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COVER: (A) Three-dimensional structure of pancreatic porcine lipase (PPL; PDB code 1ETH), (B) Lid of PPL (237–261, in red), (C) Catalytic triad of PPL (Serine 153, Aspartic acid 177 and Histidine 264, in green), and (D) oxyanion hole of PPL (Phenylalanine 78 and Leucine 154). Article: Extraction and Characterization of Coffee Silverskin Oil and Its Valorization by Enzymatic Hydrolysis by Cleide Mara Faria Soares et al. J Bioeng. Tech. Appl. Health 2021;4(1):21.

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Contributions and Impacts on Health Using New Technologies and Innovative Products

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This special edition of the Journal of Bioengineering and Technology Applied to Health brings a second selection of articles presented at the VI International Symposium on Innovation and Technology (SIINTEC). The SIINTEC happens since 2015. The event is annual and promoted by SENAI CIMATEC, Salvador, Bahia, Brazil. The VI SIINTEC focused on discussing challenges in science, technology, and innovation after COVID-19. We had to make changes and find immediate solutions to keep people together, and this connection provides us the opportunity of having qualified participants from all over the world sharing and building knowledge. The VI SIINTEC occurred in 2020 from October 21 till 23. The main point was providing the opportunity of joining the scientific and technological community to discuss innovation, researches, and advances promoted by the pandemic period and draw applicable conclusions to society's new routine.

Many researchers seek answers and solutions to questions and problems generated in the current pandemic scenario. Vaccine developments to combat the SARS-Cov-2 virus are being carried out by researchers around the world. But also, all scientific development, despite the difficulties imposed by quarantine, remains active. In this second volume of selected articles from VI SIINTEC 2020, the studies discussed developments involving the health impact of pollution, oil extraction, and characterization technologies, methods for characterizing and assessing water quality, and biotechnological processes.

The research presented here makes significant contributions about the evaluation of the deposition of nanoparticles in the human respiratory tract, technology as a pillar for essential oil green extraction, extraction and characterization of coffee silverskin oil, technological prospective study of green coffee processing, the effect of temperature on physical properties of Canadian maple, techniques, and methodologies used for the analysis of metals and organic compounds in wastewaters, graywater and rainwater, and the importance of occupational health and safety in biotechnological processes.

We wish you all an excellent reading.

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Address for correspondence: Lílian Lefol Nani Guarieiro. Centro Universitário SENAI CIMATEC. Av. Orlando Gomes, 1845, Piatã. Zip Code: 41650-010. Salvador, Bahia, Brazil. E-mail: lilian.guarieiro@fieb.org.br. https://doi.org/10.34178/jbth.v4i1.146.

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Evaluation of the Deposition of Nanoparticles on the Human Respiratory Tract from the Burning of Diesel/ Biodiesel/ Additive

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This study aimed to evaluate the deposition in the respiratory tract of nanoparticles (11.5nm to 365.2nm) from the burning of diesel, biodiesel, and additives. The studied fuels were pure diesel (D), a binary mixture of pure diesel with 11% biodiesel (B11), and a ternary mixture of pure diesel, with 11% biodiesel and with the biocatalyst Xmile (B11X). The impact of nanoparticles on health was assessed using the MPPD lung model. From the tests, the burning of the studied fuels showed a concentration of some particles in the accumulation mode (50nm to 120 nm). When comparing fuels, it was clear that B11 emits more particles and has a greater deposition capacity in the lung. B11X is efficient in reducing pollutant emissions as well as impacting human health.
Keywords: Deposition. Respiratory Tract. Biodiesel. MPPD.
Abbreviations: MPPD: Multiple-Path Particle Dosimetry Model.

Introduction

Diesel engines play an important role in the world economic scenario, due to higher energy productivity, higher power, and considerable durability [1]. These particularities are associated with many applications such as transportation, pumps, and electricity generators. Despite having such applicability, diesel engines are responsible for the growth of pollutants in the atmosphere, such as total hydrocarbons, nitrogen oxides, carbon monoxide, and particulate matter (PM) [2].

Atmospheric particles material (PM) consists of heterogeneous mixtures of solid and liquid particles suspended in the air that vary in size and chemical composition, such as nitrates; sulfates; elemental and organic carbon; organic compounds (for instance, polycyclic aromatic hydrocarbons); biological compounds (for example, endotoxin, cell fragments, viruses); and metals (for example, iron, copper, nickel, zinc, and vanadium) [3,4].

The PM can be classified according to its transport capacity in the air, which is associated with particle diameter sizes. Its classification is Coarse (PM10), Fine (PM2.5), and ultrafine (PM0.1) [5]. PM10 has an aerodynamic diameter smaller than 10 micrometers (µm); PM2.5 has an aerodynamic diameter smaller than 2.5 µm and PM0.1 has an aerodynamic diameter less than 0.1 µm [5]. The particulate matter emitted by diesel engines consists of a predominance of fine particles (PM2.5) and ultrafine particles (PM0.1) [6].

Improving engine performance and regulate the emission of pollutants, additives, also called oxygenated fuels, are added to diesel [7]. Oxygenated additives mixed with diesel fuels promote combustion and octane processes without emitting a high amount of pollutants to the atmosphere [8]. Generally, the most applied additives are alcohols (butanol, propanol, methanol, and ethanol), ethers (diethyl ether, tert-butyl methyl ether), and esters (acetoacetic esters, dicarboxylic acid esters, and methyl esters) [8]. The application of these additives in diesel inhibits the formation of particles considering the existence of less unsaturated micro molecules, such as C_2H_2, that contribute to the reduction of PM emissions in the combustion process [9].

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The particulate matter from diesel engines is not only responsible for a huge impact on the atmosphere but can result in cardiovascular, respiratory, and carcinogenic diseases, considering that inhalation can be a means of contact between the human organism and the PM [7]. This interaction happens in a way that the smaller the particle, the higher the capacity to absorb organic and inorganic compounds in the respiratory tract [3]. Fine particles (PM2.5), for example, when inhaled run through the bronchioles and alveolus (where gas exchange occurs) inducing carcinogenic (lung cancer symptoms) and mutagenic (breaks and changes in the genetic chain) effects [3]. Therefore, the use of additives in diesel cycle engines is not only intended to reduce the emission of atmospheric pollutants, but also to reduce the impact that particulate matter can cause on the human respiratory tract.

The current scenario of COVID-19 is disturbing, especially in countries with a high level of pollution and the incidence of deaths resulted from the emission of PM. These factors can lead to more serious symptoms with the action of the virus which has been decimating. However, when introducing the measures imposed during quarantine, it was possible to visualize a scenario with reduced emissions from transport and industries, enabling an improvement in air quality [10]. An India study from March 2020, in which the objective was measuring the incidence of pollutants in the atmosphere after the measures imposed to contain the spread of COVID-19 [11], demonstrated a significant improvement in air quality in a period when there is no intense car flow in cities due to the measures implemented during the COVID-19 pandemic [10].

The objective of this study was to evaluate the deposition of nanoparticles (11.5nm to 365.2nm) from the burning of diesel, biodiesel, and additives in the respiratory tract.

Material and Methods

The methods of this study are represented in Figure 1.

The experimental phase of the study used three fuels: pure diesel, B11 (a binary mixture of pure diesel with 11% biodiesel), and B11X (a ternary mixture of pure diesel, with 11% biodiesel and with the biocatalyst Xmile). An Agrale diesel engine, model N-790, speed 1700 rpm was used, coupled to a hydraulic dynamometer (Schenck) with a maximum rotation of 10,000 rpm. Integrating this system, a partial dilution tunnel was used to sample the particulate matter with a partial exhaust dilution rate of 24.

A Nanoscan SMPS 3910 particle counter was coupled to the exhaust system to measure the concentration and distribution of the particulate material size (11.5nm to 365.2nm) according to the variation of its concentration, in a 10 minutes time range with three replicates for each fuel (D, B11, and B11X).

We used the MPPD software (Multiple-path Particle Dosimetry Model) (version 3.04) with the experimental data of this study to evaluate how the variation of particle sizes from the vehicle emission behave in the respiratory tract. This software is based on a lung geometry model by Yeh and Schum (1980) that simulates the deposition of particulate material in different regions from the anatomy of the species studied, by adopting a dichotomous branch in the airway structure [11]. It consists of simple and multiple path methods to track the airflow and calculate the aerosol deposition in the lungs.

The single path method calculates deposition in a typical path by airway generation, while the multipath method calculates particle deposition in all airways in the lungs [12]. This model provides the study of regional deposition, extrathoracic, tracheobronchial, and alveolar regions, where morphometric options are available to idealize the lung. Data such as PM properties and exposure conditions must be provided by standards or values specified by the user, in which the deposition fraction can be estimated for particles with a size range between 1 nm and 100 μm [12].

The model chosen in this study was the stochastic model that aims to calculate the

Figure 1. Flowchart of the methods applied in the study.

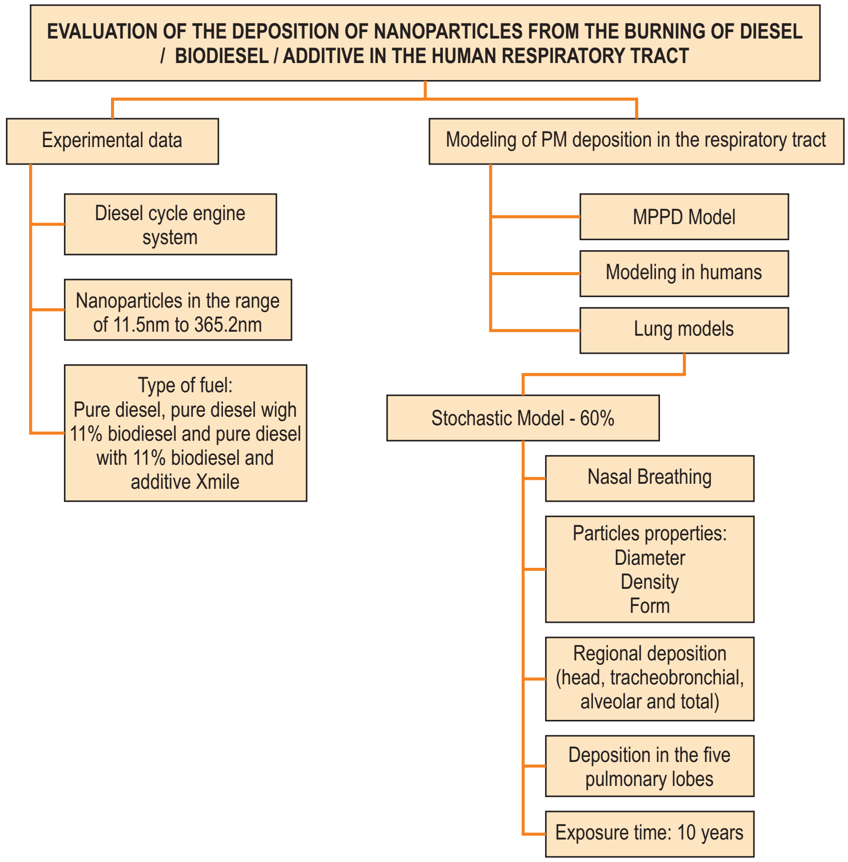
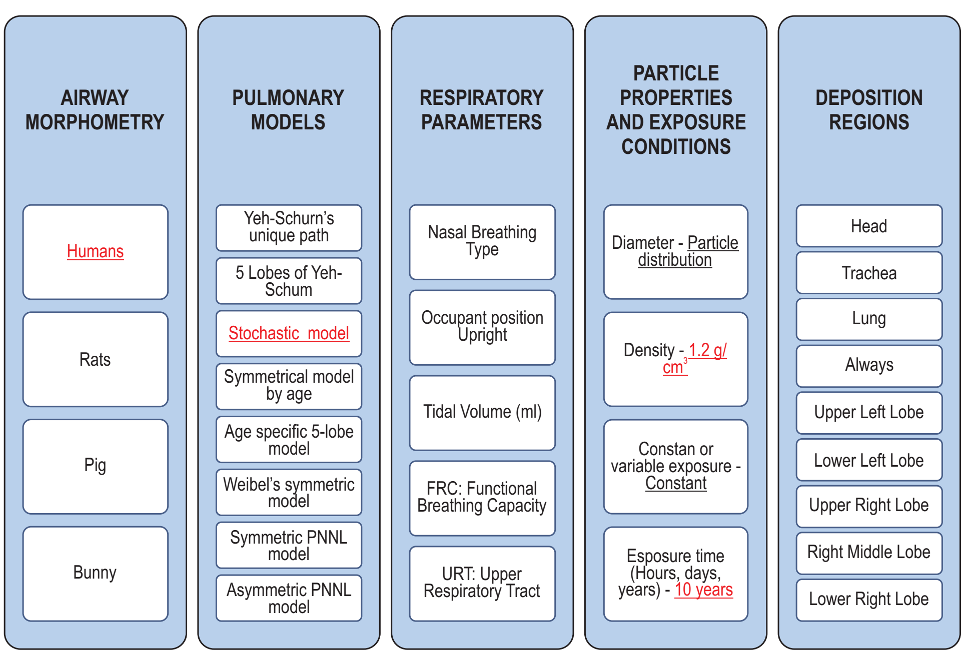


Figure 2. The flow of MPPD modeling.



deposition of PM in the lung in some locations of the human respiratory tract, such as: regional (head, tracheobronchial, alveolar, and total) and lobular (in the five pulmonary lobes) [12]. This model provides an estimate of the variability of the lung dose received by humans, generating more realistic deposition results. Modeling in MPPD occurs according to the input data steps, essential to measure the level of PM concentration in the lung (Figure 2).

Results and Discussion

The emissions of particulate material for the three fuels tested presented accumulation mode concentrations (50 nm to 160 nm) (Figure 3).

According to the literature, particles emitted by diesel engines are in the accumulation mode, in the range of 50 nm to 200 nm [13]. It means that the results obtained were satisfactory. It is also possible to observe that in a large part of the graph the error bars overlap, emphasizing that the three fuels have a statistically similar size and the number of particles distribution. However, in the size range from 50nm to 160nm, a difference in this distribution was observed. The addition of biodiesel promotes the reduction of the total mass of PM, but when compared to pure diesel it emits more ultrafine particles which are more harmful to health [13].

Therefore, the diameters that are included on the accumulation mode of the graphic obtained (50 nm to 160 nm) were used as input data in the MPPD. The main goal of this simulation was to evaluate the impact of PM on the human respiratory tract.

Considering that the B11 fuel had the highest concentrations of PM emission, Figure 4 shows the deposition of PM for the entire lung and for the 5 pulmonary lobes. It shows that the smaller the diameter, the greater is the deposition fraction in the lung. The right lower lobe is the place of the greatest accumulation of particles when compared to the left upper lobe and right middle, in which the deposition of particles is lower. Figure 5 represents the deposition fraction for the different generations or regions (from 0 to 23) of the human respiratory tract. It also shows that the smaller the diameter, the greater the particle penetration capacity in the different regions of the respiratory tract.

Figure 6 (A-F) shows the variation in the number of particles per alveolus, in the entire lung and each lobe for the three fuels studied. It also presents that the numerical deposition per alveolus was higher for B11, especially for the diameter 64.9, which corresponds to the peak of the PM emission graph for the whole lung and the 5 pulmonary lobes. The behavior of B11X and D also corresponds to the MP emission graph of the diesel cycle engine, in which the deposition of particles by alveolus is greater in B11X than in D for all pulmonary regions. The deposition flow by size is the same, the smaller the diameter the greater the deposition fraction in the respiratory tract.

The simulation considered the following scenario of exposure to pollutants: the individual at the bus stop waiting for 1 hour a day, for 7 days a week, for 10 years. The sizes 64.9nm and 86.6 were chosen to show how this type of exposure occurs, considering the B11 fuel (Figure 7).

The exposure to particulate material increases over the years, however, for the two diameters chosen, the level of exposure is almost the same.

This work focused on the evaluation of the deposition of nanoparticles (11.5nm to 365.2nm) for pure diesel, the B11 fuel, and the B11X fuel. We concluded that B11 emits more ultrafine particles in comparison to pure diesel despite the reduction of the total PM mass. The addition of the additive Xmile proved to be efficient because it contributed to reducing particulate emissions, especially the ultrafine ones.

The same result was observed in the analysis of the impact of particulate emissions from these fuels studied on the respiratory tract. As it emits more small particles, the B11 fuel was the one with the greatest capacity for depositing particles in the pulmonary regions, which proves that the smaller

Figure 3. Distribution of the number and size of fuel particles D, B11, and B11X.

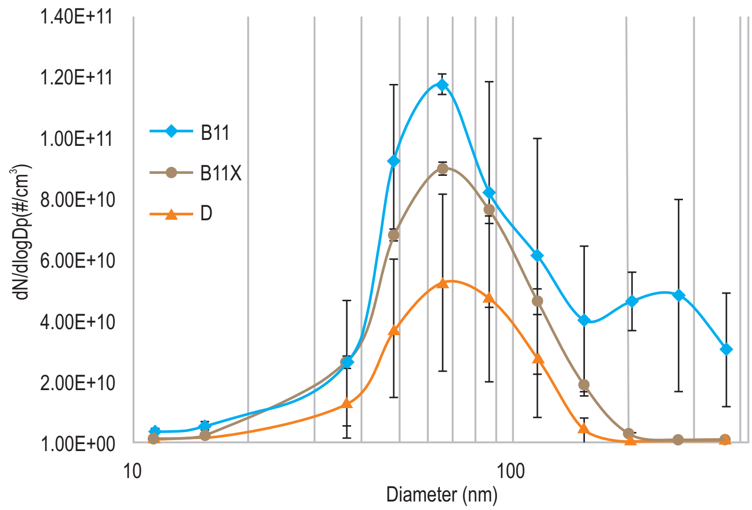


Figure 4. Fractional deposition of MP in the airways in the lung lobes for the B11 fuel.

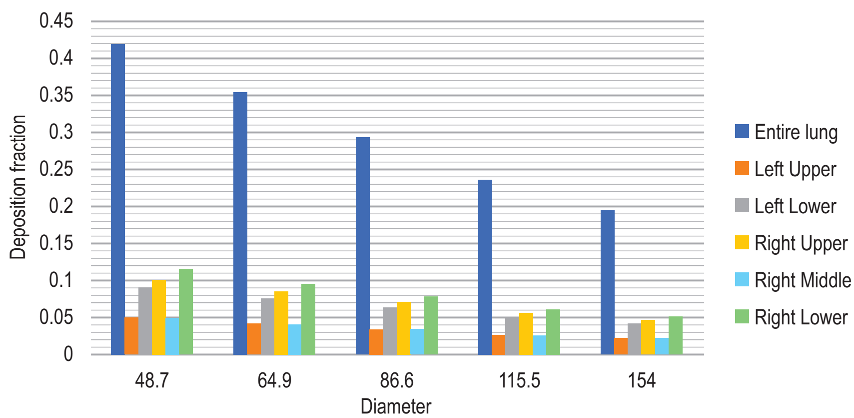


Figure 5. Fractional deposition of B11 fuel particles by generation number for each aerodynamic particle diameter.

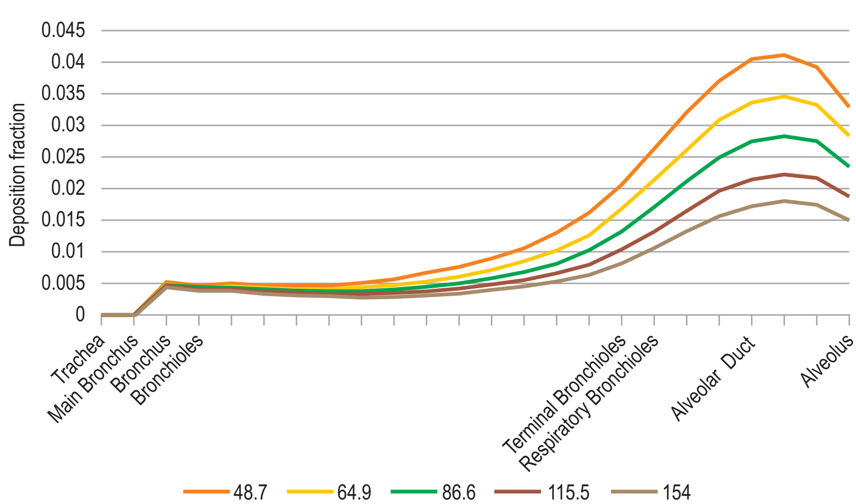


Figure 6. Deposition fraction of the number of particles per well for the B11, B11X and D. A. Entire Lung. B. Left upper. C. Left lower. D. Right upper. E. Right middle. F. Right lower.

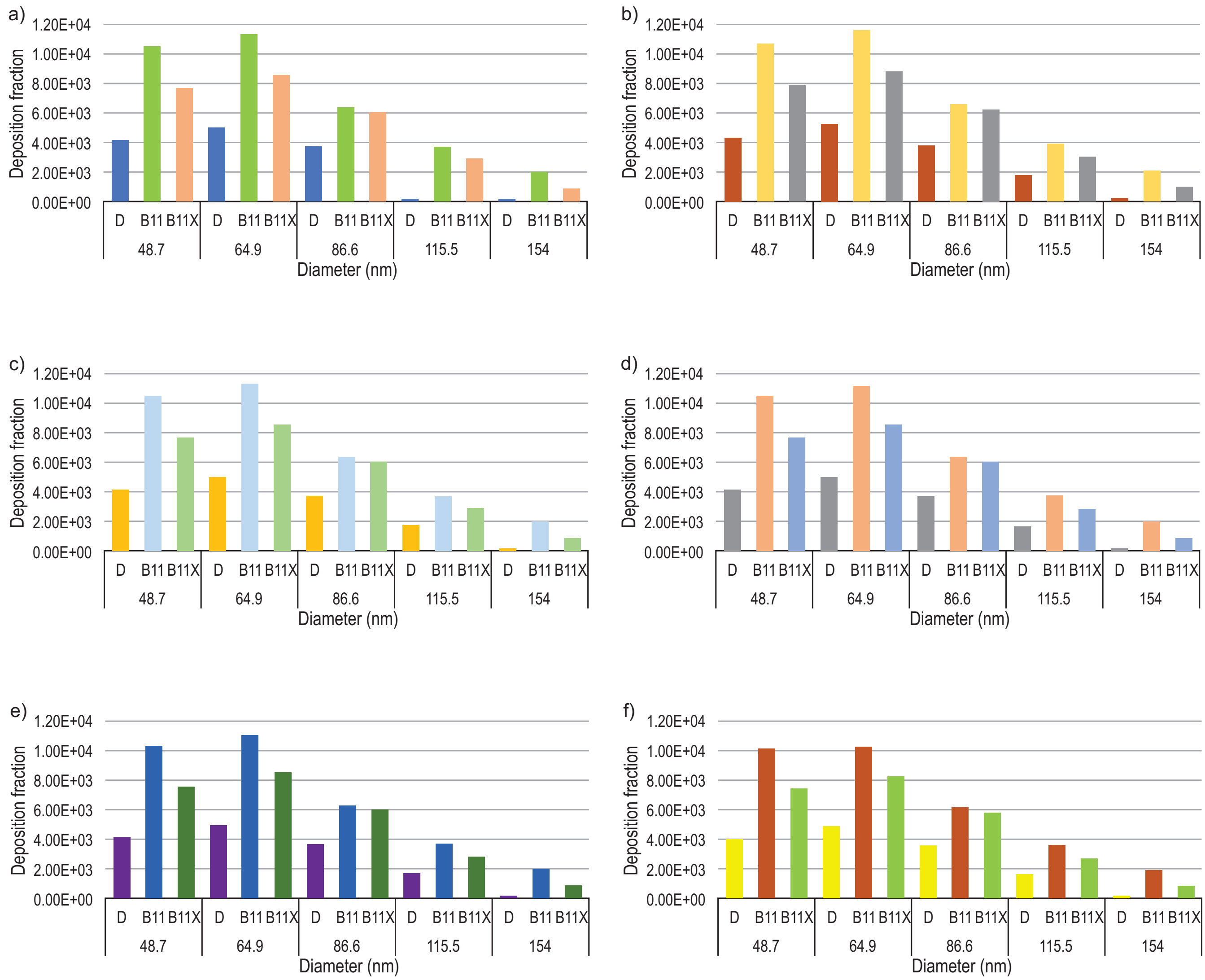
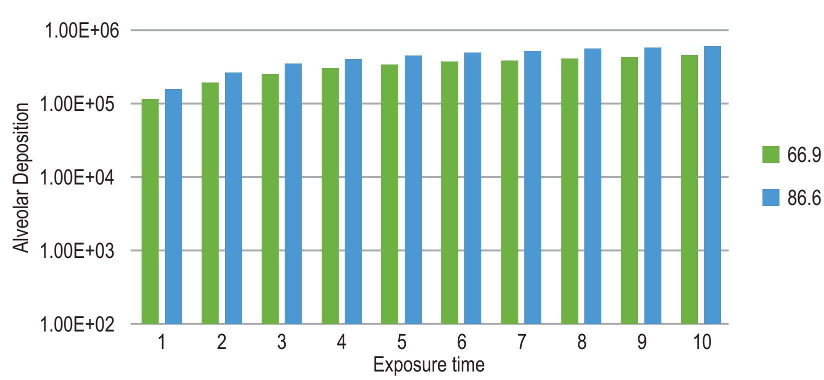


Figure 7. Alveolar deposition over 10 years for particles with 64.9 nm and 86.6 nm in diameter for the B11 fuel.



they are, the bigger the chance of penetrating the lungs, especially the alveolus. On the other hand, the addition of Xmile additive promotes the reduction of particle emissions and contributes to less impact on the human respiratory system.

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Technology as a Pillar for Essential Oil Green Extraction

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This paper focuses on essential oil (EO) extraction via steam distillation and the technological possibilities to enhance both operational and environmental performances. Steam distillation is the most common extraction method (93% of the worldwide volume), the opportunities in these production systems become a concrete target for improvements and are reflected in the businesses overall results. This paper brings the green extraction approach and the technology upgrade as an evolutionary path for this industry. A real process conception, in its current technology level, was assessed under the light of digital technology focus in order to enhance process effectiveness both in terms of material and energy balances, with direct effects over environmental performance and quality.
Keywords: Essential Oils. Green Extraction. Digital Technology.

Introduction

The remarkable growth of the natural products market is justified by consumers' movement from industrialized food to natural products. The plant extracts market size reached US$ 23.7 billion in 2019, projecting US$ 59.4 billion by 2025, according to marketsandmarkets.com [1]. The essential oils (EO) market size, part of this value, is mentioned by alliedmarketsearch.com [2] as US$ 8 billion in 2018, reaching approximately US$ 16-17 billion by 2026.

Green extraction principles subsidize the pursue of a more efficient process with a reduced number of unit operations, optimized process time, energy requirements, and minimum or zero waste generation. This industry segment comprises a myriad of small producers, without access even to basic technology developments [3, 4].

Figure 1 shows the six green principles [4] applied to inputs and outputs of an extraction process, with direct impact over environmental performance but with ultimate effect on efficiencies and business overall results, including financial margins, when optimized.

Digital technology, lately under the label industry 4.0, when properly applied, is a set of tools capable to accomplish the green principles proposals [5]. The essential oil extraction industry still needs attention in the basic engineering aspects, such as energy recovery, efficient thermal insulation, and pre-heating capabilities [6]. Nevertheless, the focus of this paper is to point out opportunities attached to technology updates, serving as a watch out for those in charge of production administration and/or company owners, with evident impact on environmental performance. So, from the plant floor reality to the upper management levels, the control, monitoring, and management of the essential oil extraction industry is a concrete subject for this renewal wave, meaning that operational and environmental excellence cannot exist without these attributes. In Figure 2, the evolution from conventional to the new technologic trend is shown in three levels: the first operates at shopfloor and it is represented by the sensors, the programmable logic controller (PLC), and process control level (SCADA – Supervisory, Control, and Data Acquisition system. The second level (plant management system), the Manufacturing

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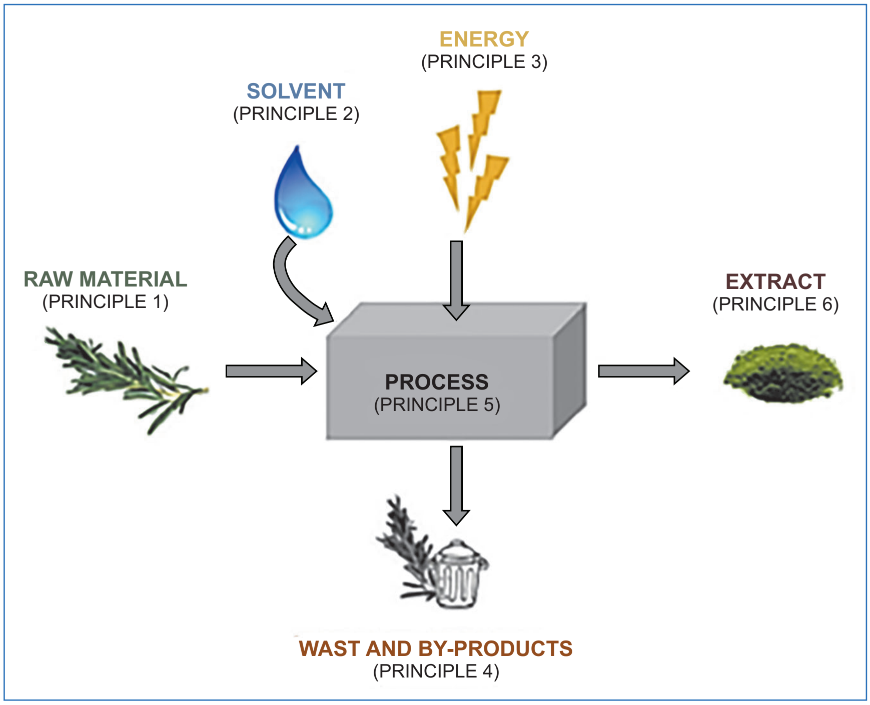
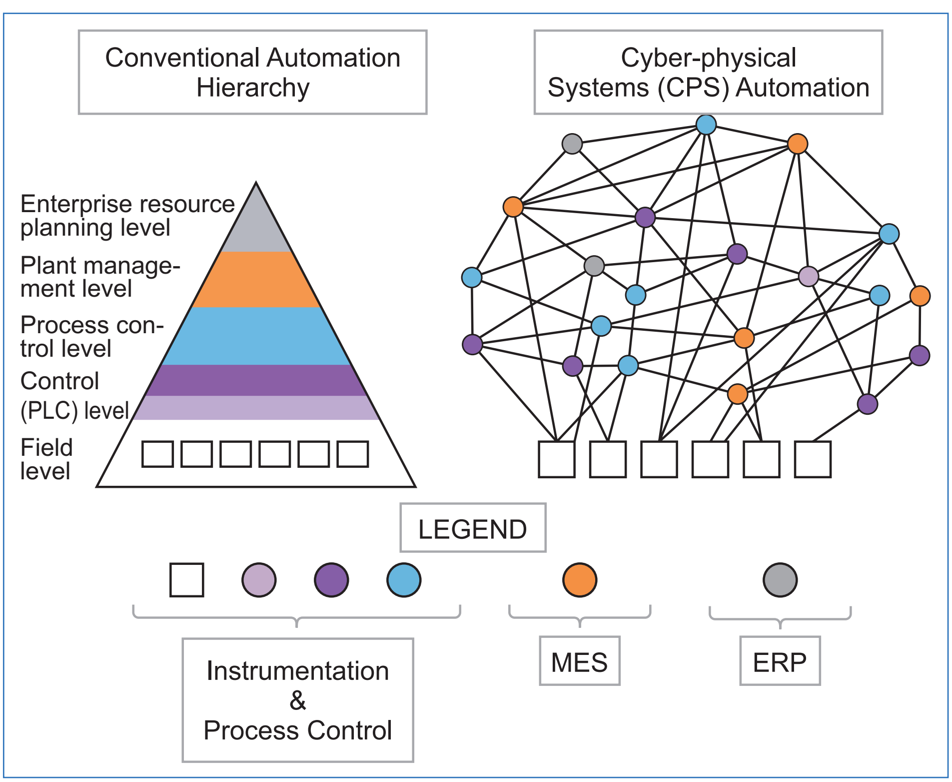
Figure 1. Green principles applied to extraction processes.



Adapted from Chemat [4].

Figure 2. Evolution: from conventional to 4.0 configuration.



Adapted from www.foodengineeringmag.com [7].

Execution System (MES), connects all productive activities to the Enterprise Resource Planning (ERP), which is the third one. ERP consists of the company's financial and organizational areas, for management purposes [7]. MES can be considered the enabler to administrate the manufacturing ‘in progress’, step by step and in real-time: overall manufacturing control, time-to-market, overall manufacturing visibility, capacity allocation, and other capabilities. MES evolution, within the 4.0 scenario, is integrated into the so-called cyber-physical space (CPS), where multilevel virtual and real worlds are merged [8].

Table 1 reflects some of the technological possibilities applicable to the six green principles, enlightening but not restricting the objectives of the present paper. The columns are connected from left to right, demonstrating – through the arrows – the way the basic systems subsidize the next ones.

Each business has its own peculiarities and direction for investments in new technologies. Financial analysis indicates the best options and their impact on business results: ROI - return on investment; NPV – net present value, among other analysis tools, encompassing the business with competitiveness. Therefore, the objective of this work is to unveil technology possibilities as a leap toward operational excellence for the essential oil extraction industry, applied to a real process, owned by Linax Indústria e Comércio de Óleos Essenciais Ltda.

The organization readiness must be assessed in terms of maturity to support such breakthrough. People must be prepared with proper skills and training. Bill Gates reinforces that: "the first rule of any technology used in a business is that automation applied to an efficient operation will magnify the efficiency. The second is that automation applied to an inefficient operation will magnify the inefficiency”, meaning that that the more developed is the organization the broader is the reach of the investments [9]. In this sense, Table 1 highlights the objective of this paper, presenting possibilities and bridging the green principles and technology, as a strategical lever for both academic and industrial developments.

Material and Methods

The methodological steps are outlined as described below:

- Starting point: status of the process in its current conception, within Linax company
- Steps for technology improvements:
  - Basic Instrumentation and plant floor level control via PLC.
  - Monitoring via SCADA.
  - MES and ERP.

Essential oil extraction system, as commonly operated by the company Linax, works under usual basic conditions (Figure 3). Then, the extraction operation consists of applying steam to a green mass through the extraction vessel and a post-condensation and separation, in a “blind” process, performed without sensors and monitoring systems, meaning that the control tasks are restricted to producers’ manual actions based on their historic experience. This weak technological scenario delivers variable quantities and quality, high energy requirements, and equipment idling due to unprepared production sequences and planning. The environmental performance suffers the consequences of this lack of control, representing a large field of opportunities for improvements. The understanding of the process “as is” allows the identification of weaknesses and propositions discussed in the sequence of this article.

<u>Basic Instrumentation and Plant Floor Level Control</u>

Figure 4 shows a basic proposition for instrumentation, according to ISA [11] as the first step to improve control, when compared to the absolute simplicity of the original design (Figure 3).

Instrumentation and control enable material and energy balance improvements as well as optimize process time and repeatability, with direct effect on environmental performance and quality.

Table 1. Technological possibilities applied to EO industry.

	Instrumentation & Process Control	Big Data & Analytics	Simulation & Machine Learning
Raw Material (Principle 1)	Analytical Values for humidity, apparent density, targeting yield improvement.	Data is intelligently analyzed to find correlations and determining parameters for self-configuration.	Self-configuration parameters are optimized by advanced simulation like digital twin. The proposed parameters will reduce batch time, idling, energy consumption.
Solvent (Principle 2)	Steam process variables impact extraction efficiencies (yield). Variations cause undesired effects as the channeling [10]	The best configuration for steam parameters will be determined for next batches.	Simulation proposes fine adjustments via machine learning. These optimized parameters can be fed into the control system for next batches.
Energy (Principle 3)	Sensors and control for steam and cooling water loops.	Best configuration for setpoints and process times.	Simulation indicates best values for steam and cooling water.
Waste & by products (Principle 4)	Solid and liquid residues (hydrosol) can be analyzed and commercialized as valuable products.	Composition of Essential oil and hydrosols indicate process trends for cooling water and time of residence parameters.	Composition of hydrosols in condensed water is predetermined from raw materials and process conditions.
Process (Principle 5)	Sensors for all variables inside/outside the extraction vessel are relevant to detect undesired conditions.	Process data is valuable to feed real tome simulators as well as to determine correlations.	Real time process simulators (digital twin) detects deviations from ideal process behavior.
Product (Extract) Principle 6	Instruments to determine quality analysis of the finished product and quantitative indicators (yield).	Statistic treatment to find correlations between raw material, process conditions and the quality indicator of the EO.	Process parameters are continuously improved when correlations are identified.

Figure 3. Essential oil extraction original status: without sensors and controls.

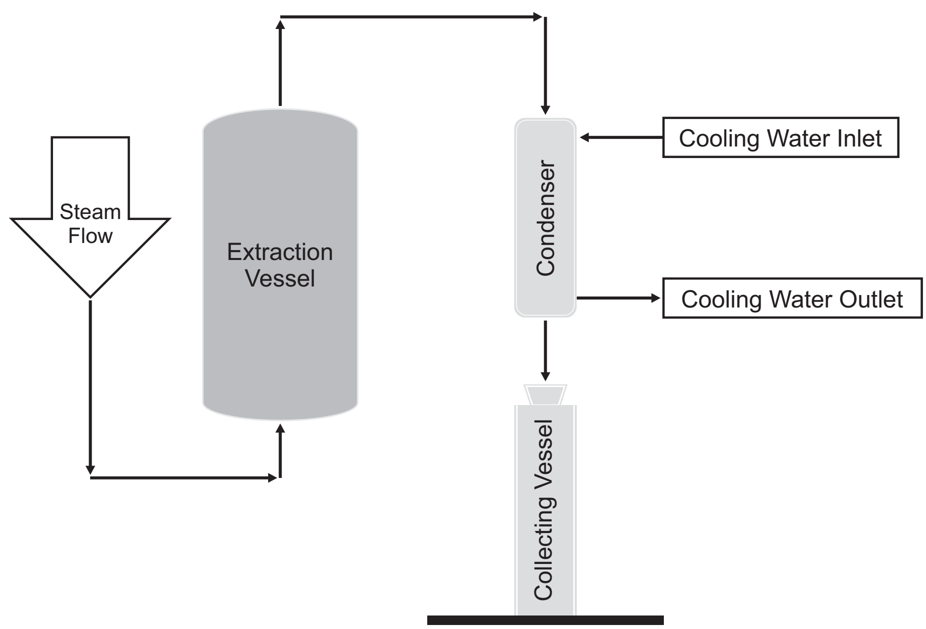
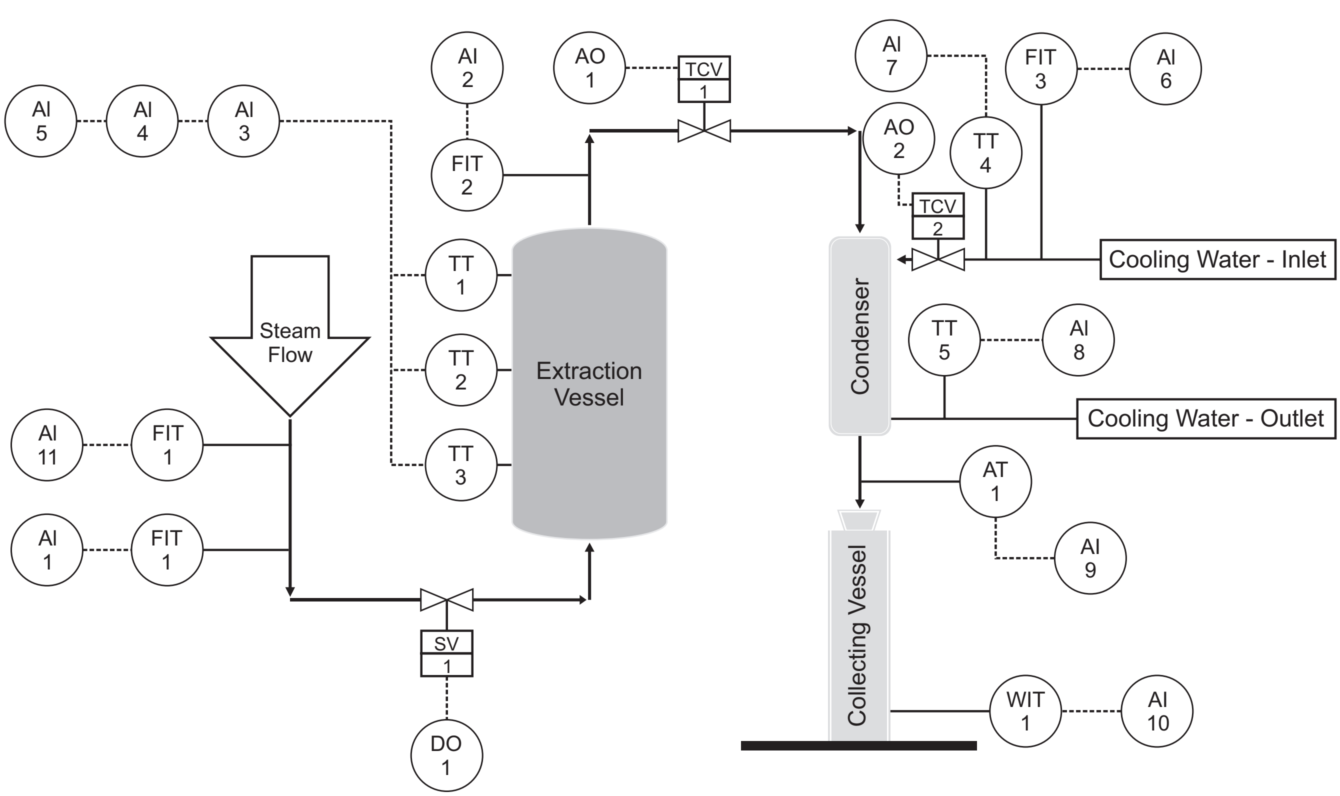


Figure 4. Essential oil extraction process with basic instrumentation.



Monitoring: SCADA – Supervisory, Control, and Data Acquisition System

Beyond the plant floor level (Figure 4), there are countless possibilities for controlling, monitoring, and managing the essential oil extraction process. Figure 5 shows how EO plant floor structure could be connected into a 4.0 proposition [7], using a SCADA system, which can either connect plant floor operation with upper systems or, staying in this level with a richer MMI – Man-Machine Interface and friendly access to process parameters, receipts, and historic data.

MES and ERP

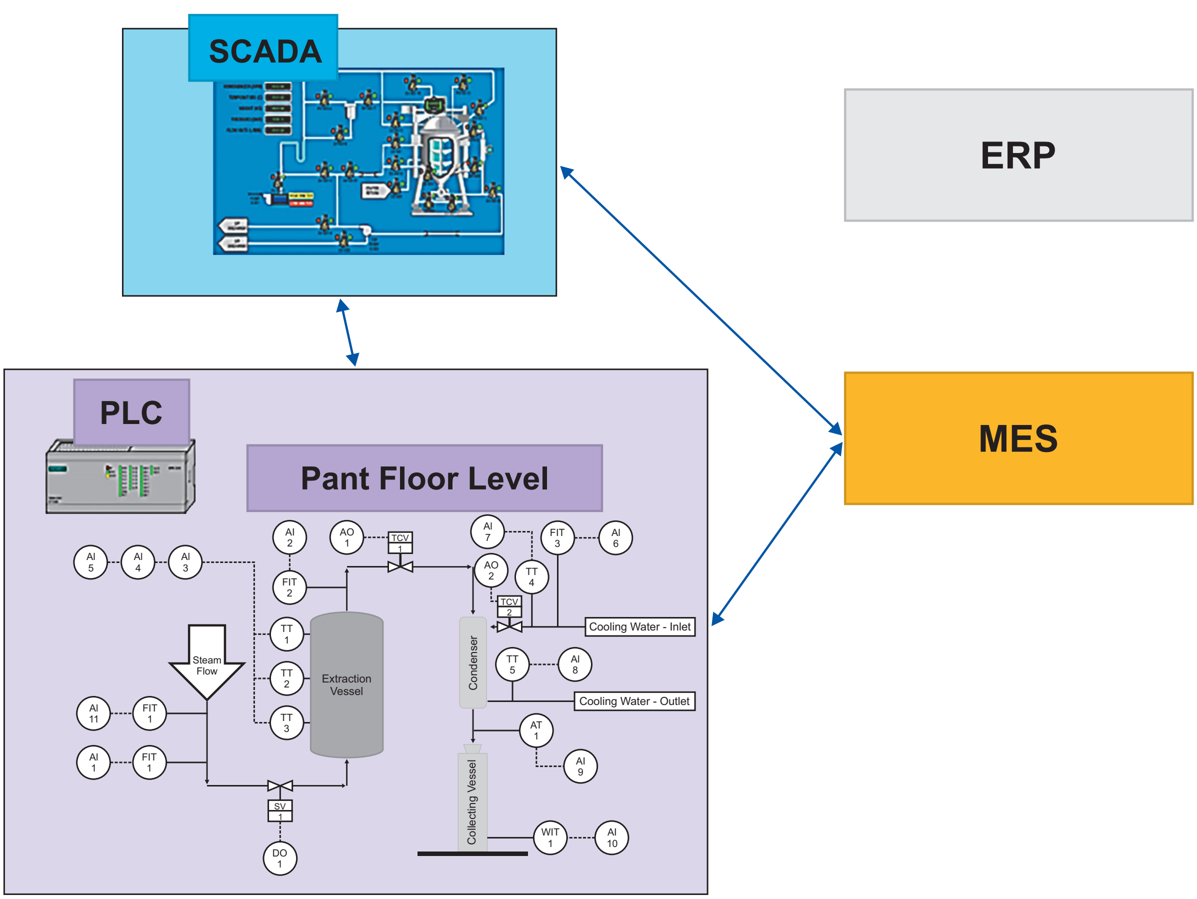
A complex manufacturing structure requires systems with broader scope for management purposes. For example, companies with a multi-factory structure, geographically distributed, part of a cooperative mode (Figure 6) can interconnect facilities to better serve business purposes as well as customer's expectations [8].

The complexity and the set of choices depending on the selection of the right investment, proper planning activities, and excellent installation.

Results and Discussion

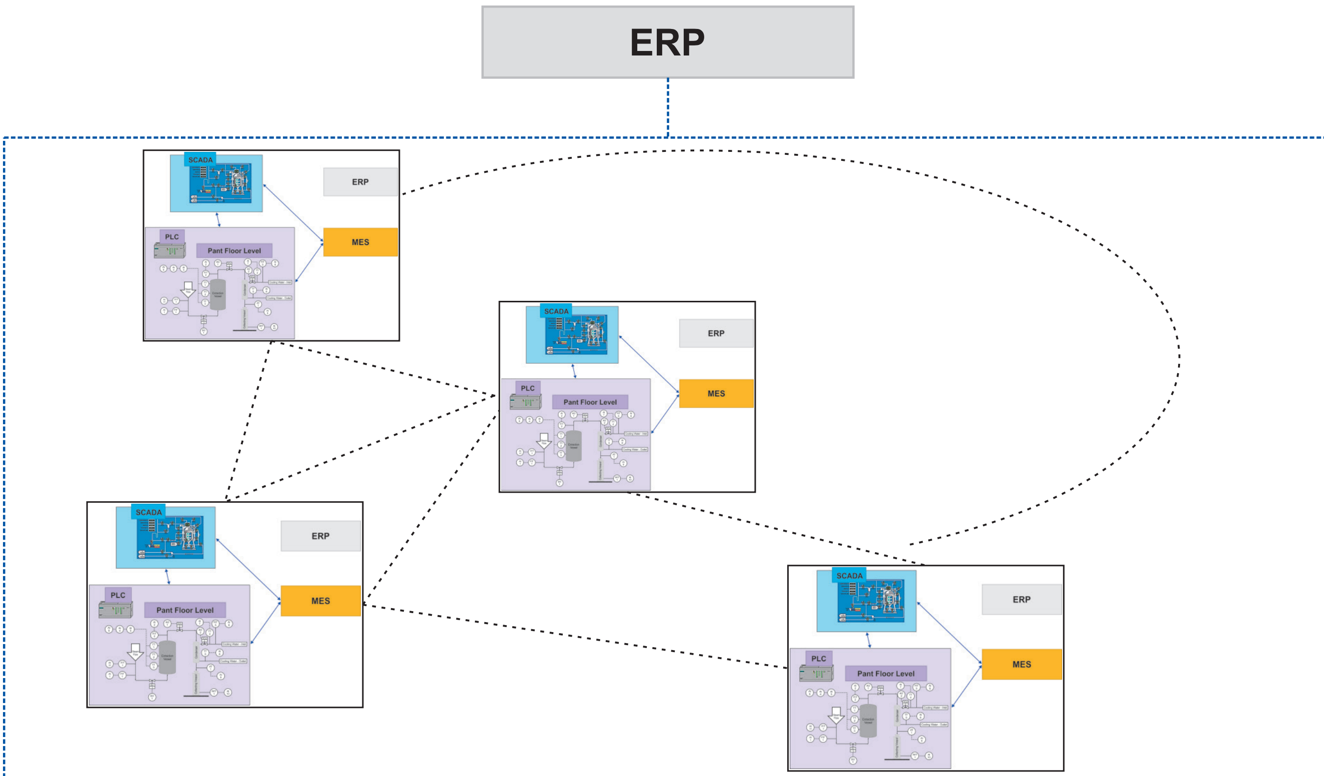
Technological enhancement possibilities for the EO extraction industry can significantly and positively impact quantities, extraction time and energy consumption through steam distillation. These improvements start in the plant instrumentation and control design, following to data acquisition and analysis, process simulation,

Figure 5. Example control, monitoring, and management configuration for EO.



Source: Adapted from mechatrone.com.

Figure 6. Multi-Factor structure view.



and machine learning which generates optimized parameters [13]. The possibilities brought in this paper aims at motivating readers to pursue the technological transformation in the extraction industry and continuous process improvement within organizations constantly developed to deliver customer, business, people, and better environmental results [3]. Steam distillation method can benefit from such technological advances and, as it uses water as a solvent, become one of the most environmentally friendly methods of extraction [4].

The innovation will add value and structure the business perpetuity as well as environmental performance. Green extraction processes are those qualified to consume less solvent (water) and energy, diminish waste generation and reduce or eliminate environmental impacts, in parallel to the benefits in the business bottom line: all in line with the industry 4.0 menu of possibilities.

The improvements explored in this paper are just a starting point for a profitable journey. Application of renewable energy, minimization of product quality degradation, better use for subproducts like the condensate (hydrosols) and solid matter remaining from the extraction cycle are side by side with robust control, monitoring, and management systems in the relentless quest for environmental care industry performances.

Conclusion

The extraction industry of essential oils presents excellent opportunities for technology updates, aiming at better yields, optimized energy consumption, and minimum waste generation. The search for operational excellence consists of a set of actions and projects, both technological and organizational, that will impact the business overall: safety, quality, reliability, good manufacturing practices, costs, and the reduction or elimination of environmental impacts, focus of this paper, reaching the level of what can be called green extraction.

The wave 4.0 brings a comprehensive portfolio of ideas to be converted into projects, enablers for better yields, quality, capacity management, and energy efficiency, as well as a considerable improvement in environmental performance.

Acknowledgments

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Extraction and Characterization of Coffee Silverskin Oil and Its Valorization by Enzymatic Hydrolysis

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This study investigated the coffee silverskin (CS) crude oil extraction process and characterization of physicochemical properties and enzymatic hydrolysis for fatty acids production. The soxhlet and ultrasonic extractions showed CS oil yield similar to 3.8% and 3.1%, respectively. CS oil extracted by soxhlet presented favorable physicochemical properties with the quality and was used as the feedstock for fatty acids production by enzymatic hydrolysis. The porcine pancreatic lipase showed hydrolytic activity of 1156 U.g-1 ± 13.4. Therefore, we verified the potential of application in biotransformation reactions of oils with biocatalyst with fatty acids production and valorization of coffee industry waste.
Keywords: Coffee Silverskin. Crude Oil. Enzymatic Hydrolysis. Fatty Acids.
Abbreviations: CS: coffee silverskin; PPL: porcine pancreatic lipase; SE: soxhlet extraction; UE: ultrasonic extraction; SCG: spent coffee grounds.

Introduction

Coffee is one of the most consumed beverages in the world and global consumption of 161 million of 60 kg coffee bags per year. So, there is a production of coffee byproducts such as coffee silverskin (CS) [1-3]. The CS is the thin tegument that covers the two coffee seeds and it is the only byproduct generated during green bean roasting and represents about 4.2 % (w/w) of coffee beans. From eight tons of coffee roasted, around 60 kg of CS is produced [1]. Therefore, CS disposal needs to be properly managed due to the increasing coffee production and the environmental impact of waste accumulation [1-3].

Some studies on the utilization of coffee waste have been advanced worldwide [4,5]. CS is a byproduct with the potential for application in the manufacture of functional paper having a low water absorbency [5]. Furthermore, CS can be used in the cosmetics, nutrition, and health industry, from the bioactive extract [4]. However, there is a promising approach to be explored that aims at the utilization of residual CS oil. CS oil is mainly composed of linoleic and palmitic acids [6]. Fatty acids can be applied in cosmetics, lubricants, and the food industry [7]. The hydrolysis of vegetable oils is the common method for fatty acid production and the reaction can be catalyzed by enzymes.

In the past years, there has been an increased interest in the isolation and valorization of compounds from the coffee industrial waste as a possibility to avoid their loss. Based on this context, the objective of this study was the valorization of coffee silverskin wastes. CS crude oils extraction process was investigated and the characterization of physicochemical properties was performed for further enzymatic hydrolysis for fatty acids production.

Material and Methods

Materials

Coffee silverskin samples were supplied by a factory, located in the city of Itabaiana-Se (Brazil).

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Hexane for oil extraction was obtained from Synth (Brazil). The porcine pancreatic lipase (PPL) was purchased from Sigma Chemical Co. (St. Louis, MO, USA). Other chemicals were of analytical grade.

Methods

Extraction of Coffee Silverskin Oil

The moisture removal of CS samples for subsequent oil extraction was accomplished via drying at approximately 60 ± 2 °C for 24 h before lipid extraction.

Soxhlet Extraction (SE)

For oil extraction, we used 20 g of CS with 150 mL hexane and refluxed by 8 h using Soxhlet apparatus. Following an extraction, lipids remain dissolved in the solvent solution and rotary evaporation was used to rapidly remove the excess solvent by applying heat to a rotating round-bottomed flask at reduced pressure.

Ultrasonic Extraction (UE)

The ultrasonic extraction study was performed with a 20 g silverskin sample for 30 minutes, (3 times in sequence) with 50 mL of hexane. The ultrasound equipment used was Ultronique (model USC-2800), frequency 25 kHz and power of 220 W. After each extraction of 50 mL of solvent, the solid fraction was separated by filtration. After the extractions were mixed, the division of the oil and solvent was by rotevaporation.

Any remaining traces of solvent were removed by nitrogen-assisted evaporation. All extraction methodologies were performed in triplicate and the yield (Equation 1) was calculated for later characterization of physicochemical properties, in which W_1 is the weight of the empty glass vial, W_2 is the weight of the vial plus the extracted oil and W_3 is the weight of the dry CS with,

$$\%\text{ oil recovered} = \frac{W2 - W1}{W3} \times 100 \qquad (1)$$

Physicochemical Properties

The quality of the oil was monitored through the physicochemical properties: acid value, free fatty acid content, iodine value, saponification value, peroxide value, density, kinematic viscosity, water content, and refractive index, according to standard analytical methods recommended by Official Methods of Analysis [8].

UV specific absorbances (K_{232} and K_{270}) assays were carried out following the analytical methods described by the Commission Regulation of the European Union for olive and olive-pomace oils (EEC) Nº 2568/91 [9].

The functional groups of oil were analyzed by Attenuated total reflection Fourier transform-infrared (ATR-FTIR) spectroscopy (AGILENT CARY 630 FTIR, Agilent Technologies, USA). ATR–FTIR measurements were performed by using approximately 5 µL of oil sample on the ATR crystal plate. with a scan range from 500 cm^{-1} to 4000 cm^{-1}.

In silico Analysis of Pancreatic Porcine Lipase

The open crystal structure of PPL (PDB code 1ETH) was obtained from Protein Data Bank. In silico analysis (lid identification, catalytic triad, and oxyanion hole on lipase three-dimensional structure) was performed using the BIOVIA Discovery Studio software [10].

Fatty Acid Production by Enzymatic Hydrolysis of Coffee Silverskin Oil

The enzymatic hydrolytic activity of free lipase was measured by the titration of the fatty acid which comes from the hydrolysis of CS residual oil [11]. The substrate was constituted by 50 mL CS crude oil with 50 mL gum arabic solution (3% w/v) and the addition of Triton X-100 (18%). The hydrolytic activity of the biocatalysts was determined according to Equation 2, in which one unit (U) of activity was defined as the amount of enzyme that liberates 1 µmol free fatty acids per min (µmol.min^{-1}) under the assay conditions.

$$\text{Hydrolytic Activities } (\text{U.g}^{-1}) = \frac{(V_A - V_B) \times N \times 10^3}{t \times m} \quad (2)$$

V_A corresponds to the volume of KOH spent in the titration of the sample (mL), V_B is the volume of the KOH spent in the titration of the blank (mL), N is the normality of the KOH solution, t is the reaction time in minutes and m is the mass of free (g).

Results and Discussion

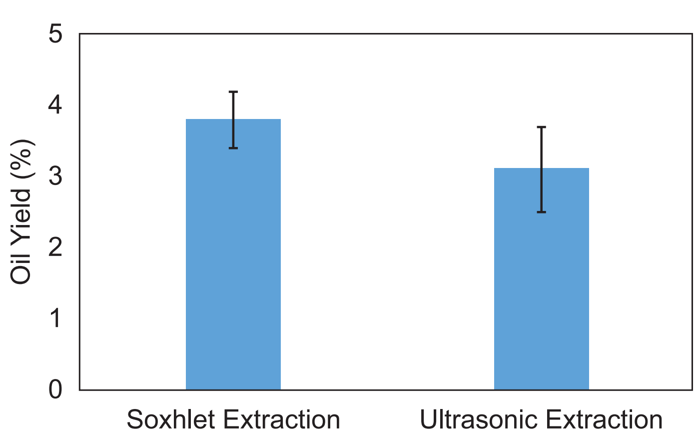
Extraction of Coffee Silverskin Oil

Figure 1 described the results of CS oil yield extractions by different methods (SE and UE). The soxhlet extraction using hexane presented 3.8% of extracted lipids, while ultrasonic extraction 3.1% (no significant differences; $p \geq 0.05$). The yield lipid of the silverskin analyzed in this study was complete following the values with the literature, between 2.4-3.4% [3,12]. The variation found in CS lipid content can be partially attributed to factors such as the different blends of coffee varieties, the origin of the coffee beans, and the processing. However, the oil extracted by soxhlet was shown to have a physical aspect (viscosity, coloring) more suitable for future applications. On the other hand, the oil obtained from ultrasound-assisted extraction was affected due to shear forces generated by the ultrasound cavitations. So, cell wall ruptures occurred, increasing the contact area between the solvent and the materials, intensifying the general oil extraction process and other compounds [13]. Considering the yields and quality of the extracted oil, the soxhlet extraction was selected as the most promising for the characterization of physicochemical properties and hydrolysis of the crude oil.

Physicochemical Properties

Table 1 presented the physicochemical properties related to the quality of the crude CS oil. However, in the literature, there is the characterization of the physicochemical properties of oil from other residues from coffee processing, as the spent coffee grounds (SCG) (Table 1). The acid value of CS oil was 13.5 mg_{KOH}/g, an important quality parameter related to the extent of oil degradation by hydrolysis, releasing free fatty acids [14]. The iodine index was responsible for expressing the degree of oil unsaturation by breaking the double bonds and then the iodine is inserted and is directly related to its oxidative stability [15]. The analyzed saponification index was 158.3 mg_{KOH}/g, just below the expected range for vegetable oil (180 and 200 mg_{KOH}/g). The relatively low levels of saponified matter mean that the oil remains viscous and does not freeze easily, making it suitable for applications in oil transformation [14]. The peroxide value was

Figure 1. Extraction yield from coffee silverskin oil by soxhlet extraction and ultrasonic extraction.



5.9 meqO_2/kg, which indicates high resistance to oxidation of CS oil, and that it can be stored for longer [15]. Density at 40 °C amounted to 0.90 g/cm³ and kinematic viscosity at 40 °C was 73.5 mm²/s. The unsaturated oils have higher densities than those saturated oils. The refraction index at 40 °C was 1.46, in which a larger hydrocarbon chain will deflect a greater amount of light, resulting in greater refraction. The content of water in oil was 0.6%. The determination of oil moisture is important, as water favors the growth of microorganisms and product degradation. The low values of K_{232} and K_{270} in both crude CS oil indicated a low extent of oxidation. For crude oils, K_{232} is related to the first stage of oxidation with the presence of conjugated hydroperoxides, while K_{270} is related to the presence of secondary oxidation products, like aldehydes, ketones, and short-chain fatty acids [16].

Figure 2 shows the FTIR spectrum used to analyze the main functional groups present in the silverskin oil. The absence of a peak after 3000 cm^{-1} indicates very low concentrations of impurities contained in hydroxyl groups (OH), such as free glycerol and water, which corroborates the moisture data (0.6%) obtained in this study. The two intense bands at 2852 cm^{-1} and 2924 cm^{-1} were due to CH2 asymmetric and symmetric stretching vibrations, attributed to the fatty acids present in the oil. Peaks between 722 cm^{-1} and 1466 cm^{-1} are associated with various CH groups. The bending of cis C=C was observed at peak 722 cm^{-1}, the vibration of –C–O ester groups which corresponded to the large area at peak 1158 cm^{-1} and C=O stretching related to peak 1720 cm^{-1} [17].

In silico Characterization of Pancreatic Porcine Lipase (PDB: XX) and Potential Application in Hydrolysis of Coffee Silverskin Oil

PPL is a protein with 50 kDa and a specific sequence of 449 amino acids that play a key role in PPL specificity (Figure 3A). Figure 3B presents the three-dimensional structure of PPL has an α-helical flexible lid (constituted by amino acids between 237 and 261, in red). In closed conformation, the flexible lid covers the enzyme catalytic triad (inactive state). On the other hand, PPL open conformation is based on lid movement exposing the amino acid from enzyme catalytic triad, Serine 153, Aspartic acid 177, and Histidine 264 (Figure 3C), to interact with substrates in organic media and the water/lipid interfaces. The amino acid residues, Phenylalanine 78 and Leucine 154 (PPL oxyanion hole), play a significant role in

Table 1. Physicochemical properties of oil extracted from coffee silverskin.

Properties	**Determined values**	**Haile et al. [15] SCG**	**Al-Hamamre et al. [14] SCG**
Acid value (mg_{KOH}/g)	13.5 ± 0.2	9.8	7.3
Free fatty acid (mg_{KOH}/g)	6.7 ± 0.2	4.9	3.6
Iodine value (gI_2/100g)	74.6 ± 2.8	79	ND
Saponification value (mg_{KOH}/g)	158.3 ± 1716	7.3	173.9
Peroxide value (meqO_2/kg)	5.9 ± 0.3	ND	ND
Density at 40 °C (g/cm³)	0.90	0.92	0.92
Kinematic viscosity at 40 °C (mm²/s)	73.5	42.6	55.5
Refractive index	1.46 ± 0.003	ND	ND
Water content (%)	0.6 ± 0.3	0.03	ND
K_{232}	0.26 ± 0.004	ND	ND
K_{270}	0.33 ± 0.003	ND	ND

Values are mean ± SD of triplicate determinations. ND = not determined.

Figure 2. FTIR spectra of extracted silverskin oil.

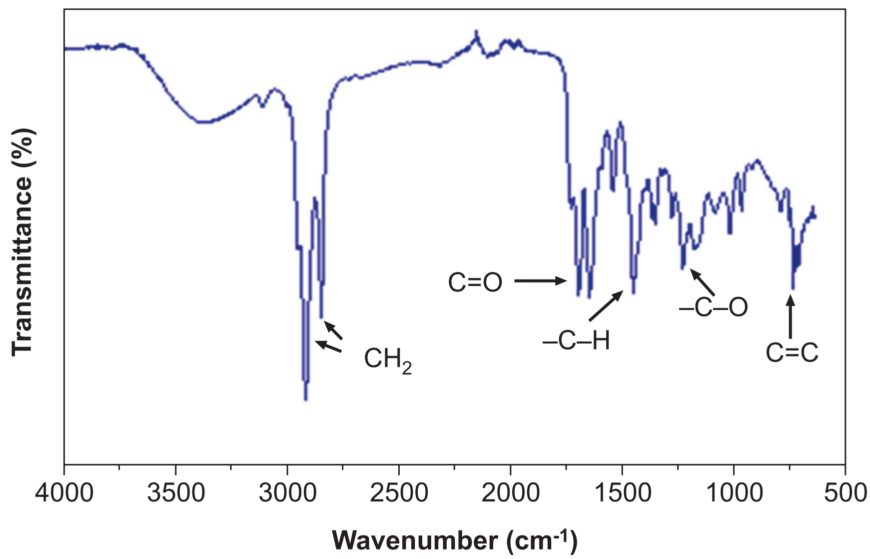
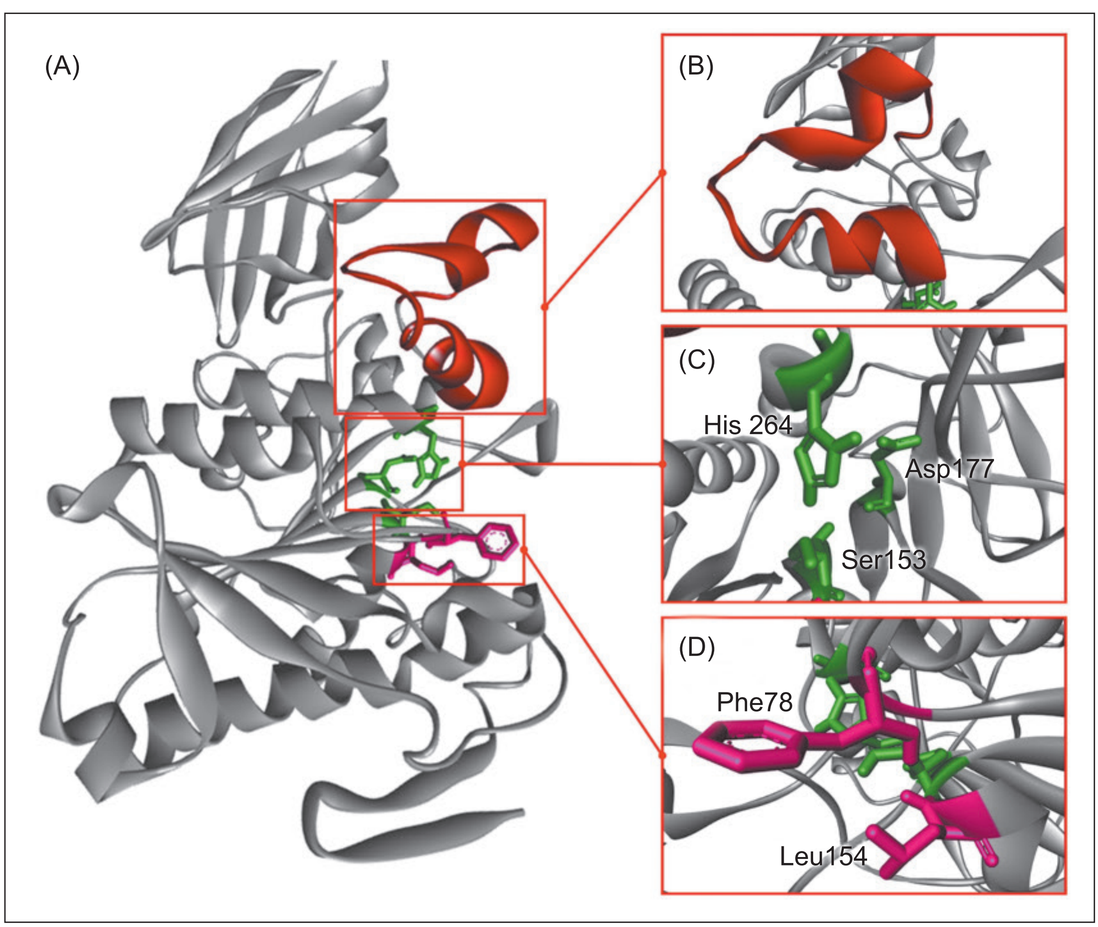


Figure 3. (A) Three-dimensional structure of pancreatic porcine lipase (PPL; PDB code 1ETH), (B) Lid of PPL (237–261, in red), (C) Catalytic triad of PPL (Serine 153, Aspartic acid 177 and Histidine 264, in green), and (D) oxyanion hole of PPL (Phenylalanine 78 and Leucine 154).



lipase catalysis reaction, stabilizing the negatively charged tetrahedral intermediates by hydrogen bonds with substrates (Figure 3D) [18].

The crucial requirement to produce fatty acids by enzymatic hydrolysis is biocatalyst hydrolytic activity. PPL is an *sn*-1,3 regiospecific lipase that preferentially catalyzes positions 1 and 3 of triacylglycerides in hydrolysis reaction [19,20]. Thus, PPL was used as a biocatalyst for biotransformation of CS oil by enzymatic hydrolysis, showing the hydrolytic activity of 1156 $U.g^{-1}$ ± 13.4 after 10 min of the hydrolysis reaction. Based on these results, PPL showed to be an effective and sustainable biocatalyst to obtaining fatty acids from CS oil, a bioproduct of interest to many industrial sectors, such as food, pharmaceutical, cosmetic, and fuel.

Conclusion

Based on the results, and considering the energy matrix and utilization of the coffee silverskin with residual oil, a potential of application in biotransformation reactions of crude oils was verified with favorable physicochemical properties for the application, with the conversion of food byproducts into value-added products.

Acknowledgements

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Technological Prospective Study of Green Coffee Processing

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This article aims to identify patents referring to coffee processing and to correlate them with the exportation scenario of the processed coffee. The research relates the keywords "coffee" and "treatment" with the International Patent Codes, in the Espacenet database. The CIP A23F5/02 has predominance, with the United States figure as the largest holder (20) and Brazil with only one patent deposit. The article suggests that countries that promote research in technology become more competitive in the exportation of processed coffee, even without producing the grain. This explains the need for policies aimed at valuing research in technological innovation in the national industry.
Keywords: Export. Coffee. Treatment.
Abbreviations: CIP: International Patent Codes; CONAB: National Supply Company; MDIC: Ministry of Development, Industry and Foreign Trade; Espacenet: European Patent Office; EU: European Union; us: United States; USDA: United States Department of Agriculture; CECAFÉ: National Council of Coffee Exporters of Brazil; SEAGRI: Secretariat of Agriculture, Livestock, Irrigation, Fisheries, and Aquaculture.

Introduction

Coffee came from Africa and was introduced into Brazil in the 17th century. Here it found favorable climatic and social conditions to make the country a reference in production. The history of coffee grain cultivation is inherent to the country's development, it was significant for the generation of financial resources, social evolution, and today it occupies second place in world wealth, second only to oil [1]. According to the National Supply Company (CONAB), Brazil stands out as the largest producer and exporter of green coffee in the world [2,3].

However, some references of economic power are emerging in the world panorama, concerning the production and export of processed coffee. A study published by the Ministry of Development, Industry and Foreign Trade (MDIC) signaled that countries such as Germany, Spain, Indonesia, Italy, Mexico, and Switzerland are investing in green coffee treatment technologies [4]. The study warns about the fact that Brazil has competitive advantages compared to other countries, as it has a large and diversified coffee park, in addition to the considerable number of coffee growers who respond to stimuli in technology for production [5].

The cycle of green coffee begins in the planting of seedlings and goes to the processes that involve the harvest and ends in the drying of coffee beans, which are subsequently known as green coffee. From there, the processed coffee production cycle begins, which is set off with the change from raw (green) coffee to roasted coffee, moving through the processes of removing impurities, selection of beans before and after roasting, and finally ends with the grinding processes.

Material and Methods

The research is not linked to any educational or agrarian research body. Developed and financed by the authors themselves, the research objective was to elaborate a technological prospection study and map the patents deposited to correlate to the world panorama of processed coffee exports to

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assess which technologies and measures Brazil should take to become more competitive in the export of processed coffee.

So, a search was carried out in the database of the European Patent Office (Espacenet), using the keywords "coffee" and "treating" and the International Patent Classification (CIP). It was developed between the months of January and June of 2020 and divided into four phases: Search for Information, Treatment of Information I/II, Representation of results and techniques to propose future scenarios.

In the first phase, it was identified that the patents of the A23F family - "Coffee; Tea; their substitutes; manufacture, preparation, or infusion thereof" and linked to patents code A23F5/00: "Coffee; Coffee substitutes; Preparations thereof"; these patents adhere to the purpose of the article. It was observed that the most frequently found CIPs were A23F5/02; A23F5/04; A23F5/10; A23F5/16 and AF23F5/2. However, the patents A23F5/04, A23F5/16, and A23F5/20 combined processes for removing unwanted substances. For this reason, CIP A23F5/04 was elected as the representative of this process (Figure 1).

For phase 3, the patents that relate to CIP A23F5/02 were eligible due to the resemblance with the patents that relate to codes A23F5/04 and A23F5/1. In Espacenet, the documents were select, imported with the CSVed 1.4.9 software, compiled, and exported to a Microsoft Excel table as part of the analysis phase (Figure 2).

Table 1 presents the documents found in Espacenet based on combinations of keywords and CIP, adopted by the National Institute of Intellectual Property, which could enrich the discussion about the objects of this study.

For being restricted to one process for the treatment of green coffee, the patents whose CIP code A23F5/04 and A23F5/10 directly correlate to the CIP code A23F5/02 were eligible in phase 3. This shows how it is connected to the other codes

Figure 1. The first and the second phase of the methodological flow.

Phase 1	**Search for information** - Search option: "Advanced Search". - Use of the keywords: "coffee" and "treating" in the "title" and "summary" fields. - Identification of patents in the A23F family. - Adoption of patents linked to code A23F5/00.
Phase 2	**Treatment of information I** - Selection of patents A23F5/02, A23F5/04 and A23F5/10 due to their relevance. - Use of the keywords: "coffee" and "treating" correlating with the patents found. - Making a table with data obtained (Table 1).

Figure 2. The third and the fourth phase of the methodological flow.

Phase 3	**Treatment of information II** - Exclusion of patent documents belonging to the same family. - Selected the patent code A23F5/02 as the focus of the objective. - Choose of the CSVed 1.4.9 software to compile the information.
Phase 4	**Representation of results and techniques for reflection on the future** - Import of document information citing patent A23F5/02 to CSVed 1.4.9. - Do the preview and editing of the table proposed by the software. - Export the table to Microsoft Excel. - Editing and analysis of data relevant to the topic.

Table 1. Search for patents by patents and code (CIP).

Coffee	Treating	A23F5/02	A23F5/04	A23F5/10	Total
*					10.000
*	*				1.015
*	*	*			64
*	*		*		46
*				*	27
*	*	*	*	*	5

related to the treatment of green coffee beans (Figure 3).

Results and Discussion

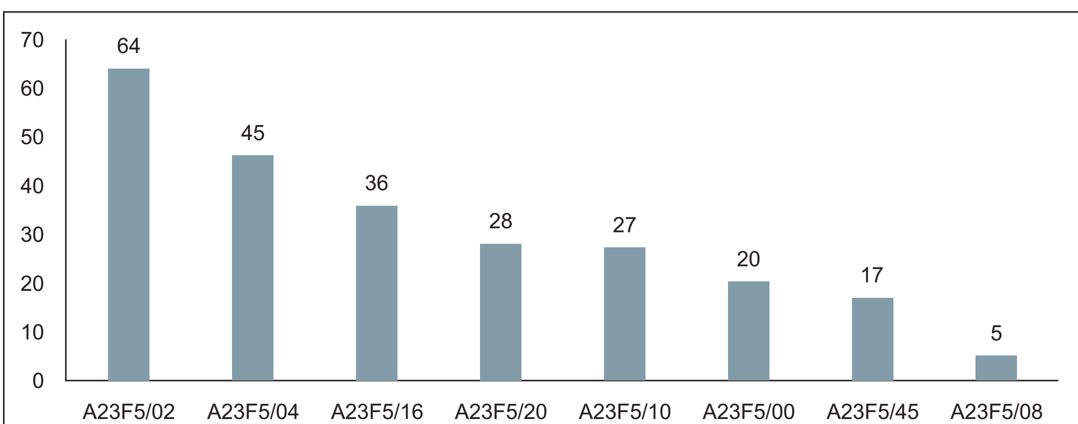
During the research, the CIP most found was code A23F5 / 02, which refers to the process of green coffee (coffee in its post-harvest state) in general and its preparations. Then the codes for the removal and treatment of impurities and residues, whose codes are A23F5/04, A23F5/16, and A23F5/20. Finally, with 5 citations, the code A23F5 / 08, which refers to coffee grinding methods.

Patent filings related to the treatment of green coffee dated since 1912 had significant growth in the last two decades, with the years 2014 and 2015 standing out with 4 filings. Brazil is the author of only one deposit, dated in 2007. The United States (US) stands out, with 20. The European Union (EU) emerges with 17. In Asia, Korea and Japan are the leaders, with 4 and 16 patents respectively (Graph 1).

The depositor with the highest number of patents for the treatment of green coffee is Nestlé S.A., a Swiss company, responsible for 5 patents.

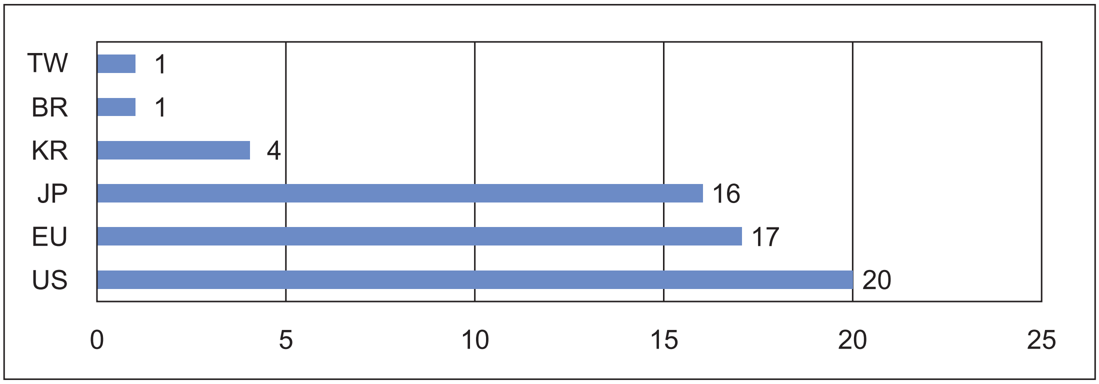
The American Verdurin Company and the Japanese Suntory LTD follow right behind (Graph 2).

Figure 3. Distribution of patents related to coffee processing by codes.



A23F5/02: *Treatment of green coffee; Preparations produced thereby.*
A23F5/16: *Reduction or removal of alkali content.*
A23F5/04: *Removal of unwanted substances.*
A23F5/10: *Processes for the treatment of roasted coffee.*
A23F5/20: *Recuction or removal of alkali content; preparations produced by this means; extracts or infusions thereof.*
A23F5/08: *Coffee grinding methods.*
A23F5/00: *Coffee; coffee substitutes; your preparations.*
A23F5/46: *Coffee aroma; Coffee oil; Coffee flavoring or coffee extract.*

Graph 1. Countries with the highest number of patent filings.



TW: Taiwan; BR: Brazil; KR: Korea; JP: Japan; EU: European Union; US: United States.

According to the United States Department of Agriculture (USDA) in 2020, Brazil is the largest coffee producer in the world (Table 2) [6,7].

The country's leadership is also seen in the ranking of green coffee exports (Table 3) [6,7].

However, the country is limited to the supply of raw material (green coffee) to exporters of processed coffee [8]. In this second cycle of coffee, some countries focus on investing in research and technology to add value to the product, according to the ranking of processed coffee exporters. In this ranking, it is possible to identify the importance of the company Nestlé SA patent filings to the relevance of Switzerland in the exportation of the processed coffee world scenario, a country that does not possess appropriate climatologic and geographic characteristics to cultivate the bean. (Table 4) [6,7].

According to the study, the focus of these countries is on technologies aimed at the selection of grains and removal of unwanted substances, CIP A23F5/04, both for green coffee and for subsequent processes of changes in the impurities of the grain after roasting or grinding. This observation serves as a guide for the use of policies to encourage research and technology development that can change the production criteria from a focus on volume to a focus on quality and identity [5]. A strategy that has to be initiated by cooperatives or associations with administrative and technological support to producers, and support by the local government [9,10]. The National Council of Coffee Exporters of Brazil (CECAFÉ), released the ranking of the destination of Brazilian green coffee (Graph 3), it is possible to notice the presence of the countries that hold the largest

Graph 2. Companies responsible for the largest number of patent filings.

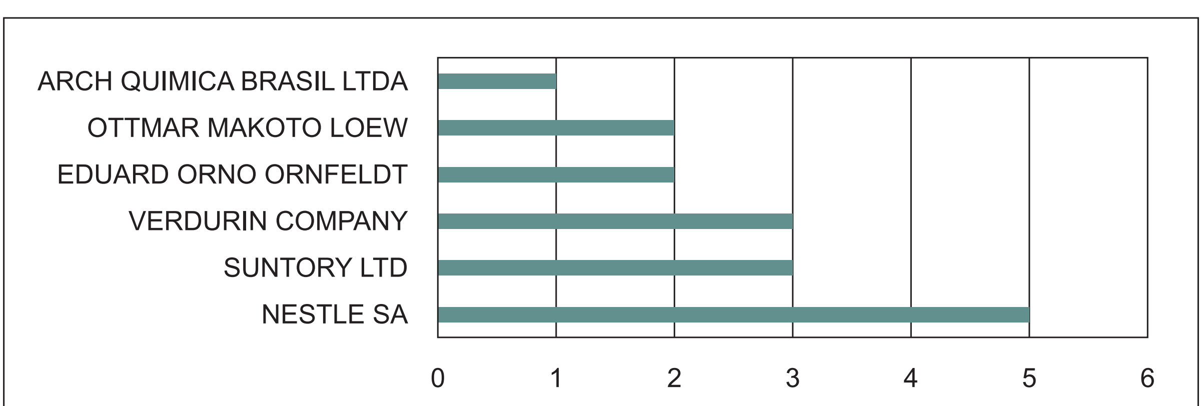


Table 2. The highest coffee producer in the world.

Position	Country	2019/20 Ton-60kg Bag	2020/21 Ton-60kg Bag
1	Brazil	59,300	67,900
2	Vietnam	31,300	30,200
3	Colombia	13,800	14,100
4	Indonesia	10,700	10,300
5	Ethiopia	7,450	7,500
6	Honduras	5,600	6,125
7	India	4,890	5,310

Table 3. The highest green coffee exporters in the world.

Position	Country	2019/20 Ton-60kg Bag	2020/21 Ton-60kg Bag
1	Brazil	32,700	37,000
2	Vietnam	24,000	24,000
3	Colombia	12,000	12,400
4	Indonesia	6,096	5,900
5	Honduras	5,500	5,575
6	Uganda	4,000	4,500
7	Peru	4,360	4,265

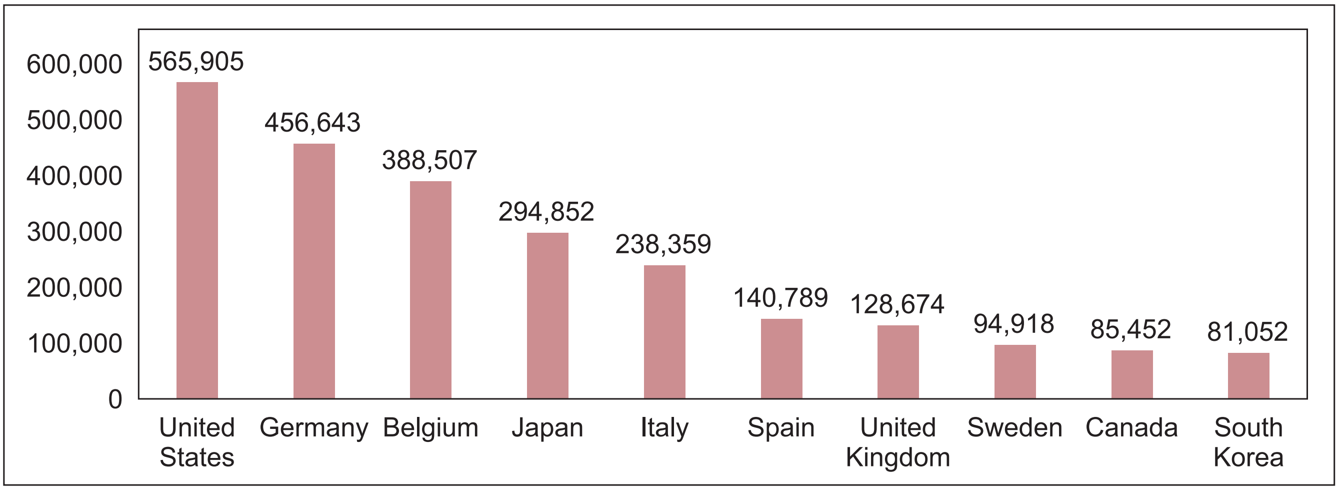
Table 4. The highest exporters of processed coffee in the world.

Position	Country	2019/20 Ton-60kg Bag	2020/21 Ton-60kg Bag
1	Europe	1,775	1,500
2	Switzerland	1,425	1,400
3	Vietnam	550	550
4	Colombia	120	300
5	Mexico	230	230
6	Indonesia	56	50
7	China	25	25
8	Brazil	24	24

number of patent deposits related to the processing of green coffee, previously shown in Graph 1. The analysis corroborates with the Secretariat of Agriculture, Livestock, Irrigation, Fisheries and Aquaculture (SEAGRI), in a 2011 report, where the authors state that most producers, especially small ones, do not use the most modern technologies available for coffee growing, especially about coffee processing [11].

Although the country stands out as the largest coffee producer in the world, the number of patents related to the treatment of green coffee reflects the world panorama of processed coffee. In Brazil, the coffee is exported and used as an input for the expansion of the industrial sector in other countries, which in some cases, do not even have a geographical and climatic condition for planting. This reinforces the thesis that there are ways to add value to green coffee and have to be adopted in small and medium coffee industries in the country. Reference countries in technology and innovation invest in research to add value to the product. The

Graph 3. The highest destinations for the Brazilian green coffee bean.



United States, for example, has 20 patents filed. Brazil, despite being the world's largest coffee producer, has only one deposit, made by a chemicals company in the biotechnological industry.

Thus, it is possible to affirm that Brazil has the potential to figure as an important exporter of processed coffee in the world. However, for this panorama to become a reality Brazil must reflect countries that invest in technology and research, such as the countries with the largest numbers of patent filings. There is a favorable, broad market for the country, which can boost the generation of jobs and strengthen national technology while favoring the Brazilian economy.

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Effect of Temperature on Physical Properties of Canadian Maple (*Acer saccharum marsh*) Syrup

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The optimization of industrial operations requires knowledge of thermodynamics related to the process, which can be determined either experimentally or by predictions based on an appropriate model and a set of data. Although maple syrup is a nearly unprocessed natural product, its industrial manufacture applies usual chemical-mechanical fluid operations. So, appropriate equipment designs are conditioned by sufficient information on mixing thermodynamics. In this paper, we analyze the temperature effect on maple syrup and its aqueous dilution in terms of different properties, trying to explain their special physicochemical behavior to explore the strength of the interactions among heavy covalent macromolecules and shorter chain polar solvents.
Keywords: Food Engineering. Canadian Maple Syrup. Thermodynamic Properties. Theoretical Model.
Abbreviations: P: density; u: ultrasonic velocity; Lf: free length; Z: specific acoustic impedance; b: van der Waals' constant; S: collision factor.

Introduction

Canada produces more than 78 percent of the world's maple syrup. In 2016, Canadian producers exported 45 million kg of maple products, with a value of US$381 million. Canada's share of the world's maple production increased over 225% in the last decade, exporting to more than 50 countries. The most important export market is the United States, to which Canadian producers send 65% of total exports. Other principal markets are Germany (11%), Japan (7%), United Kingdom (4%), Australia (4%), and France (4%). The chemical complexity of the maple syrup taste is not completely known yet. Flavor compounds of maple syrup include volatile phenolic compounds, carbonyl compounds, and alkyl pyrazines [1], typical products of the advanced stages of the Maillard reaction, which have been the subject of numerous studies because of the impact on the flavor and color of different foods [2]. The most widely accepted mechanism for the formation of pyrazines in food systems is via the Strecker degradation of amino acids, which in the presence of a-diketones result in the formation of a -aminoketones and Strecker aldehydes [3]. The formation of pyrazine compounds is considered to require sugar fragments. It has been reported that alkaline conditions promote sugar fragmentation and result in increased formation of pyrazines. These compounds, mostly found in heated foods, have organoleptic characteristics [4]. Different aminoacids [5] and sucrose, glucose, or fructose [6-7] present in the maple sap are the main precursors of the pyrazines in maple syrup. Maple syrup is considered a better alternative to traditional refined sugar and many other available natural sweeteners, due to its oligo-elements profile and high amount of bioactive compounds with well-known antioxidant potential action [8-10]. Despite the economical and nutritional importance of this natural product, only a few studies in the last years have been developed closely related to chemical determination [11-12], the application of instrumentation techniques for quality control, adulteration, and compounds identification [11, 12] or treatment procedures. Most of them are related to narrow operational conditions and the chemical constitution of maple sap or syrup, but not with thermophysical characteristics, their temperature dependence, or

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potential applications in industrial elaboration. Regarding the unit operation field, optimization of industrial operations requires knowledge of the thermodynamics of compounds and mixtures related to the process, which can be determined either experimentally or by predictions based on an appropriate model and a set of data. Although maple syrup is a nearly unprocessed natural product, its industrial manufacture applies usual chemical and mechanical fluid operations, so the optimization and adequate designs of equipment are conditioned by sufficient knowledge of mixing thermodynamics. Operations such as pumping, evaporation, or filtration are required for the sap treatment and for quality control during the process, which is based on the evolution of physical properties of the sap throughout the process. Refractive techniques are usually applied to determine the mature point of evaporation and the quality of the maple syrup, although no bibliographic data has been found in the open literature.

In this paper we analyze the temperature effect (278.15-323.15 K) on the maple syrup and aqueous dilution of this product, in terms of density and isentropic compressibility, assuming that in the last steps of maple syrup concentration no significant chemical changes take place and only water is removed. We have attempted to explain the physicochemical behavior of the mixtures indicated above, to explore the strength and nature of the interactions among the complex components evolved.

Material and Methods

Due to the importance of theoretical knowledge on industrial design, the prediction of physical property values was realized by applying different methods. For density, a modified equation of Subbiah-Barber, and an empirical equation for ultrasonic velocity. The obtained results were analyzed and commented upon. Various parameters such as intermolecular free length (Lf), specific acoustic impedance (Z), van der Waals' constant (b), collision factor (S), and compressibility hydration number (nh) were computed. The analysis of these volumetric and acoustic magnitudes pointed out the availability of intense effects among solute + solvent molecules at a determined range of concentration and temperature. Attending to the deviation in computed data, we conclude that the application of these models shows close agreement with the experimental data reported in this paper. The present study of thermodynamics shows the strong dependence of these properties on temperature and the amazing trend of the isotherms, showing them as an accurate alternative procedure for determining the optimal point of syrup concentration by sap evaporation.

Results and Discussion

Maine law requires maple syrup to be evaporated to a density greater than 66% Brix at 68 degrees F. Parenthetically, syrup with a density reading below 66% Brix is illegal since it is more likely to ferment. With density above 68% Brix, it may crystallize, causing consumer complaints. Various instruments can be used to check the density: hydrometers, hydrothermal, refractometers, light transmittance meters, and many others. While the particular grade of pure maple syrup is largely determined by color, all grades of syrup must meet minimum density standards. In most maple syrup producer countries, the minimum allowable density of maple syrup is 66% by weight of soluble solids (66.0 degrees Brix at 68 degrees F). Although syrup density can be measured in three ways - (1) weight, (2) use of an optical refractometer and (3) use of a hydrometer -, only the refractometer and hydrometer methods are recommended for producer use. Syrup weight may be used as an estimate of volume, but it is too imprecise to be used as an indicator of density. While the minimum syrup density of 66.0 degrees Brix is a legal requirement in most states, there are also several practical reasons for carefully controlling the finished density of maple syrup. Viscosity, a measure of a fluid's resistance to flow, is an important characteristic of maple syrup. Until the sugar concentration of maple sap exceeds 30 degrees Brix, an increase in sugar percentage has relatively little effect on viscosity. However, as the sugar concentration increases toward and through that of standard density syrup, the increase in viscosity is more pronounced. Maple syrup has a density only 0.5 degrees to 1 degree Brix below standard density syrup feels and tastes thin. Conversely, an increase of only 1 degrees Brix above standard density causes the syrup to acquire a thick, pleasant feel to the tongue, and the perception of considerably increased sweetness. This explains why some producers finish their syrup slightly above standard syrup density; customers can tell the difference between 66 degrees and 67 degrees Brix and prefer the heavier syrup. Syrup density also affects how well quality is maintained when the syrup is stored. Light density syrup spoils faster. Syrup with a density of more than 67 degrees Brix may precipitate sugar crystals when stored at room temperature for extended periods. Finally, the higher the density at which syrup is finished, the less that can be made from a given amount of sap. Using a refractometer to determine the density of syrup by measuring its refractive index is a relatively accurate, yet simple method. This possibility has been checked in earlier works for another kind of mixtures. A refractometer works by measuring the refractive index of a solution (syrup) which is directly related to the number of dissolved solids (sugar) present in the solution. Refractometers are precise instruments and are particularly well suited for determining the density of syrup in Brix units at room temperatures. They are not well suited for measuring the density of hot syrup (180 degrees F and above) but are very convenient for larger operations of buying and selling syrup. They are also commonly used to determine the density of syrups entered in various competitions. But as far as we know, there is no open literature data of refraction for maple syrup taking into account this magnitude is strongly dependent on temperature. This fact potentially is the cause of wrong determination of the optimal point of dehydration, due to inaccurate data of refraction to translate experimental measurements and inaccuracy in controlling the temperature of samples to be measured. Moreover, the computation of density through refraction leads to errors in the final density values. To avoid these problems, it is necessary the use direct magnitude measurements and the disposable of its temperature dependence. The measured physical properties were correlated as a function of temperature using Eq. 1:

$$P = \sum_{i=0}^{N} A_i T^i \qquad (1)$$

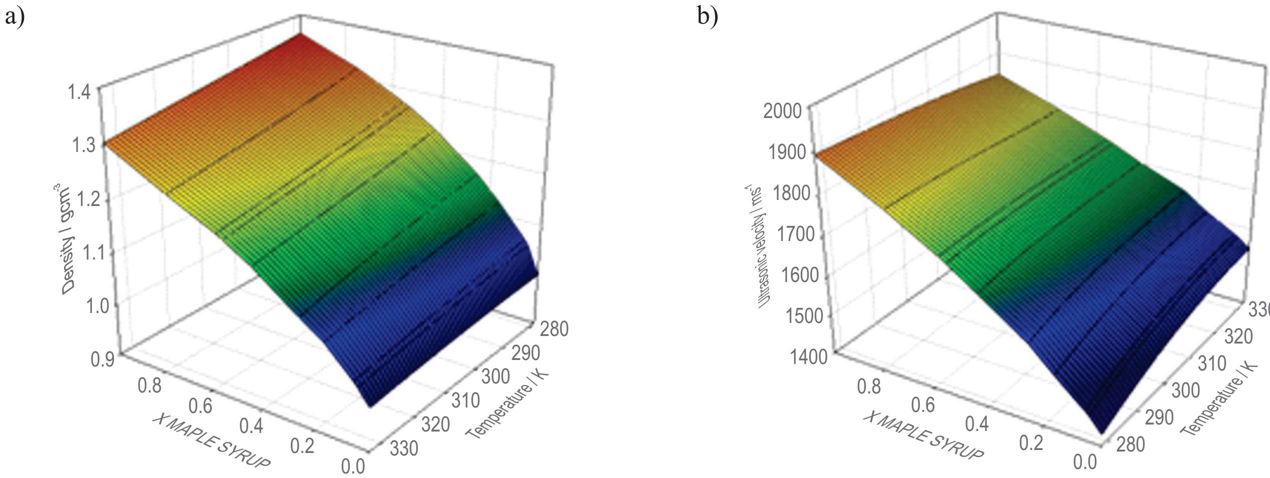
in which P is density (gcm^{-3}) or ultrasonic velocity (ms^{-1}), T is the absolute temperature in Kelvin and Ai are fitting parameters. N stands for the extension of the mathematical series, optimized through the Bevington test. The fitting parameters were obtained by the unweighted least squared method applying a fitting Marquardt algorithm. The root means square deviations were computed using Eq. 2, where z is the value of the property, and nDAT is the number of experimental data.

$$\sigma = \left(\frac{\sum_{i=1}^{n_{\mathrm{DAT}}} \left(z_{\mathrm{exp}} - z_{\mathrm{pred}} \right)^2}{n_{\mathrm{DAT}}} \right)^{1/2} \qquad (2)$$

In Figures 1a and 1b, the temperature trend of density and ultrasonic velocity are gathered.

We have attempted to explain the physicochemical behavior of this mixture, to explore the strength and nature of the interactions between the components by deriving various thermodynamic parameters from the new collection of density and ultrasonic velocity. The parameters derived from the experimental measured data were intermolecular free length (Lf), specific acoustic impedance (Z), van der Waals' constant (b), and collision factor (S). As observed, intermolecular free length decreases

Figures 1a and 1b. Effect of temperature for (a) density and (b) ultrasonic velocity of Canadian maple syrup + water.



x: molar fraction of maple syrup.

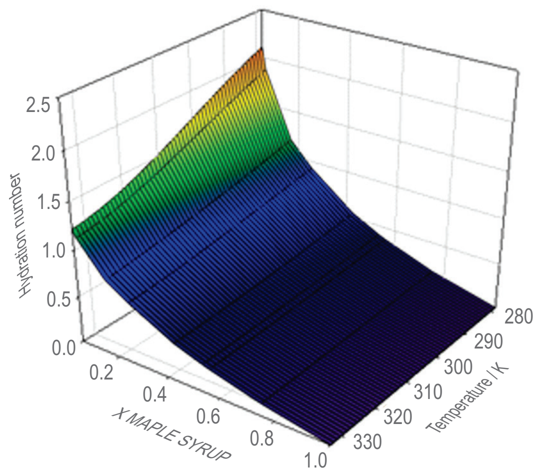
from pure solvent (water) towards pure solute (maple syrup), showing the lowest values for low temperatures, as expected. While van der Waals constant gathers a linear performance in terms of composition or temperature effect, the specific acoustic impedance and collision factor show an inverse trend of the enclosed pure substances, mainly due to the nature of the complex collection of covalent molecules enclosed into the "maple syrup concept". That goes to show how much resistance an ultrasound beam encounters as it passes through the liquid phase, or, in other words, as the probability of collision among molecules rises for high concentration compositions and low temperatures.

Despite solvation numbers of covalent molecules into the aqueous solution being key parameters necessary when discussing intermolecular interactions or interfacial phenomena, this data is extremely scarce and dispersed into open literature. If the search for such data was related to a solvent other than water, the situation is worse. Solvation numbers are based on isentropic compressibilities (computed by the Newton-Laplace equation from density and ultrasonic velocity), a parameter easily derived from acoustic measurements, as previously commented. The compressibility solvation numbers, or compressibility hydration numbers for an aqueous environment, are calculated using the following equation, attending to the usual expressions:

$$n_S = \left(\frac{n_{solvent}}{n_{solute}}\right) \cdot \left(1 - \frac{\kappa_S}{\kappa_{So}}\right) \quad (3)$$

in which nsolvent and nsolute are the mol number of solvent and solute into a binary mixture, respectively. The equation used for computing compressibility hydration number assumes that the solvation layer around the corresponding solute molecule is incompressible, which is not the case. Despite this, it provides an acceptable approximation of the extent of interaction of the solute or solutes with solvent. These parameters are derived from isentropic compressibility measurements and therefore account for the first two layers of solvent around the solute. For example, Figure 2 shows the evolution of the compressibility hydration number for the mixture maple syrup + water as a function of temperature, gathering the strong diminution of disposable solvent molecules for the establishment of layers around each theoretical solute molecule. As observed, only a slight effect is produced by variation of temperature at the studied range. When the temperature is increased, there is a corresponding decrease in the ultrasonic velocity for concentrated solutions, and then an increment of the entropy

Figure 2. Effect of temperature for compressibility hydration number of Canadian maple syrup + water.



x: molar fraction of maple syrup.

of the system, the strongest values of solvation numbers being observed for low temperatures. The physical property packages used in powerful chemical simulators typically rely on generalized equations for predicting properties as a function of temperature, pressure, etc. In the last few years, despite the success of developing several procedures of density estimation for pure compounds or mixtures, only a few of them may be of practical application and high accuracy for fats and oils. The procedure proposed by Subbiah et al. for the description of the density of aqueous sucrose using a polynomic expansion has been proven accurate, only requiring a description of pure sucrose density dependence with temperature as suggested by Barber:

$$1/\rho = \sum_{i=1}^{N} \frac{w_i}{\rho_i} \tag{4}$$

$$\rho_{sucrose} = a + b \cdot w_{sucrose} + c \cdot w_{sucrose}^2$$

$$a = 1662.7 - 2.5025 \cdot T + 0.0306 \cdot T^2$$

$$b = -57.953 + 2.2511 \cdot T - 0.0417 \cdot T^2$$

$$c = -40$$

in which r is the density of the mixture, and wi is the mass fraction of the mixture.

Ultrasonic velocity has been systematically measured in the last years but this kind of thermodynamic data is still extremely scarce for biological solutions, specifically for food engineering. The experimental data were compared with the values obtained by the Junjie equation, which is dependent on the values of density and ultrasonic velocity of each component into the mixture:

$$u = \frac{\sum_{i=1}^{N} \left(x_i M_i / \rho_i\right)}{\left(\sum_{i=1}^{N} \left(x_i \cdot M_i\right)\right)^{1/2} \left(\sum_{i=1}^{N} \left(x_i M_i / \left(\rho_i^2 u_i^2\right)\right)\right)^{1/2}} \tag{5}$$

in which Mi is the molar mass of each component and xi is the molar fraction composition. Table 1 shows the deviation of these estimation methods.

Maple syrup and sugars during refining are examples of complex solutions in a high polar environment. The physical properties of such systems are necessary for an adequate design and optimization of processes and a deeper understanding of the behavior of the final product. Literature shows limited disposable data and even less rigorous analysis of the physical properties of maple syrup. A fundamental thermodynamic approach provides an effective basis for the analysis and prediction of these properties.

Table 1. Deviation of the estimation methods for density and ultrasonic velocity for the mixture Canadian maple syrup + water at 298.15 K.

Mixture	Subbiah-Barber equation	Junjie equation
Maple Syrup + Water	0.18693 gcm^{-3}	33.81ms^{-1}

The main focus of this study was to increase volumetric and acoustic property data as a function of temperature for aqueous solutions of Canadian maple sugar graded as Canada Grade A Golden (delicate taste, ≥75.0 %T), former Canada #1, Extra Light, compute derived thermodynamic properties and analyze the accuracy of theoretical empirical models for predicting data.

Conclusion

From the experimental investigation and the above discussions, the following conclusions have been drawn:

1. The tested methods Subbiah-Barber equation (SBE), and the Junjie equation (JE) showed the accurate capability of prediction of the measured magnitudes at the range of application, especially for low compositions, despite their empirical character and complexity of the studied solutions. These models have better predictive capacity at low temperatures for density, and high temperatures for ultrasonic velocity. The consideration of maple syrup as a concentrated solution of sucrose was a simplification, but the applied model deviations were acceptable.

2. A review of volumetric and acoustic properties of Canadian maple syrup revealed an important gap in disposable open literature thermodynamic data, despite its economic importance and its strong influence as a necessary tool for the accurate establishment of the optimal point of thermal operation, the gathered data being a new contribution of consistent technical information for industrial maple operators.

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Techniques Used for Metals' Analysis of Organic Compounds in Wastewater, Greywater and Rainwater: A Brief Review

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Water recycling is a sustainable way of managing water resources because of the large consumption of fresh water in the world caused by population growth, urbanization, and industrial development. However, the reuse of freshwater requires serious care due to the appearance of contaminants after its use, such as active chemicals, micropollutants, and pharmaceutical products. This study presents a systematic review of articles that includes terms of techniques used to assess metals and organic compounds in wastewater samples (a combination of effluents and water originated from bathrooms, showers, and kitchen sinks, and rainwater between the years 2000 and 2020).

Keywords: Systematic Review. Characterization. Wastewater. Greywater. Rainwater.

Abbreviations: PAHs: polycyclic aromatic hydrocarbons; ICP OES: inductively coupled plasma optical emission spectrometry; SBSE: sorting stir bar extraction; GC-MS: gas chromatography coupled to mass spectrometry; GC-ECD: gas chromatography-electron capture detector; SPME -HPLC-UV: solid phase microextraction with detection by high performance liquid chromatography; ICP MS: inductively coupled plasma mass spectrometry; AAS: atomic absorption spectrometry; F AAS: flame atomic absorption spectrometry; GF AAS: graphite furnace atomic absorption spectrometry; HG AAS: hydride generation coupled to atomic absorption spectrometry, CV AAS: cold vapor atomic absorption spectrometry; DGT: gradient in the thin films; DPASV: differential pulse anodic stripping voltammetry; FIA: flow injection analysis; CLE-ACSV: competitive ligand exchangeadsorptive cathodic stripping voltammetry; DPCSV: differential pulse cathodic stripping voltammetry; SIA: sequential injection analysis; XRF: X-ray fluorescence; HPLC: high performance liquid chromatography; HTC: high temperature combustion; FT-ICR MS: cyclotron ion resonance mass spectrometry by ESI Fourier transformation; HPLC-DAD: liquid chromatography coupled to a photodiode matrix detector; LC-APCI-MS: chemical ionization ions by atmospheric pressure; LC-MS/MS: liquid chromatography coupled to two mass spectrometers; GC-FTD: thermoionic flame detector.

Introduction

Freshwater consumption is increasing worldwide due to the acceleration of population growth, followed by urbanization and industrial development [1]. Water resources have been exploited throughout history, which has generated water pollution, making it useless for humans. This increase in water demand is linked to some processes such as climate change and river pollution [1-3]. Agriculture, dams, and changes in land use are also reshaping the rate, expansion, and distribution of consumption and replenishment of freshwater [4].

One of the sustainable solutions in the management of water resources is the recycling of wastewater. The treatment of wastewater in the 20th century highlighted the theme of protecting public health, reducing pollution, and preventing environmental degradation [4]. On the other hand, wastewater consumption can affect human health due to the presence of active chemicals and endocrine disruptors, micropollutants, including pharmaceuticals and personal care products, PAHs, phosphorus flame retardants, plasticizers, pesticides, and pathogens. Additionally, other factors that ultimately affect human health are soil quality due to accumulation of salinity and toxic metals, as the contamination of groundwater by salts, and the quality of crops [2,5,6,7].

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There are also alternative sources for nonpotable supply, with emphasis on the use of rainwater and greywater. Greywater can be defined as wastewater originating from bathrooms, showers, washbasins, washing machines and tanks, and kitchen sinks [8].

The origin and destination of these waters and their characterization is important for public health. The analysis that one can be sure that the water distributed is reliable if it is free of microorganisms or harmful chemicals to human health and the environment.

Park and colleagues (2009) [9] examined the effects of γ-ray treatment on wastewater toxicity at a rubber plant in Korea using Daphnia magna, a small planktonic crustacean that belongs to the Phyllopoda subclass. ICP OES was used to analyze Al, Cd, Cu, Cr, Fe, Pb, and Zn. The results showed the gamma-ray treatment did not completely remove the toxicity of wastewater and effluents from a rubber factory, suggesting that the main toxic agents were probably cationic metals [9].

Pang and colleagues (2016) [10] used an SBSE with chemical derivatization to preconcentrate 29 biogenic carbonyl compounds in rainwater samples in Yor, United Kingdom. For the detection and quantification of species, they used GC-MS. The sensitivity of the method using SBSE was evaluated in terms of LOD. The SBSE LODs of the 29 species studied ranged from 0.02 to 0.24 μg / L. The LODs of the SBSE-GC-MS technique for carbonyl measurements employed in this work were lower than those of GC-ECD and SPME -HPLC-UV [10].

So, the following work aimed to carry out a systematic review on the main techniques used for the assessment of metals and organic compounds in wastewater, greywater, and rainwater, highlighting the journals with the largest number of articles, the countries that most published about this subject, the years with the largest number of publications 2000 and 2020, and the most applied techniques between the years.

Material and Methods

To find the techniques used for the evaluation of chemical compounds in different types of wastewater, gray water, and rainwater, a systematic review was used in four databases: Science Direct (https://www.sciencedirect.com" https://www. sciencedirect.com), Web of Science (https:// www.webofknowledge.com/" https://www. webofknowledge.com/), Scopus (https://www. scopus.com/home.uri" https://www.scopus.com/ home.uri) and Scielo (https://www.scielo.org/" https://www.scielo.org/). To start the systematic review, search filters were selected using the keywords: wastewater; gray waters; rainwater; metals; organic compounds. The research focused on the period between 2000 and 2020.

Results and Discussion

The application of the systematic review resulted in 83 studies found according to the established filters. Table 1 shows the number of publications found for each investigated database. The works were found in 41 scientific journals, among which the "Atmospheric Environment" stood out with 7 published articles, followed by "Revista Brasileira de Engenharia Agrícola e Ambiental " and "Water Research" with 6 articles published in each journal.

Table 1. Number of publications found for each database.

Database	Number of publications
Science Direct	20
Web of Science	33
Scopus	17
Scielo	13

Brazil was the country that showed the most interest in the characterization of recyclable waters (wastewater, greywater, and rainwater), presenting a total of 19 articles, followed by China with 8 published articles and the United States with 7 articles. Figure 1 shows the countries that published articles related to the researched topic followed by the number of publications.

Figure 2 presents the publications of the articles distributed over the years in an eventual way. The Figure 2 does not show a sequential growth in the number of publications each year, but a growth followed by a decrease each year, with a distinction of the period between the years 2008 and 2011, in which 27 articles were published (33.3% of the 83 articles published in this period).

At least 18 techniques were used for the determination of metals in wastewater, greywater, and rainwater. The metals most frequently found in the articles were Cd, Cu, K, Na, and Pb. ICP OES and ICP MS totalized 15 applications for the assessment of metals in the aforementioned waters. Jambers and colleagues used both ICP OES (detection limits 0.2-3.0 ppb; accuracy 10%) and ICP MS (detection limits 1-100 ppt; accuracy 10%) for the inorganic characterization of rainwater collected above the North Sea [11]. ICP based techniques have been highlighted for their versatility and detection capacity. A plasma spectrometer usually reaches a temperature of 8,000 K and causes a less reactive chemical environment than an atomizer flame. The high temperature determined by the plasma source

Figure 1. Countries that published on the topic.

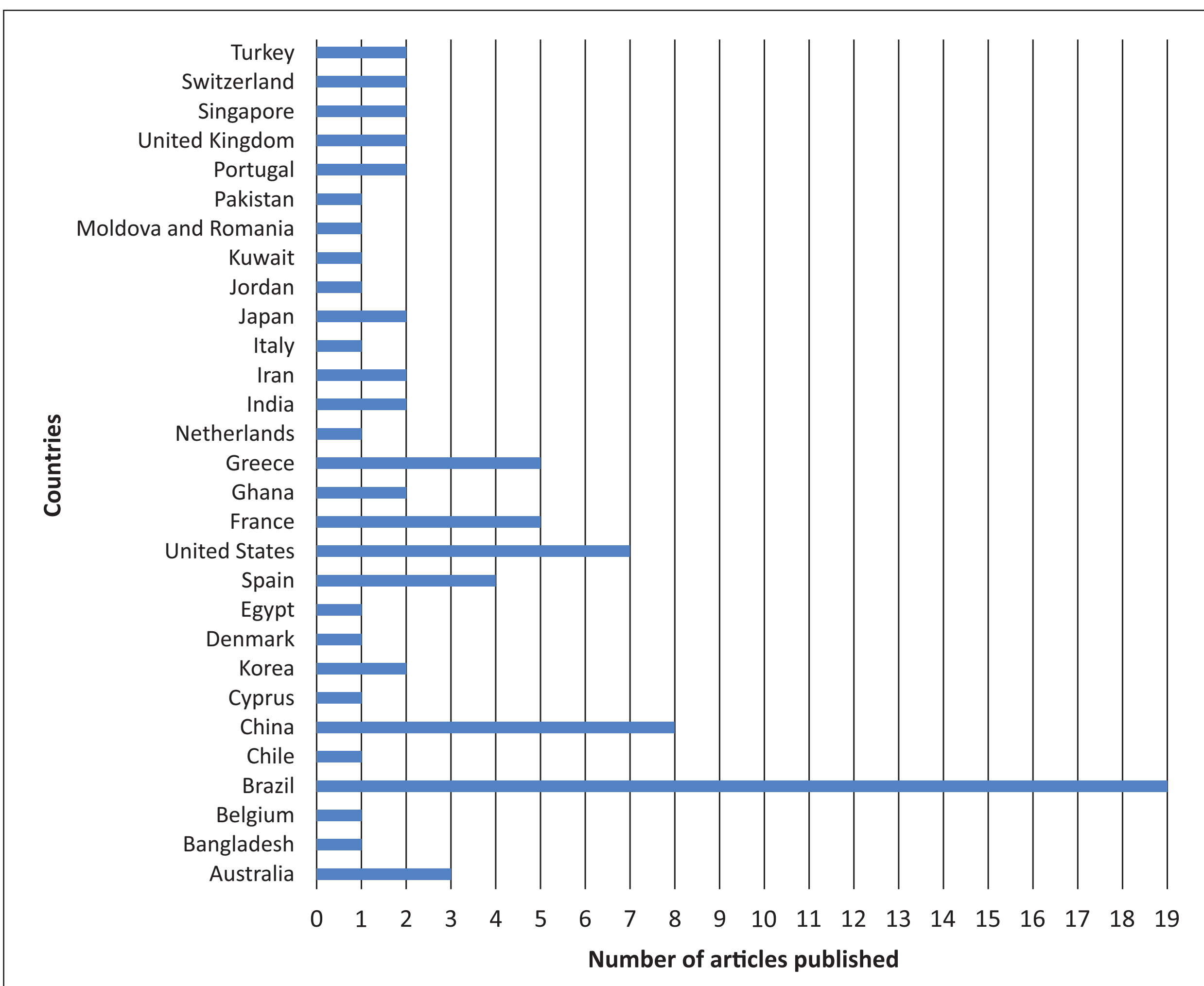
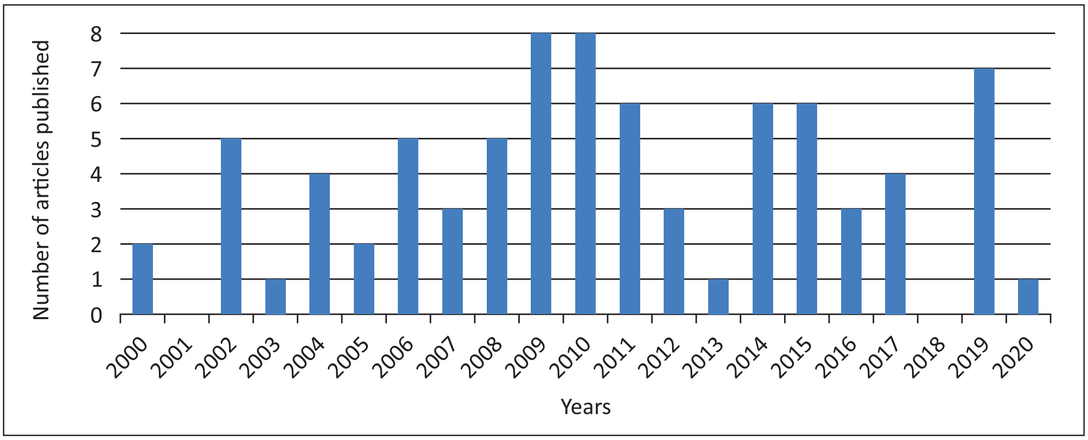


Figure 2. Number of articles published per year.



allows a highly sensitive determination of common elements detected by other analytical techniques, such as refractory metals or form refractory oxides, rare earth elements, and light elements like boron [12].

Other techniques are AAS. F AAS, GF AAS, HG AAS, and CV AAS had a sum of 18 applications. AAS, also widely used, has been compared throughout history with ICP. Its advantages compared to ICP are lower equipment and operational costs, ease of operation, and a reduced number of spectral lines, allowing less interference by overlapping lines. However, AAS has a small linear working range, less analytical frequency, and some non-metallic elements are not easily determined, such as phosphorus and sulfur, and it mainly considered a mono elementary analytical technique, its greatest disadvantage [13]. Buzier and colleagues (2006) [14] used GF AAS to determine copper and cadmium in wastewater samples after using DGT as a tool for metal speciation, concluding that DGT can be very useful to provide an operational fractionation of metals in wastewater [14].

Other techniques also used in the studies analyzed, such as flame photometry to determining sodium in gray waters [15]; ion chromatography with conductometric detection, used by Fontenele and Pedrotti to determine copper, lead, cadmium, as well as major cations and anions in rainwater samples [16]; DPASV, used by Prestes and colleagues [17] to determine copper, lead and cadmium in rainwater samples [17]; in addition to FIA with anodic stripping voltammetry detection; CLE-ACSV; atomic emission spectrophotometer with flame atomization; voltammetric determination by anodic stripping using a chitosan modified carbon paste electrode; colorimetry; titrimetry; DPCSV; infrared spectroscopy; SIA, XRF; and UV absorbance, totaling the use of 20 techniques used with different methodologies in 56 of the 83 articles found.

GC-MS has been the most used technique for the determination of organic compounds in wastewater, greywater, and rainwater in the last 20 years [18]. GC-MS applies to volatile and thermally stable compounds at the relatively high temperatures employed during the chromatographic separation process. These requirements are similar to those required for compounds to be ionized through IE and IQ2 [19]. An analytical strategy involving the use of GC-MS certainly has the advantage of enabling identification with excellent sensitivity and reproducibility for compounds that occur in complex matrices [20]. Noutsopoulos and colleagues (2017) [18] characterized greywater samples from Greek households using GC-MS according to Samaras and colleagues (2011) [21] to assess micropollutants present in the samples.

Then, the technique with the most appearances was HPLC. HPLC uses small columns, filled by a mobile phase that is eluted under high pressures.

This technique can perform separations and quantitative analyzes of a large number of compounds present in various types of samples in a few minutes, with high resolution, efficiency, and sensitivity. Due to its characteristics, it is widely used in the pharmaceutical industry. Eschauzier and colleagues (2010) [22] used HPLC to determine perfluorinated compounds in the infiltrated water of the Rhine and rainwater infiltrated in coastal dunes.

A wide variety of organic compounds was found in the studied waters, such as recalcitrant compounds, biogenic carbonyl compounds, perfluorinated compounds, aldehydes, phenolic compounds, hydroquinones, among others.

Other techniques appeared less frequently, such as cyclic voltammetry with vitreous carbon electrode modified with bismuth film, used by Santos and colleagues [23] to determine 2,4-dinitrophenol (2,4-DNP) in rainwater from regions of Santa Catarina; in addition to UV/visible spectroscopy; fluorescence spectrophotometry; thermo-optical analyzer; HTC; capillary electrophoresis; hightemperature catalytic oxidation; FT-ICR MS; HPLC-DAD; and sources of LC-APCI-MS; LCMS/S; GC-FTD, totaling the sum of 13 techniques employed with different methodologies in 42 of the 83 articles found.

Conclusion

The systematic review was able to identify a considerable amount of specific research articles from the last 20 years, making it possible to evaluate databases, journals, countries, years of publication, and techniques used for the analysis of metals and organic compounds in wastewater, greywater, and rainwater, facilitating a possible choice and future implementation of techniques for the characterization of water samples. The characterization of these waters is of paramount importance to ensure their potability, verifying their quality from different sources, reaching the standards of demand for their use.

Acknowledgments

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Occupational Health and Safety in Biotechnological Processes: A Review and Future Directions

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An option to change partially or completely conventional chemical methods is a biotechnological process. It enables the development of environmentally friendly and innovative means. The safety of this process has not been fully examined, thus, the lack of awareness about risk management is a great concern. This work aims to elucidate the importance of recognizing, assessing, and controlling potential risks, and developing appropriate risk management to develop bioprocesses safely. For this purpose, qualitative research was carried out through scientific studies and current legislation. Safe development of biotechnological procedures allows for occupational safety throughout the processes. It was observed that control measures should be adopted to obtain a safe work environment for everyone. These measures can be carried out through anticipation, recognition, assessment, and control of existing risks or that may exist in the process. Also, it was found that the involvement of all adequate risk management is fundamental. Therefore, biotechnological processes must be developed safely for workers, the environment, and society.
Keywords: Occupational Safety. Occupational Health. Risks. Bioprocesses.
Abbreviations: CLT: Consolidation of Labor Laws; NR: Regulatory Norms.

Introduction

Processes that involve several stages of transformation through biological agents, such as enzymes, microorganisms, or animal and plant cells, are called bioprocesses [1]. Bioprocesses have attracted a lot of attention due to being a sustainable and innovative alternative for the industry [2]. Thus, scientific and technological research has sought to develop and transform processes and products by biotechnological processes to reduce negative impacts on the environment and the use of fossil fuels. In this context, bioprocesses have been used in several applications, such as for fuel and pharmaceutical products [3,4].

In bioprocesses, the main operations are fermentation, microbial and enzymatic catalysis [5]. Bioprocesses are promising alternatives that are justified by their lower impact on the environment compared to conventional chemical processes. On the other hand, there is little discussion on the safety of their development. It is important to highlight that a good amount of organic solvents for extraction from aqueous solutions can be used in bioproduct processing. Thus, the steps of processing, recycling, control, and safe disposal are necessary for both organic solvents and microorganisms [6].

The use of bioprocess technologies in research and industrial development activities has grown in the world. Risks are directly related to the means and conditions in which operations occur [6]. Because of this, there is a need for special attention to the hygiene and safety in bioprocesses to preserve the health, integrity, and safety of workers and the environment. Along with the accelerated use of this process, a great problem arises, which is the little knowledge and awareness of risk management systems to mitigate the risks [7]. Moreover, the occupational health and safety of such procedures have been little discussed. Therefore, this work aims to elucidate the importance of recognizing, assessing, and controlling potential risks, to develop safer

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bioprocesses for workers, the environment, and society.

Material and Methods

Research on occupational health and safety in bioprocesses was carried out through important national and international bibliographic databases. The information was collected from scientific studies such as articles and books, published in indexed and specialized journals. Also, Consolidation of Labor Laws (CLT) [8] and Regulatory Norms (NR) [9] were the current legislation used as a basis. Among the NR, NR 9 (Environmental Risk Prevention Program), NR 12 (Machines and Equipment), NR 15 (Unhealthy Activities and Operations), NR 16 (Dangerous activities and operations) e NR 25 (Industrial Waste) were used, since these regulatory norms cover activities carried out in biocatalytic processes. Figure 1 shows the flowchart of the methodology performed.

Results and Discussion

Occupational health and safety have been widely discussed in several areas in the past 20 years (Figure 2). Figure 2 shows the increase in the number of articles when the keywords "occupational health" (Figure 2A) and "occupational safety" (Figure 2B) were used separately in the Web of Science database. However, when the keywords "occupational health" and "biotechnological processes" were combined, only 2 articles were found, and when the keywords "occupational safety" and "biotechnological processes" were combined, only 1 article was found. These results showed that little has been discussed about occupational health and safety in biotechnological processes, demonstrating, thus, the need for a greater discussion to preserve the occupational health and safety of workers and the environment.

There are notorious benefits of developing the safety of bioprocesses for industries, companies, workers, and society. This effort promotes the

Figure 1. Qualitative research developed in this work.

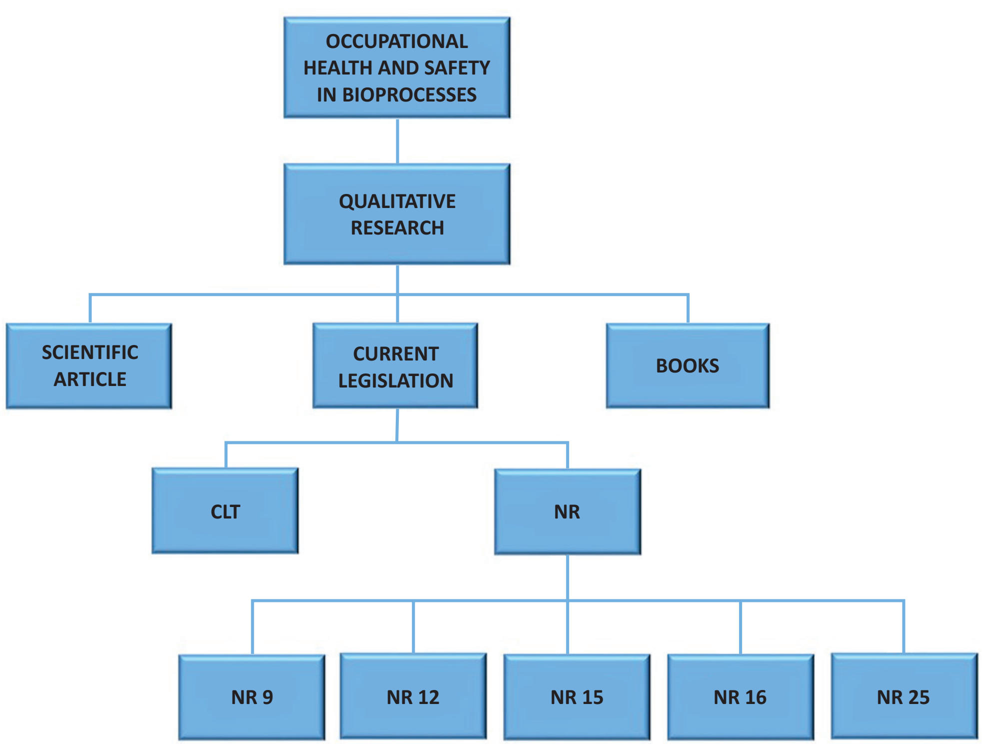
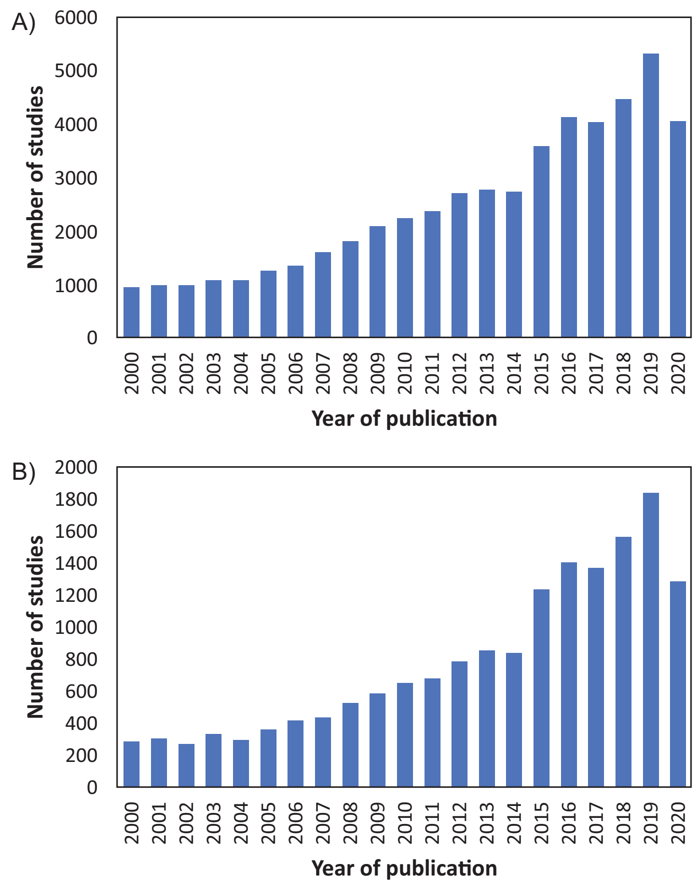


Figure 2. The number of published articles per year between 2000 and 2020 in Web of Science with the keywords: A) "Occupational Health" and B) "Occupational Safety".



safety of workers throughout the enzymatic and fermentative processes. Among the benefits, the propagation of biotechnological processes is associated with both social and commercial development, which include high-paying jobs, the use of waste, and innovative products that address critical social problems in materials, health, transport, energy, and pollution. Moreover, safer processes lead to greater safety for the worker, through sensors that detect dangerous agents, appropriate protective equipment, and others [10].

To achieve this safety, security measures must be adopted in biotechnological practices. Health risks arising from exposure to biotechnological processes must be eliminated or reduced to guarantee the health and integrity of workers. It is contradictory to say that the development of bioprocesses is responsible, if the health and safety of workers are negatively affected, as well as the environment. This understanding corroborates with NR 9 [11], which explains that employers must develop and implement the Environmental Risk Prevention Program to ensure the health and integrity of workers and the environment with some measures: anticipation, recognition, evaluation, and control of the environmental risks that exist or will exist in the workplace [11].

Despite being an arduous task, the safe and responsible development of bioprocesses and any other industrial process depends on the health and safety of workers and the environment, since both are linked. Also, risks, dangers, and exposures must be understood by everyone involved, to avoid possible accidents that compromise the health and integrity of the worker and the environment. It is important to note that employers must assess all risks inherent in the processes to which workers are exposed, and employers must inform their employees [12]. In this sense, NR 9 establishes that all environmental risks present or that may exist in the work environment must be communicated by employers to all employees, as well as possible resources to avoid or mitigate these risks [11]. Moreover, the government must inspect companies/industries, analyzing whether the control of workers' exposures to risks is being carried out properly and there is no damage to workers or the environment [12].

One of the most critical factors that increase the risk is exposure [12]. Thus, there is a need to identify the agents and control exposures to these agents in the work environment, to develop risk management appropriately. In this scenario, employers must be aware and assess the frequency of exposure to risk agents and their magnitude. To establish proper occupational exposure to bioprocesses, it is necessary to obtain information about the monitoring of risk agents [13]. Identification, evaluation, and monitoring are essential to preserving the health of workers and the environment, avoiding unhealthy activities and operations. According to NR 15, activities and operations are considered unhealthy when they are above the tolerance limits (annexes 1, 2, 3, 5, 11, and 12), in which the tolerance limit is the maximum or minimum concentration or intensity related to the nature and the time of exposure to the agent which will not cause damage to the health of the worker during his working life [14].

For the safe and responsible development of bioprocesses, exposure assessment is a very important factor, as mentioned before [13]. However, it is important to emphasize that just assessing the risks is not enough; there is a need for communication about risks between employers, government agencies, and organizations promoting occupational safety and health. Thus, the data of exposure to the risks of processes, when properly disclosed, assist in the decisions about risk management in biotechnological processes [15]. Biotechnological processes can also be safe with adequate knowledge of the procedures and mechanisms used in these processes, in addition to the adoption of control measures, such as eliminating risks, neutralizing risks, training, and hygiene practices.

In bioprocesses, the complexity of risks inherent to the procedures is very large, in addition to the limited knowledge related to safety. Today, the authorities have pointed to the importance of gathering knowledge about the application of bioprocesses and exposure control. It is important to highlight that employers are responsible for proper risk management and preserving worker health [16]. In cases of dangerous activity and operations, NR 16 states that according to article 195 of the CLT, it is using a technical report prepared by an Occupational Physician or Occupational Safety Engineer that the employer is also responsible for the characterization or the mischaracterization of the hazard [17].

Special attention is also needed in the phases of design and use of machines and equipment since they can cause damage to the health and physical integrity of the worker through accidents and illnesses at work. NR 12 has details about occupational safety in regards to machinery and equipment, determining technical references, principles, and protective measures, to guarantee the safety and health of workers. In this sense, NR 12 says that protective measures must be adopted for work on machinery and equipment by the employer, enabling the preservation of health and physical integrity of workers [18].

Another issue that needs special concern is relate to industrial waste that results from processes. NR 25 states that companies are responsible for making decisions that prevent industrial waste from causing damage to workers' health and safety. Also, companies must adopt measures that minimize the generation of waste, preventing this waste from compromising the health and safety of workers and the environment [19].

Regulatory agencies request the execution of good risk management conduct, although some general regulations fit the requirements for biological and related processes to develop safe and responsible biotechnological processes. There have been studies reporting the need for the development of safe biotechnological processes, as well as regulations that make this possible. In general, the works show global parameters for the safe exercise of bioprocesses (Figure 3) [5, 6, 20].

In general, the adoption of safety measures, knowledge of the processes, risks, dangers, and the engagement of all involved enable the development of biotechnological processes responsibly and safely. Furthermore, past mistakes can serve as lessons to prevent future problems, which is very advantageous for both scientific and industrial society. Thus, for the development of safer and more responsible biotechnological processes, it is essential that the health and integrity of workers, as well as the environment and society in general, be considered through knowledge and current legislation.

Conclusion

This work highlighted the importance of developing biotechnological processes safely, guaranteeing the health and safety of workers and the environment. This work also demonstrated the benefits of developing safety regulations for companies, industries, workers, the environment, and society. A safe development is only possible if security measures are adopted via anticipation, recognition, assessment, and control of the risks present in the processes. Moreover, it is necessary that everyone is involved and well informed about risks, dangers, possible ways to mitigate or eliminate such risks, industrial hygiene practices, and adequate supervision. Proper risk management is also a crucial factor for safe biotechnological processes. Therefore, there must be special attention and greater discussion about safety and health in biotechnological processes, to protect the health and well-being of workers, the environment, and society.

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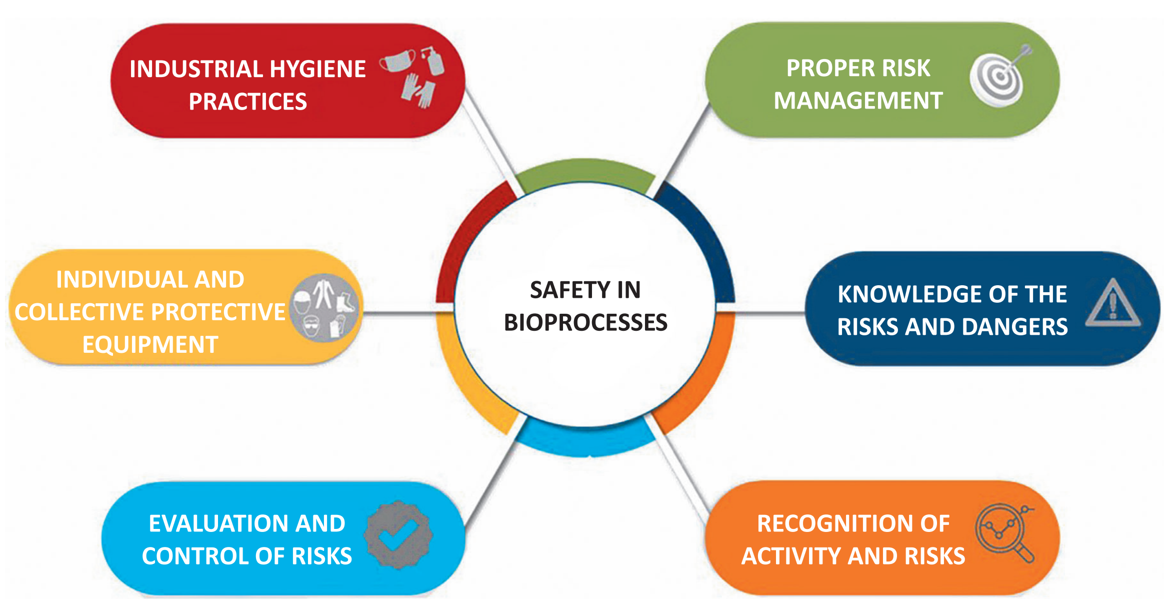
Figure 3. Global parameters for the safe exercise of bioprocesses.



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