
I_{FL}	4	3
$(UEL - LEL)_{VOL\%}$	10.8	11.5
I_{EX}	1	1
$(I_{TOX} + I_{FL} + I_{EX})_{max}$	7	6

Now, the last parameter to consider, for the calculation of the chemical inherent safety index corresponds to the corrosion subindex, $I_{COR,máx}$, which is directly associated with the construction material required in the biorefinery. For this, the materials that could be used with each chemical were consulted in chemical compatibility tables. Due to the presence of corrosive substances, such as sodium bisulfite, chlorides and NaOH, some equipment required stainless steel as the material, therefore, $I_{COR,máx}$=1.

According to the above, chemical inherent safety index of the process, calculated with Eq. (2), has a value of 15.

Figure 2. Calculated subindexes for chemical inherent safety index and total score.

Figura 2. Subíndices calculados para el índice de seguridad inherente químico y puntuación total.



From the indicators shown in Figure 2, the importance of the compounds involved in the process can be noted. The highest values were obtained for the main reaction and flammability, because the chitosan formation reaction is highly exothermic and the most dangerous substance (acetone) is highly flammable. To decrease the value of the I_{CI} the use of a less dangerous solvent than acetone could be evaluated in the second depigmentation stage such as deep eutectic acid.

3.2. Process inherent safety index

This parameter, I_{PI}, expresses the safety of the equipment and the operating conditions of the process itself, it involves subindexes related to the inventory managed, operating temperature and pressure, safety equipment and structure of the process [15]. The expression used to calculate this index is shown below in Eq. (3).

$$\mathrm{I_{PI}} = \mathrm{I_I} + \mathrm{I_{T,máx}} + \mathrm{I_{P,máx}} + \mathrm{I_{EQ,máx}} + \mathrm{I_{ST,máx}} \tag{3}$$

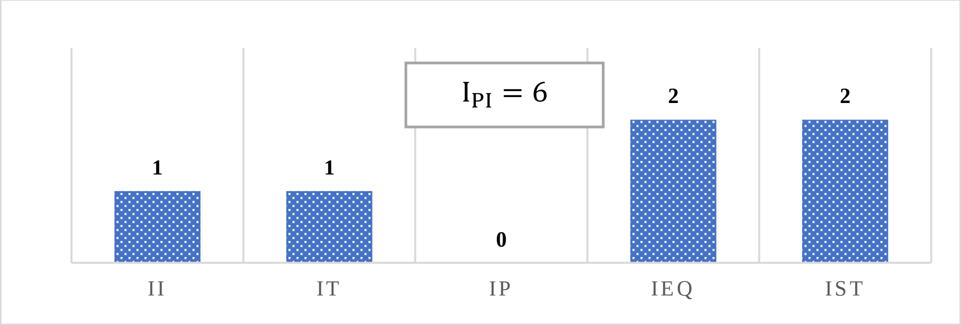
The inventory subindex, $\mathrm{I_I}$, is defined according to the mass flows handled by the process considering that large inventories in one place are unfavorable in the event of fire or the rupture of a vessel (15). The total inventory of the biorefinery located in North Colombia was calculated as the sum of all the feed flows entering the plant in one hour. These flowrates were calculated according to the total fresh shrimp production and reagents consumption leading to 6.2 t/h, which is equivalent to an inventory indicator equal to 1.

For the most part, the shrimp biorefinery operates at environmental conditions, however, it has a maximum temperature of 110 ° C in the deacetylation reactor, which gives it an $\mathrm{I_{T,máx}}$ value of 1. In any case, the pressure of the process is maintained under conditions close to 1 atm, so no danger related to the working pressure in the system is associated and this subindex is equal to zero.

Another very important factor regarding the safety of the process is associated with the reliability of the equipment used, the scale taken for this indicator considers furnaces as the most dangerous equipment and those that handle non-flammable and toxic materials as the safest equipment, in this order of ideas, the presence of reactors distributed throughout the plant sets the process in an intermediate place in terms of equipment safety (see Figure 1), with a value of $\mathrm{I_{EQ,máx}}$ equal to 2. Finally, the safe process structure refers to the description of process safety from the engineer's point of view, it describes how two equipment, units or processes work together and how they must be connected and controlled together [15]. The fact that there is no information about how safe a shrimp-based biorefinery is suggested a neutral position that is reflected in an $\mathrm{I_{ST,máx}}$= 2; however, additional studies must be performed to validate this assumption . Once all the required subscripts have been obtained, the process inherent safety index is calculated with the Eq. (3), the final result is $\mathrm{I_{PI}}$=6.

Figure 3. Calculated subindexes for process inherent safety index and total score.

Figura 3. Subíndices calculados para el índice de seguridad inherente de proceso y puntuación total.



According to *Figure 3*, the parameters that had the greatest representation in calculating the process inherent safety index were those associated with equipment safety and process temperature, due to the risk that is intrinsically linked to reactors and high temperatures managed in the process.

3.3. Total inherent safety index

From the results obtained for the chemical and process inherent safety indices, the total inherent safety index, $\mathrm{I_{TI}}$,, can be calculated with Eq. (1). For a process to be considered safe, an SIS value less than 24 is recommended [15], therefore, it can be stated that the current design of the biorefinery is inherently safe.

Table 4. Inherent Safety Index calculated for the Shrimp-based biorefinery.
Tabla 4. Indicé de seguridad inherente calculado para una biorefinería de camarón.

Index	Score
I_{CI}	15
I_{PI}	6
I_{TI}	21

Now, when comparing the ISI result obtained in this research with the ISI reported by other biorefineries, it is observed that it has better performance. A biorefinery for the industrial production of levulinic acid via acid-catalyzed dehydration [13] showed a safety-neutral performance, with an ISI equal to 24. While a lignocellulosic multifeedstock biorefinery [14] obtained an ISI of 36 in its safety evaluation, showing that process as risky. Both consulted biorefineries were presented as industrial processes, therefore, the inventories managed are much greater than that managed by a pilot plant such as the proposed biorefinery, and considering that the amount of substances present in the plant has a great effect on the degree of threat [15], a process with less inventory is considered safer. Besides, the biorefineries consulted have pressurized equipment that handles up to 24.67 and 32 atm, this confers less safety to the process than working at low pressures, such as the shrimp biorefinery by working at atmospheric pressure. Finally, it should be noted that the biorefinery of multiple lignocellulosic feeds has process stages that operate with extremely high temperatures, up to 750 ° C, which influences that the plant is not considered safe.

4. CONCLUSIONS

- This work analyzed the safety performance of a preliminary design for a pilot-scale shrimp biorefinery that obtains shrimp meat and value-added products from the processing of the shell of the crustacean, using the inherent safety index method to evaluate the social component of sustainability for this process. The biorefinery was designed to process 4,534 t / year of fresh shrimp. Overall, the process performed well in terms of inherent safety, with chemical and process inherent safety indices equal to 15 and 6, respectively. The highest subindex values corresponded to the heat of reaction released by the chitin deacetylation and the acetone flammability, which is the most dangerous substance in the process; both subindexes are associated with the chemical component of ISI. The evaluation of a solvent different than acetone in the second depigmentation could improve the intrinsic safety of the process. However, with a total inherent safety index of 21, it is reasonable to affirm that this process is inherently safe as it has an ISI of less than 24, as recommended. As future work, the incorporation of green solvents in depigmentation stages must be analyzed to enhance the inherent safety performance of the biorefinery.

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