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Ecological soap production using green chemistry principles

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ABSTRACT. The reuse of fatty materials for soap production is considered a viable alternative to minimize environmental problems such as the eutrophication of lakes and rivers and to reduce the high costs of effluent treatment and domestic water supply. This research presents protocols for ecological soap production from the determination of the saponification index (SI) using the principles of Green Chemistry. The chemical greenness of the produced soap was assessed using mass and holistic metrics. The SI measurement ensured a final product without residues, aligning with the principles of Green Chemistry: principle 1 (waste prevention) with a Factor E of 0 and an Atomic Economy of 100%. Additionally, the Green Matrix and Green Star analyses demonstrated a more sustainable experimental approach for bar soap production, with 45% higher greenness compared to traditional soap and 95% greenness for ash soap. The changes in the saponification process by the principles of green chemistry allowed ecological soap production without residues, an innocuous product to health and the environment. The methodology proposed in this research can contribute to minimizing an environmental problem related to the incorrect disposal of non-biodegradable oil.

Keywords: saponification reaction; sustainability; environmental chemistry; green chemistry; green matrix; green star.

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Introduction

Soap is a commonly utilized cleaning agent. According to Silva and Puget (2010), soap is produced through a process called saponification which involves alkaline hydrolysis using sodium hydroxide (NaOH) or potassium hydroxide (KOH), along with a specific type of ester known as triglycerides. The saponification reaction occurs in multiple stages. In the initial step, the bonds in the triglyceride molecule are broken through alkaline hydrolysis. The subsequent step leads to the formation of glycerol and an organic salt, shown in the mechanism of Figure 1:

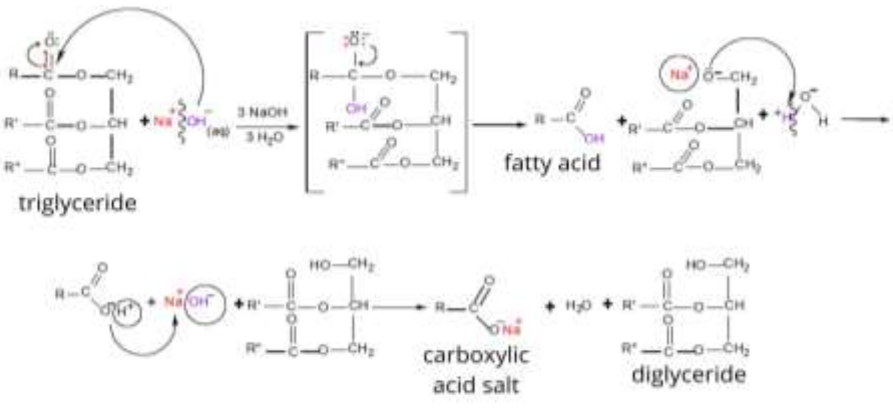


Figure 1. Triacylglyceride saponification mechanism.

The physicochemical soap composition depends on the feedstock used in the saponification process. In the traditional method, animal fats such as tallow or lard are commonly employed, along with additives to enhance the appearance of the soap (Félix, Araújo, Pires, & Sousa, 2017). According to Borsato, Moreira, and Galão (2004), alcohol plays a crucial role in solubilizing fatty materials and imparting transparency to the final product. Furthermore, factors such as temperature, water content, and impurities can significantly influence the saponification process.

Recently, there have been several studies on the production of ecological soap using recycled frying oil (Mello, Gomes, Giusti, Sandri, & Robaert, 2019; Schaffel et al., 2019; Neves, Albuquerque, & Yamaguchi, 2020; Dutta & Kumar, 2021; Weyer & Dalla Nora, 2015). Oils, fats, greases, hydrocarbons, and detergents can interfere with biological processes, leading to inefficient oxygenation and water eutrophication. Therefore, there is a growing importance placed on recycling and alternative synthesis methods to reuse these substances (Prado, 2003).

According to Mello et al. (2019), the reuse of frying oil in ecological soap production helps in reducing environmental impacts. To make soap production more economically and environmentally efficient it is important to evaluate the saponification index (SI) of the raw materials to minimize the waste of reagents and avoid health damage (Mello et al., 2019).

In this way, the evaluation of the greenness of an experimental laboratory or industrial protocol can be performed by mass metrics and holistic metrics. The holistic metrics, namely the green matrix (GM) and green star (GS) aim to provide a systemic analysis of greenness, encompassing chemical, environmental, and energy aspects (Sandri & Santin Filho, 2017). The Green Matrix (GM) involves identifying positive and negative aspects related to predefined objectives. This internal analysis helps identify strengths and weaknesses. Additionally, an external analysis considers external influences on the object, enabling the identification of opportunities and threats. The findings of the GM analysis are presented in tables, often in the form of a SWOT matrix. The objective of this analysis is to evaluate the greenness of an industrial process or experimental protocol based on the 12 principles of Green Chemistry (GC) (Ribeiro & Machado, 2012; Machado, 2014 Ferreira, Rocha, & Silva, 2003). Each point on the Green Star (GS) represents a principle to be analyzed. The larger the area of the star corresponding to a principle, the greater the chemical greenness, thus measuring the overall system being studied (Machado, 2014).

In this context, the objective of this research is to present protocols for the production of ecological soaps utilizing the saponification index as a raw material parameter. Additionally, the study aims to construct the Green Matrix (GM) and Green Star (GS) to assess the greenness of the soap formulations. The research seeks to establish adapted formulations for both bar soap and ash soap, with an emphasis on ecological considerations.

Material and methods

Soap formulation with saponification index (SI)

Table 1 shows the soap formulations. Column A1 shows the bar soap formulation suggested by Borsato et al., (2004). Columns B1 and C1 indicate the proportions for bar and liquid soap, respectively, with the substitution of bovine fat with frying oil. The bovine fat (tallow) used in the experiment was donated by a local butcher.

Table 1. Soaps formulations.

Reagents	(A1) Soap Formulation in Traditional Bar	(B1) Formulation of Ecological Soap Bar	(C1) Formulation of Liquid Ecological Soap
Water	600 mL (room temperature)	600 mL (room temperature)	600 mL (room temperature) + 15 L (boiling water)
NaOH 99 %	200 g	200 g	200 g
Ethanol	860 mL	860 mL	860 mL
Fat/Oil	1.080 kg tallow	1.080 kg frying oil	1.080 kg frying oil
SI theoretical	185 mg of NaOH 1 g^{-1} $_{(oil/fat)}$	185 mg of NaOH 1 g^{-1} $_{(oil/fat)}$	185 mg of NaOH 1 g^{-1} $_{(oil/fat)}$

For the soap production process, the fat/oil was heated gradually, and 860 mL of ethanol was added. The mixture was homogenized. The temperature was reduced to 60°C, and 185.51 g of NaOH, pre-diluted in water, was added while stirring until a paste-like consistency was achieved. The mixture was kept at rest at room temperature (Borsato et al., 2004). The difference between the formulation of bar soap (B1) for liquid (C1) is 15 L of water.

To minimize waste resulting from excessive NaOH usage, the saponification index (SI) of both tallow and residual frying oil was determined. It is worth emphasizing that following the determination of the SI, the formulation was adjusted, leading to the production of bar soap (B2) and liquid soap (C2).

To determine the saponification index (SI), a procedure was followed. Initially, a sample weighing between 3 to 4 g was measured and placed in an Erlenmeyer flask. Then, 50 mL of 0.5 mol L-1 NaOH solution (alcoholic solution) was added to the flask. The sample was subjected to reflux boiling for a duration of 30 minutes, ensuring complete dissolution. Finally, the sample was removed from heating and 1 mL of phenolphthalein solution was added. With the mixture still heated, titration was carried out with hydrochloric acid (HCl) 0.5 mol L-1. The SI equation (Eq. 1) proposed by Borsato et al. (2004) was adapted with the molar mass of NaOH:

$$SI= (V_2-V_1)x\ f\ x\ N\ x\ 40)/m \quad (1)$$

N= normality of HCl; V_1= volume of HCl spent in the titration; V_2= volume of HCl of the blank sample; f= HCl correction factor; m= mass in grams of the oil or fat.

Evaluation of the chemical greenness of ecological soap by the Green Matrix

The chemical greenness evaluation includes several levels for each of the 12 principles. It is essential to maintain a consistent evaluation scale for these principles to enable comparisons between different alternatives. However, it is important to note that the accuracy of assessing each principle may vary. Certain principles, particularly those related to risk, may have lower levels of assessment accuracy. As a result, the number of levels for these principles might be limited. The high uncertainties imply a restricted number of levels, the development of the GS takes into account three levels, which must follow the determined requirements and score from 1 to 3: Score 3 - Full green (ideal case: substance, reaction benign); Score 2 - Moderately green (acceptable with some restrictions); Score 1 - Total absence of chemical greenness (malignant/red cases) (Machado, 2014). Table 2 presents the dimensions of the internal analysis of the GM according to Ribeiro and Machado (2012) along with the criteria used to assess the strengths and weaknesses for evaluating the chemical greenness of ecological soap (B2).

Table 2. Dimensions of internal analysis and criteria for accounting for weaknesses / strengths.

Analysis dimensions	Strong points	Weaknesses
1-Risks to health and the environment of waste	There is no formation of residues or the residues have low risks to health and the environment	There is a formation of residues with moderate/high risks to health or the environment
2-Excess reagents and formation of co-products (water is not considered)	Excess reagents ≤10% and no formation of co-products (water is not considered)	Excess reagents >10% or there is a formation of co-products
3-Risks to health and the environment due to the substances involved	The substances involved have low risks to health and the environment	The substances involved have moderate/high risks to health or the environment
5-Risks to health and environment from solvents and/or other auxiliary substances	Solvents or other auxiliary substances are not used or are used, but have low risks for health and the environment	Solvents or other auxiliary substances are used with moderate/high risks to health or the environment
6-Pressure and temperature	Environmental pressure and room temperature	Different pressure or temperature
7-Use of renewable substances (water is not counted)	All reagents/raw materials involved are renewable (water is not considered)	At least one of the reagents/raw materials is non-renewable (water is not considered)
8–Derivatization	Not used	Used
9-Use of catalysts	Catalysts not needed or have low risks to health and environment	Catalysts with moderate/high risks to health or the environment are used
10-Use of degradable substances to harmless products (water is not considered)	All substances involved are degradable to harmless products	At least one of the substances involved is not degradable to harmless products
12-Risks of chemical accident due to the substances involved	The substances involved have a low risk of chemical accident	Substances involved have a moderate/high risk of chemical accident

Source: Ribeiro and Machado, P. 1879-1883, 2012.

Opportunities were considered as aspects that have the potential to contribute to the fulfillment of the unreached principles. On the other hand, threats were identified as external constraints that may pose difficulties in achieving the necessary improvements to fulfill the principles. Table 3 presents an analysis of these dimensions according to Ribeiro and Machado (2012) and Machado (2014).

The atomic economy or atomic efficiency (AE) is related to the evaluation of the first principle (P1) in the GM. It is calculated by determining the ratio between the mass of atoms of reactants incorporated in the desired product and the total mass of atoms in the reactants, based on the stoichiometry of the reaction, as shown in equation 2 (Machado, 2014):

$$\%\ EA = (\text{molar mass of the main product/total mass of all reactants})^* \quad (2)$$

Table 3. External analysis dimensions.

Opportunities	Threats
- Substitute moderate/high-risk substances for low-risk substances. - Eliminate the use of solvents or replace the solvents used by others with low risks. - Process optimization to increase atomic economy (stoichiometric or near-stoichiometric conditions). - Optimization of the process from an energy point of view: normal pressure and room temperature. - Use of catalytic reagents with low risks instead of stoichiometric reagents. - No derivatization -Substitute non-degradable substances for other degradable ones, with harmless degradation products. - Replace non-renewable substances with renewable ones.	- Difficulties in carrying out the conditions mentioned in the opportunities for economic reasons or there are no known alternatives.

Source: Ribeiro and Machado, p. 1879-1883, 2012.

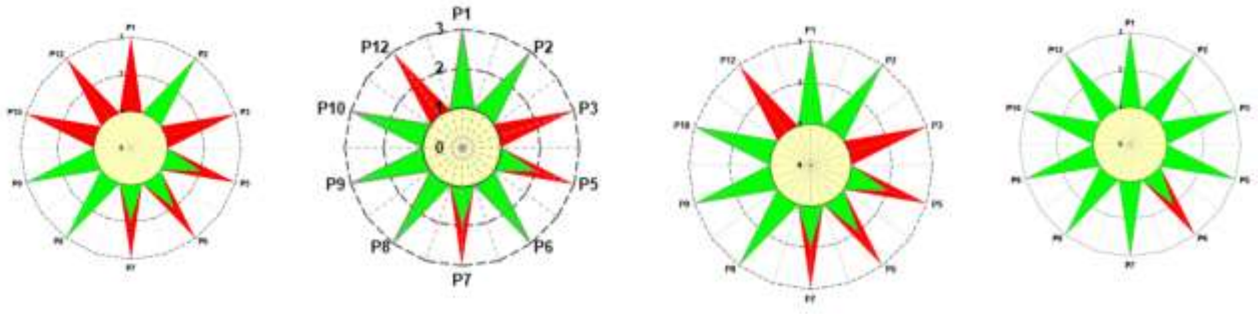
Reactions that have high atomic efficiency are called green reactions, while reactions that offer low atomic efficiency are considered brown reactions. The degree of greenness is determined by the proximity to 100% atomic efficiency, where a higher value signifies a greener process (Van Aken, Strekowski, & Patiny, 2006). Atomic efficiency yields of 90% are excellent, 60% are reasonable yields, and 20% or less are considered low. This efficiency or yield calculation does not consider all the material (such as waste or co-products) obtained beyond what is desired, as well as the reagents and auxiliaries not incorporated in the final product (Lenardão, Freitag, Dabdoub, Batista, & Silveira, 2003).

The factor E considers the amount of waste for each kilogram of product obtained and its determination contributes to the evaluation of principle 1. Waste refers to any material produced in excess of the desired product. Factor E is calculated as the ratio of the sum of the masses of secondary products by the mass of the desired product, as shown in Equation 3 (Lenardão et al., 2003):

$$\text{Factor E} = \text{waste mass (kg) product mass (kg)}^{-1} \quad (3)$$

Factor E considers all substances used in the reaction, including solvents (except water) and any remaining reagents. The higher the value of Factor E, the less environmentally acceptable is the process. Factor E makes it possible to estimate the performance and efficiency of the reaction process. The ideal value of Factor E is zero since the mass of residue/waste is equal to zero. Factor E provides a straightforward measure for assessing the efficiency and sustainability of the chemical industry (Sheldon, 2017).

Before the construction of the GS, it was necessary to classify the hazards associated with the substances used in the formulation of ecological bar soap (B2). To accomplish this, the risk codes of the reagents used in the formulation were researched in the Safety Data Sheets for Chemicals (FISPQ) and the GHS (Global Harmonized System of Classification and Labeling of Chemicals) and these risks were compared with Regulation (EC) No. 1272/2008 (European Parliament and the Council of the European Union, 2008). The hazard codes found were recorded in the table shown in Figure 2. These hazards were scored according to the GHS, where the scores correspond to the following risk level: p1-low risk; p2-moderate risk, and p3-high risk. To construct the GS, an Excel spreadsheet was utilized to compile information about the experiment, including details about the reagents, physical and environmental risks, health risks, biodegradability, and renewability.



(a) GS Soap A1 45% (b) GS Soap B2 70% (c) GS Soap C2 65% (d) GS Ash Soap 95%

Figure 2. Green Stars (GS) of (a) A1, (b) B2, (c) C2 and (d) Ash Bar Soap Formulations.

Results and discussion

The frying oil is susceptible to degradation reactions, occurring through oxidation and hydrolysis reactions caused by heating, and contact with air and water. Therefore, it is necessary to determine the saponification index (SI) for the use of frying oil in soap production. The SI will indicate the amount of NaOH or KOH needed to saponify 1 g of oil or fat. This determination involves carrying out a complete saponification reaction using a known quantity of alkaline base, followed by titration to determine the excess base (Uchimura, 2007). In addition to waste reduction, controlling the SI also provides a pH between 9 and 10.4, aiming to prevent any potential harm or damage to the skin (Agência Nacional de Vigilância Sanitária [ANVISA], 1999) and reducing damage to the aquatic environment with increasing pH, as most aquatic species do not tolerate pH in the range of 12 to 14. Higher pH levels may lead to the solubilization of metallic salts, which can be toxic to aquatic organisms. By controlling the pH and keeping it within the specified range, the potential negative impact on the aquatic environment can be minimized (Sampaio, Boijink, & Rantin, 2013).

Resolution RDC nº 482 ANVISA (1999) provides for an SI between 189-195 mg_{NaOH} g^{-1} for soybean oil and a SI between 193-202 $mg_{NaOH} g^{-1}$ for tallow. The lower SI values for residual oil (186.51 mg_{NaOH} g^{-1}) and for tallow (169.19 mg_{NaOH} g^{-1}) were probably caused because of the presence of unsaponifiable co-products from the decomposition of residual oil during the frying process and the presence of unsaponifiable contaminants originated in the tallow production process, respectively. Table 4 presents the adapted SI.

Table 4. SI of Ecological Soaps.

Reagents	(A1) Borsato et al.(2004) Formulation	(A2) Formulation with tallow after SI calculation	(B2) Solid ecological soap formulation produced with residual frying oil after SI calculation	(C2) Liquid ecological soap formulation produced with residual frying oil after SI calculation
SI (mg NaOH g^{-1})	185 (15.6 mg excess)	169.19± 1.85	186.51± 2.15	186.51± 2.15
NaOH excess	8.43%	No excess	No excess	No excess

The formulation was adapted (A1 to A2) because the SI shows the reduction of NaOH in the formulation from 185 mg to 169.51 mg of NaOH per gram of fat. For the liquid ecological soap (C2), formulation B2 was initially developed, and an additional 15 L of boiling water was incorporated. The SI proved that the soap production methodology must be adapted according to the different types of fat or oil, as the residual oil required a higher quantity of NaOH for complete saponification. The modified mixtures B2 and C2 both required 186.51 mg_{NaOH} g_{fat}^{-1} to achieve the desired saponification level.

The results show the importance of calculating the SI to prevent the excessive use of NaOH. The degree of saponification can vary depending on the fatty materials used, especially in the case of frying oil, which may have different origins and lipid contents (Félix et al., 2017). Mello et al. (2019) consider that the formulation of soaps should be modified for all different raw materials, as soaps with a high content of NaOH can pose risks to health and skin damage.

The GM was used to verify which chemical principles can be contemplated by the production of ecological soap with residual frying oil, a potential environmental contaminant. In addition to health risks, environmental risks, and physical risks, information on the renewability and biodegradability of the reagents and products of the saponification reaction was also verified. The GM shows that in the evaluation of 10 principles, a total of six principles were considered strengths (P1, P2, P6, P8, P9, P10), four weak principles (P3, P5, P7, P12), and P4 and P11 do not apply to laboratory analysis as proposed by Machado (2014), as they involve industrial processes.

Analyzing the GS (Table 5), six principles were fully attended (P1, P2, P6, P8, P9, P10), as well as in the GM. P5 and P7 were partially attended in the GS and not attended in the GM analysis. P3 and P12 were not reached (Table 5).

Table 5. Comparative Analysis of Results Obtained in GM and GS.

Green Matrix (GM)	Green Star (GS)
Principles achieved: P1, P2, P6, P8, P9, P10	Principles achieved: P1, P2, P6, P8, P9, P10
-	Partially achieved principles: P5 e P7
Principles not achieved: P3, P5, P7 e P12	Principles not achieved: P3 e P12

When comparing the GM results with the GS results, P5 and P7 were considered weak points in GM whereas they were partially achieved in the GS evaluation. The GM analysis allows a more comprehensive internal qualitative analysis of the procedure and external predictions which facilitate the improvement of experimental greenness.

On the other hand, the GS evaluation involves a semi-quantitative analysis that presents the greenness in the form of a graph. Despite this difference, both the GS and GM evaluations complement each other. The GS facilitates the visualization of the experimental results allowing to notice that the P7 was partially attended, accepting partial chemical greenness when at least one renewable substance is present, as exemplified by ethanol. While in the GM analysis, principle P7 was not fully met due to the requirement of NaOH, a non-renewable substance, in the saponification process. The GM evaluation allowed an internal analysis of the saponification procedure, which is described below:

- In principle P1 (Prevention), the evaluation focused on the careful and responsible use of reagents that possess physical, environmental, and health risks, with the aim of minimizing or eliminating the generation of residues. In this case, the residual oil (waste) was converted into a biodegradable product;

- In principle P2 (Atomic Economy) the focus is on the efficient use of reagents, minimizing or avoiding excess amounts. In the formulations, the SI was determined, ensuring that there was no excess NaOH used (which is a strong point). By carefully controlling the addition of NaOH during soap preparation, all the reagents and the co-product of the reaction (glycerin) are fully incorporated into the soap. Therefore, the atomic economy of the process reaches 100%, which can be called a green reaction. It is worth noting that even though the saponification reaction involves a nucleophilic addition process followed by the elimination of a leaving group (glycerin), it is considered atom-efficient since it does not produce any co-products with potential environmental degradation (Domingues, Magalhães, & Sandri, 2022).

- In principle P3 (Synthesis of less hazardous products), the objective is to propose a synthesis that involves the use and generation of substances that pose minimal risks to both human health and the environment. The soap itself is considered biodegradable, presenting minimal risks to the environment and health. However, NaOH used in soap formulation has a high health risk (toxic if ingested and causes severe skin and eye damage) and a moderate risk to the environment (harmful to aquatic organisms). Ethanol also poses a moderate health risk (causes serious eye irritation; respiratory tract irritation; drowsiness or dizziness). Therefore, both caustic soda and ethanol are considered weak points in meeting the criteria P3;

- P5 (Use of safe solvents and auxiliaries) seeks to avoid the use of auxiliary substances, and if they are used, they must be harmless. The saponification procedure used ethanol, representing a weakness in the VM;

- P6 (Energy consumption) analyzes the use of minimal energy and the exploration of renewable energy sources. If saponification is carried out on hot days, there is no need to heat the residual oil, as the heat of the dissolution of caustic soda in an aqueous medium is sufficient for the reaction to occur (strong point). On cold days, the procedure should be performed at higher temperatures (heating between 60 and 75°C);

- P7 (Use of renewable substances) - although the cooking oil and ethanol used in the formulation are renewable substances, caustic soda is not. Thus, principle 7 is not evaluated as a strong point;

- P8 (Avoid the formation of derivatives) is related to the use of some substances as blockers, to prevent a chemical reaction from happening in more than one step in the synthesis. In this criterion, soap production meets P8, with no need to use blockers or changes that generate waste;

- P9 (Catalysis) evaluates the use of catalysts. The proposed saponification did not employ catalysts (strength).

- P10 (Design for degradation), emphasizes the importance of designing chemical products that, after their use, degrade into harmless byproducts and do not persist in the environment. In the case of soap production, this principle is a strong point since soap is known to be biodegradable.

- P12 (Intrinsically safe chemistry for accident prevention), The substance used in a process and its method of use aim to minimize chemical accidents. Therefore, in terms of chemical safety, the handling of caustic soda is considered a weak point due to the potential risks it poses, including the possibility of causing burns to the skin and mucous membranes. External analysis indicates that an alternative approach in soap production is to use an alkaline mixture of water and ash to replace or reduce NaOH in the saponification process. However, ash soap tends to have a pastier consistency (soft) compared to traditional soap formulations. The replacement of wood ash with KOH is one of the improvements to soap. Another reagent generally used in soap formulations is ethanol, because it increases the cleaning power and transparency of the soap in addition to its bactericidal action. However, it also has moderate health risks and low risk for the environment, which can be mitigated by the formulation of alcohol-free soaps, thus contemplating P5.

The proposed adaptations have the potential to address and align with 10 principles, thereby enhancing the overall sustainability of the soap production process. However, there are a few additional considerations that can further increase the greenness of the soap:

- The external analysis also guides the use of Individual Protective Equipment (IPE) during soap production (Freitas, 2018).

- There is the possibility of adapting the A1 formulation by Borsato et al. (2004), by replacing 50% or even 100% of tallow with residual oil, which would result in a slightly greener soap. However, it is crucial to calculate the Saponification Index (SI) to ensure that the process is carried out without the risk of producing soap with excess caustic soda. Although it is a commonly used approach, where soap formulas are often adapted by reducing or increasing the quantity of reagents to accommodate different fatty materials, it is crucial to emphasize the importance of conducting the Saponification Index (SI) calculation before formulating the soap. Soap produced using various fatty materials can exhibit different properties, and the SI calculation helps ensure the appropriate amount of base is used to prevent excess. By determining the SI beforehand, the soap formulation can be adjusted accordingly, optimizing the process and avoiding potential issues associated with excess base.

In the assessment of the chemical greenness of soap, holistic metrics play a significant role, particularly the Green Metrics (GM). The GM offers the advantage of analyzing an experiment before its execution, allowing the identification of areas to enhance its greenness. The GS has some limitations, as pointed out by Costa (2011). Firstly, it does not consider whether an activity is conducted on a microscale or not. Additionally, it cannot differentiate between experiments in which all substances involved pose a risk and those where only one substance is hazardous and, it does not take into account the amount of waste formed, which can be addressed through the concurrent utilization of the GM and mass metrics.

Before the development of the GS, an evaluation of hazard phrases was conducted using the FISPQ and GHS for the substances employed in the production of the ecological soap bar (B2) which were also used for the construction of the GM. The risk codes were then compared to the corresponding risk levels specified in Regulation (EC) No. 1272/2008 (European Parliament and the Council of the European Union, 2008), as shown in Table 6.

Table 6. Hazards and Information Regarding Renewability and Biodegradability in Reagents and Saponification Products according to the Globally Harmonized System of Classification and Labeling of Chemicals (GHS).

	Risks				Biodegradability and/or renewability
	H-phrases Physical Hazards	Health (p*)	Environment (p*)	Physical (p*)	
Reagents					
NaOH	H290 - Corrosive to metals			P2	- Resistance to degradability: caustic soda is harmful to aquatic life by increasing the pH. Most aquatic species will not tolerate pH in the range of 12 to 14 at any time. This increase in pH can also cause the release of metal salts, such as aluminum, which could also contribute to the exposed toxicity.
	H301 - Toxic if ingested.	P3			
	H305 - Harmful if swallowed and enters airways	P2			
	H312 - Harmful in contact with skin	P2			
	H314 - Causes severe skin burns and eye damage	P3			
	H317 - May cause allergic skin reactions	P2			
	H318 - Causes serious eye damage	P2			
	H402 - Harmful to aquatic organisms		P2		- Non-renewable. - Very low biodegradability.
Frying oil	-				- Renewable.
Solvents and other auxiliary substances					
Ethanol	H225 - Highly flammable liquid and vapors			P3	- Renewable
	H319 - Causes serious eye irritation	P2			
	H335 - May cause respiratory tract irritation	P2			
	H336 - May cause drowsiness or dizziness	P2			

Water	H410 – Very toxic to aquatic organisms with long-lasting effects.		P3		
	Code (H...)	Risks Health (p*)	Environment (p*)	physical (p*)	Biodegradability and/or renewability
Product					
Soap					- Biodegradable
Waste					
NaOH (only traditional formulation).		Same NaOH information			

(P*) GHS score (3 high risk, 2 moderate risk, 1 low risk). Source: From the author (2022).

Table 7 shows how the GS was constructed to evaluate and compare the greenness of the traditional soap production process, the modified process based on the SI, and the formulation involving the use of ash, as recommended after analyzing the GM. Through a thorough examination of the FISPQ, which provides information on the hazardous nature, degradability, and renewability of substances employed in soap production, the principles were assigned scores ranging from 1 to 3. These scores reflect the degree to which the principles were fully (3), partially (2), or not met (1), in accordance with the guidelines outlined in Table 7.

Table 7. Construction of the Green Star (GS) and Comparative Analysis between Formulations.

Green Chemistry Principles	(P)	Criteria	(P) A1	(P) B2	(P) C2	(P) SC	Notes
P1 - Prevention	3	All residues are harmless.	1	3	3	3	- B2 and ash soap do not form residues.
	2	Formation of at least one waste involving moderate risks to health and the environment.					
	1	Formation of at least one waste involving a high risk to health and the environment.					
P2 - Atomic Economy	3	Reactions without excess reagents (⩽10%) and formation of co-products	3	3	3	3	- Soap A1 8.43% NaOH excess. - Soap B2 0%
	2	Reactions without excess reagents (⩽10%) and with the formation of co-products					
	2	Reactions with excess reagents (>10%) and without the formation of co-products					
	1	Reactions with excess reagents (>10%) and with co-product formation					
P3 – Less dangerous synthesis	3	All substances involved are harmless	1	1	1	3	- NaOH has high health risks.
	2	The substances involved present a moderate risk to health and the environment					
	1	At least one of the substances involved presents a high risk to health and the environment					
P5 – Solvents and other safer auxiliary substances	3	Solvents and auxiliary substances do not exist or are harmless	2	2	2	3	- Ethanol has a moderate health risk.
	2	Solvents and auxiliary substances used involve moderate danger to health and the environment					
	1	At least one of the solvents or one of the auxiliary substances used involves a high risk to health and the environment					
P6 - Planning to achieve energy efficiency	3	Environmental temperature and pressure	2	3	2	2	- Formula A1 (heating the tallow between 60°C to 75°C - Cold formula B2 - Formula C2 uses 15 L of boiling water.
	2	Ambient pressure and temperature between 0ºC and 100ºC that imply cooling or heating					
	1	Pressure other than ambient and/or temperature > 100 °C or lower than 0 °C					
P7 - Use of renewable raw materials	3	All reagents/raw materials involved are renewable	2	2	2	3	- NaOH is not renewable - ethanol, oil, and soap are renewable.
	2	At least one of the reagents/raw materials involved is renewable, water is not considered					
	1	None of the reagents/raw materials involved is renewable, water is not considered					
P8 - Reduce	3	No derivatization or one step		3			- There are no

Derivatization	2	Only one derivatization or two steps					derivatization.
	1	Multiple derivatization or more than two steps	3		3	3	
P9-Catalysts	3	No catalysts are used or the catalysts are harmless	3	3	3	3	- Catalysts were not used
	2	Catalysts that involve moderate danger to health and the environment are used					
	1	They use catalysts that involve a high risk to health and the environment					
P10 - Planning for degradation	3	All substances involved are degradable with innocuous degradation products	1	3	3	3	- A1: (NaOH is not biodegradable, harmful to fauna and flora) - B2: substances are degradable into harmless degradation products
	2	All substances involved that are not degradable can be treated to obtain their degradation with innocuous degradation products					
	1	At least one of the substances involved is not degradable and cannot be treated to obtain its degradation with innocuous degradation products					
P12 – Inherently safer chemistry for accident prevention	3	The substances involved present a low risk of chemical accident	1	1	1	3	-NaOH presents a high health risk
	2	The substances involved present a moderate chemical accident hazard					
	1	The substances involved present a high risk of chemical accident					

Figure 2 shows the GSs constructed to quickly verify and compare the chemical greenness of the following soap formulas: soap A1, SI-adapted ecological soap B2, soap C2 and the ash soap proposed in the external analysis of the GM. The GSs were developed based on 10 criteria, as the P4 and P11 principles do not apply to laboratory analysis.

The GSs showed a significant enhancement in the greenness of the soap formulations. The transition from formula A1 with a Green Star Fill Index (GSFI) of 45% to formulation B2, achieved principles P1, P6, and P10, improving the chemical greenness to 70%. Formulation C2 (liquid soap) fully incorporates principles P1 and P10, and partially P2, with a GSFI of 65%. This is due to the requirement of using boiling water to dilute the bar soap. The evaluation of the GM also revealed the chemical greenness of the ash soap formulation through the GS, resulting in a GSFI of 95%. It is worth noting that green chemistry focuses on maintaining and improving the quality of life within the framework of sustainable development principles (Prado, 2003; Anastas & Kirchhoff, 2002).

Conclusion

It is important to highlight that despite the soap production going through a mechanism of nucleophilic acyl substitution (addition-elimination) that normally presents low chemical greenness, the process achieves a 100% atomic economy and an E factor of zero, indicating the absence of residue formation. The internal and external analysis of the GM of the saponification process provided valuable insights for proposing improvements in the formulation. These alternatives offer the possibility of producing a greener soap by substituting caustic soda with ash and eliminating the use of ethanol. While the GS offers practicality, the GM enables both external and internal evaluations.

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