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Influence of Lightpipes on Readers for Microtubes Fluorescence Detection

Eduardo de Araujo Rocha^{1*}, Clara Mariah Loureiro da Silva¹, Valmara Silveira Ponte¹, Valéria Loureiro da Silva¹, Vinicius Pinto Rocha², Milena Botelho Pereira Soares^{2,3}

¹Optic and Photonic Engineering Laboratory, SENAI CIMATEC; ²Institute of Innovation in Advanced Health Systems – ISI SAS; ³Gonçalo Moniz Institute, Oswaldo Cruz Foundation - FIOCRUZ; Salvador, Bahia, Brazil

Lightpipes are light guides based on total internal reflection used for LED illumination systems with many applications. This work investigates using lightpipes in a fluorescent reader for microtubes. It is part of a project to develop an RT-RPA multiplex test and fluorescence reader for SARS-COV 2 and H1N1. We investigated the lightpipes interaction with an excitation filter. The results do not show a benefit in using them on the emission side due to the capture of LED scattered light.

Keywords: Lightpipes. Lightguides. Fluorescence Readers.

Introduction

Lightpipes are used when it is necessary to direct light from the source to a particular area that requires illumination. They are made up of a transparent material, usually glass or plastic, and tiny filaments capable of transmitting light signals through internal reflections [1]. In essence, the light pipe reflects the rays of light through total internal reflection until the light reaches the pipe's end and can exit. They are often used in applications that require a homogeneous light beam and can be commonly found in stage fixtures and automotive applications [1].

The total internal reflection occurs at angles of incidence more significant than the critical angle when the light beam goes from a medium with a higher index of refraction to a medium with a lower index of refraction, as illustrated in Figure 1. The incident light ray is refracted at a critical angle tangentially to the refractive index interface. When the angle of incidence is greater than the critical angle, the incident ray is reflected [2].

In the automotive industry, there has been exponential growth in the use of lightpipes in

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lighting systems, both for external and internal vehicle lighting [3]. Furthermore, the discovery of the broad applicability of light guides, combined with the advent of powerful LED light sources, enables innovative designs and concept styles using total internal reflection [3]. This work is part of a project to develop an RT-RPA multiplex test and fluorescence reader for SARS-COV 2 and H1N1 [4]. This article investigated the use of a lightpipe for capturing the fluorescence emitted by the fluorophores. A fluorophore is a molecular functional group that absorbs the energy of a specific wavelength and reacts by emitting light at a wavelength longer than that absorbed [5].

Materials and Methods

The influence of different lightpipes from three manufacturers was investigated, whose characteristics we presented in Table 1. The reader uses a BPX61 photodiode, a PCI board for amplification, and an STM32 microcontroller to control the excitation LEDs and filter the emission signal [4]. For the tests, the photodiode was replaced by a 400 μ m optical fiber (Ocean Insight QP400-2-SR) and an Avantes spectrometer (AvaSpec-3648) to enable spectral analyses of the captured light. As fluorescent markers, the developed RT-RPA tests use three fluorophores, FAM, ROX, and Cy5. However, for characterizing the lightpipes, an aqueous solution of Rhodamine 6G with a

Received on 27 August 2021; revised 22 October 2022. Address for correspondence: Eduardo de Araujo Rocha. Rua Santa Isabela, 100, Cond. Elegance Garibaldi, Ap 2202 C, Engenho Velho da Federação, Salvador, Bahia, Brazil. Zipcode: 40221-225. DOI 10.34178/jbth.v5i4.240.

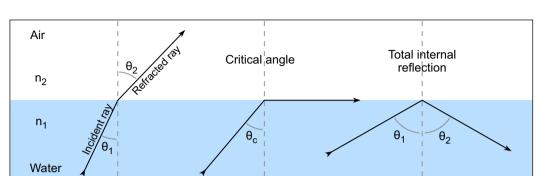


Figure 1. Illustrative image demonstrating the process of total internal reflection.

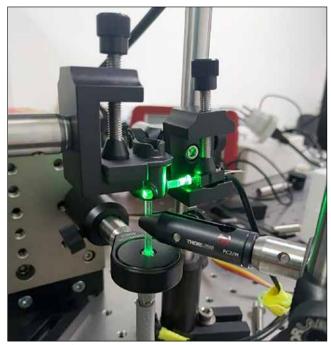
Source: Jaycon Systems.

Table 1. Physi	cal characteristics	of the analyzed	lightpipes.

Model (Manufacturer)	Length	Internal	External
		Diameter	Diameter
LFB100CTP (VCC)	25.4mm	2.84mm	3.30mm
515-1302-0900F (Dialight)	22.86mm	2.36mm	3.30mm
PLP2-500 (BIVAR)	12.7mm	2.80mm	3.30mm
PLP2-750 (BIVAR)	19.0mm	2.80mm	3.30mm

concentration of 0.01 mg/mL was used due to its high fluorescence and convenience. For the tests discussed in the article, twenty microliters were placed into a microtube, which a 3D-printed holder supported. We investigated the use of lightpipes in two locations (Figure 2). The first was to guide the light from the excitation LED to the microtube. In this position, a PLP2-750 lightpipe was used. The second lightpipe location was to collect the emitted fluorescent light and direct it to the spectrometer via the optical fiber (Figure 3).

Also, the impact of inserting an optical filter to restrict the excitation of LED spectra was analyzed. A bandpass optical filter (Proteon SRE-AA) was positioned between the LED and the excitation lightpipe to limit the amount of scattered light from the LED that overlaps with the fluorescence spectra. In the measurements, the Avasoft spectrometer software recorded the spectral data, and the data were exported to Microsoft Excel for further analysis. Figure 2. Picture of the test bench used in the experiments.



Source: Authors.

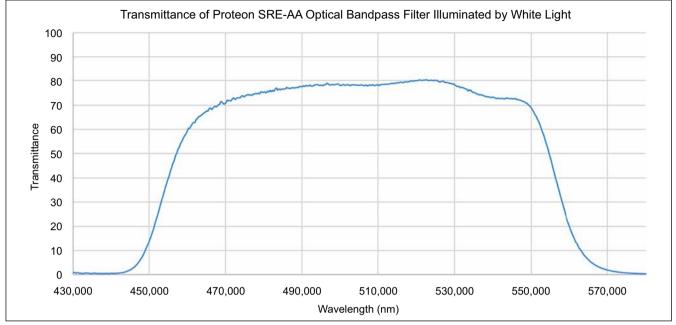


Figure 3. Measured transmission spectra of the excitation filter.

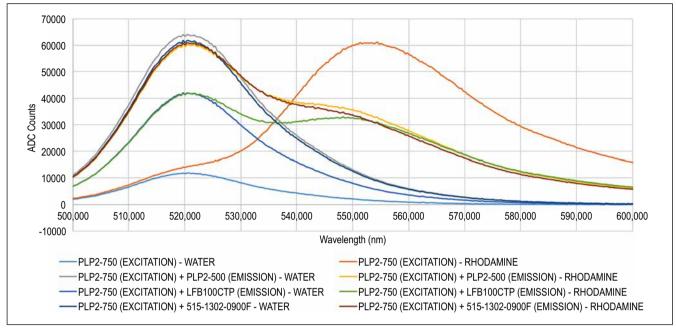
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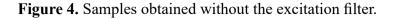
Results and Discussion

Figure 4 shows the spectra obtained without the excitation filter. The blue and grey curves correspond to the spectra obtained with the microtubes filled with deionized water. Therefore, as there is no fluorescence, the peaks around 520 nm correspond to the scattered light from the excitation LED in this case. The other curves show two peaks: the 520 nm scattered light and the fluorescence emission peak around 550 nm. Interestingly, the amount of scattered light at 520 nm in the samples with deionized water and Rhodamine 6G are the same, indicating that the deionized water is a good reference for the undesired, scattered light. The measured spectrum for the case where no lightpipe was used for capturing the fluorescence emission showed a better result, with higher fluorescence at 550 nm than the scattered light at 520 nm. The spectra for the cases where lightpipes are used catch more scattered light (520 nm) than fluorescence (550 nm). Of the lightpipes tested, the LFB100CTP captured the least scattered light.

The addition of an excitation filter (Proteon SRE-AA) changes the relationship between the scattered and emitted fluorescence (Figure 5). The captured scattered light is proportionally smaller than the Rhodamine 6G fluorescence peak. However, the overall intensity of the captured fluorescent light was reduced by five times because of the large thickness of the excitation filter used (6mm). In addition, since the LED has a high divergence, less light is captured and guided by the excitation lightpipe. These measured spectral curves also show a better result for the case where no lightpipe was used for capturing the fluorescence emission.

For clarity, Table 2 summarizes the relative intensity for the measured spectral peaks at 520 nm and 550 nm for the deionized water and Rhodamine 6G solution. The addition of the filter improves the relation between the captured fluorescence and scattered lights when a lightpipe at the emission side is used. However, when there is no lightpipe, the improvement is not so clear. The relation between the peak fluorescence and peak scattered light is similar, but the filter helps reduce the scattered light for wavelengths greater than 560 nm. However, the





Source: Authors.

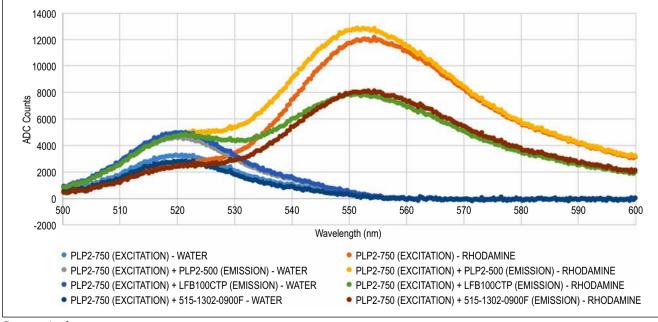


Figure 5. Samples obtained with the excitation filter.

Source: Authors.

CON	IFIGURATION	SCATTERED LIGHT	SCATTERED LIGHT	FLUORESCENCE	FLUORESCENCE AT		
FILTER	EMISSION LIGHTPIPE	PEAK INTENSITY AT 520 nm FOR DEIONIZED WATER (ADC COUNTS)	PEAK INTENSITY AT 520 nm FOR RHODAMINE 6G (ADC COUNTS)	INTENSITY AT 550 nm PEAK FOR RHODAMINE (ADC COUNTS)	550 nm / SCATTERED LIGHT AT 520 nm FOR RHODAMINE 6G SOLUTION		
	No lightpipe	12000	14000	62000	4,429		
WITHOUT EXCITATION FILTER	PLP2-500	65000	60000 36000		0,600		
	LFB100CTP	42000	41000	32000	0,780		
	515-1302-0900F	60000	60000	34000	0,567		
	No lightpipe	3500	3000	12000	4,000		
WITH EXCITATION	PLP2-500	4500	5000	13000	2,600		
FILTER	LFB100CTP	5000	5000	8000	1,600		
	515-1302-0900F	3000	2500	8000	3,200		

Table 2. The leading information contained in Figures 3-5.

results are always better without the lightpipe on the emission side, indicating the need to restrict the captured scattered light with an adequate emission filter.

Conclusion

Lightpipes are great solutions when it is necessary to guide light from a source to a specific point, and they have been used in various illumination applications. In this paper, we investigated the use of lightpipes in a fluorescence reader for multiplex RT-RPA tests. The results indicate that using lightpipes to capture the fluorescence emission is not advantageous since it captures too much-scattered light. When combined with excitation filters, the use of lightpipes in the excitation is compromised due to reduced light capture. However, spectral filtering of the excitation light can reduce the overall scattered light if combined with an appropriate emission filter.

Acknowledgments

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A Robotic Platform for Assistance in the Medical Triage Process

João Gabriel da A. Calmon^{1*,2}, Victor Guerra de Araújo e Souza^{1,2}, Caio Athayde de Oliva^{2,3},

Ruan Utah Fraga de Carvalho^{1,4}

¹Electrical Engineering Department (SENAI CIMATEC), ²Researcher at IEEE RAS, ³Mechanical Engineering Department (SENAI CIMATEC), ⁴Researcher at IEEE PES; Salvador, Bahia, Brazil

Triage is the process of partially assessing and ordering patients as to the priority of need for medical care. However, in disaster scenarios and atypical events, overcrowding of the care system can occur. In this context, a collaborative robot, able to share the work environment with health agents, could be in charge of the repetitive triage tasks, leaving the medical team with the care. Thus, this paper aims to develop a virtual prototype for medical triage assistance, nicknamed BayIEEEmax. The 3D model was created in SOLIDWORKS 2018, the electronic circuit was designed in KiCad, and the simulation was performed through ROS. Keywords: Triage. Collaborative Robots. Medicine Robots.

Introduction

Derived from the French word "trier", which means "to sort or select", triage is the medical practice of sorting patients, following their need for medical attention [1]. The term was first used around 1792 by the Surgeon in Chief of Napoleon's imperial guard, Baron Dominique Jean Larrey, to describe the necessary act of sorting the large numbers of wounded soldiers based on the criticality of their injuries [2,3].

Triage is usually employed when medical facilities are overloaded because of the great demand for people in need of medical attention but not enough resources to care for all of them properly. Overloading usually happens due to wars, natural disasters, terrorist attacks, or pandemics, like the one caused by the SARS-CoV-2 virus, also known as "COVID-19" [3,4].

Despite being essential for assessing and validating emergency procedures for many hospitals, modern triage still faces problems that can significantly decrease its ability to correctly prioritize patients most in need of clinical care [5]. Notwithstanding the need for patients to be appropriately triaged in the first few minutes after entering the hospital, many hospitals worldwide suffer from long waiting periods between procedures, both resulting and occurring as a consequence of ineffective triage systems [5,6].

Such problems derive from organizational issues with hospital management and the lack of proper training of triage nurses for the correct diagnostic and subsequent prioritization of patients [5]. Collaborative robots are a specific kind of robot designed to work side-by-side with human workers in a shared space. In general, the repetitive tasks are left to the robot, while the mental ones are executed by humans [7]. Furthermore, they have shown great promise in performing complex tasks in constantly changing environments [8]. Therefore, to improve the triage process, the insertion of robots and AI in this first step after entering some emergency departments can save time and optimize this process, especially in cases with large crowds of patients waiting for the service.

Furthermore, these insertions can automatically set all the data acquired from each patient directly in the system of the hospital or clinic, doing some easy, safe, and simple tasks in an automatic way to improve the overall scenario [9,10]. This paper's main objective is to conceptualize a virtual prototype of a robotic assistant for medical triage,

Received on 16 September 2022; revised 21 November 2022. Address for correspondence: João Gabriel da A. Calmon. Rua Péricles Cardoso, 61 - Doron, Salvador - BA - Brazil. Zipcode: 41194-035. E-mail: jgabrielcalmon1@hotmail.com. DOI 10.34178/jbth.v5i4.241.

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nicknamed "BayIEEEmax", as a possible solution to the problems faced by current triage systems. The following section presents the project's methodology, subdivided into 3D modeling, electronic design, and simulation; the third one presents the results achieved, and finally, the last section, is shown the conclusion, as well as the next steps planned for the project.

Materials and Methods

This study is characterized as qualitative and exploratory, backed primarily by the research of bibliographical material about the theme. Besides, the development of the virtual prototype itself was subdivided into three sections: the 3D model, the electronics, and the simulation, with a description of the tools for developing each section.

3D Model

To better visualize the design, we used the SOLIDWORKS 2018 software to build a 3D (three-dimensional) model that could be reviewed and modified before building the actual robot and also could adjust any necessary parameters, parts, and/or fit. In addition, building a CAD also aims to achieve not only the feasibility of building the design to fit each part, but to create a robot that is aesthetically pleasing to people.

Electronic Design

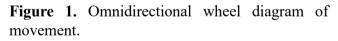
KiCad is a computational program for the computer-aided electronic design that aims to enable the conception of layouts and their conversion to printed circuit boards (PCB). Because it is Open Source, it allows the usage of 3D models and footprints created by companies or users of this software. Using KiCad allows the user to develop a circuit plan, build a board that will be made for the desired function with the selected components, and avoid expenses with the misplacement or lack of space between components. In addition, possible circuit connection faults are identified during circuit construction, and the software itself alerts the user to connection errors found.

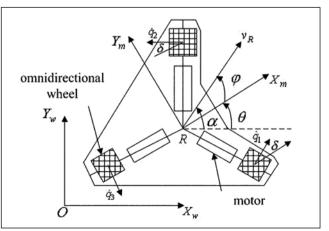
Simulation

Robot Operating System (ROS) is an opensource framework with several valuable tools for robot development. For example, it can simplify for the user the process of communicating the different components of a robot, such as the motors, sensors, batteries, and software, through a modularized system based on topics and nodes. ROS was adopted as the simulation and implementation tool of the robot logic because, besides having several packages already developed, it also natively supports the C++ and Python programming languages. Another point is that the programming can be loaded directly into embedded systems, such as the Raspberry Pi 4, the controller used as the robot's control unit, without requiring modifications in the code itself.

Results and Discussion

Omnidirectional wheels are a particular type of wheel that makes it possible to perform some moves (Figure 1) not allowed by differential movement with conventional wheels, such as rotating around its axis or moving diagonally without needing to change its orientation position. Thus, since the



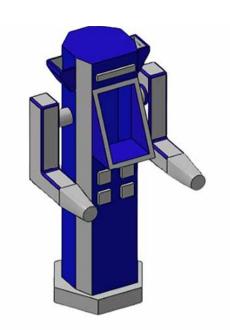


space for maneuvering a robot inside a hospital may be scarce, we adopted this wheel, which was chosen to move in limited space.

The current version of the CAD model from the project (Figure 2) contains a base to occult the omnidirectional wheels with a torso, equipped with a socket at the front to Liquid Crystal Display (LCD) Touchscreen display, two arms, and two pots in the head for several uses. The squares in the front of the torso are purely esthetical to improving the visuals of the robot. The model shown has a total height of approximately 1.65 meters and wide of 0.86 meters. He will be made up of boards of MDF (Medium Density Fiberboard) in most of your entire body with PLA (Polylactic Acid) 3D printed to fill in little details like the squares in the front part. Initially, the construction process of the electronic project was done by creating charts of functionality and electronics distribution on the robot.

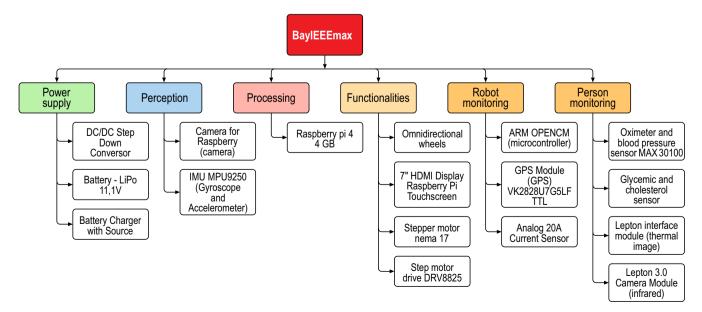
Figures 3 and 4 present the functionality and electronics distribution chart, where both were drawn in draw.io. Furthermore, Figure 3 shows the ARM microcontroller STM32F103C8 connected to an oximeter sensor, stepper motor, battery, AC/ DC converter, driver, GPS module, IMU MPU, and analog current sensor; Raspberry Pi 4 is connected

Figure 3. Diagram of BayIEEEmax functionalities.



to the module and thermal camera, two cameras compatible with raspberry, another camera for face recognition, a display, and a glucose and cholesterol sensor. And Figure 4 shows where the component will be located and its connection to the circuit.

Finally, Figure 5 presents the 3D circuit board design that was created in KiCad, where the schematic circuit and PCB layout can be drawn.



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Figure 2. The current version of the 3D model.

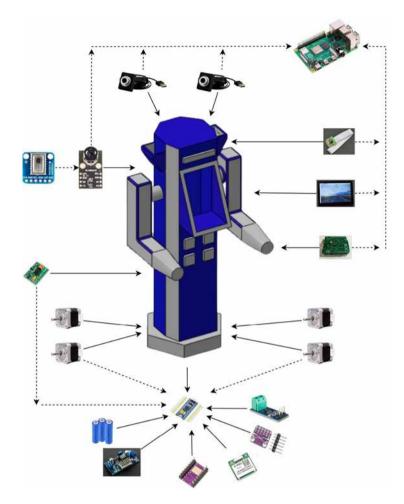
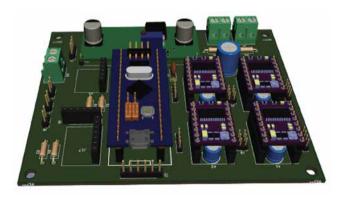


Figure 4. electronics distribution on the robot.

Figure 5. BayIEEEmax microcontroller board.



Conclusion

In this document, the current situation of the medical triage processes was presented, as well as how the occurrence of events such as wars, natural disasters, terrorist attacks, or disease outbreaks can lead hospitals to overcrowd in these critical moments. Furthermore, it was shown how the inclusion of collaborative robots in work environments could benefit the performance of activities. The progress for the 3D modeling, electronic design, and simulation of project BayIEEEmax were also shown. Considering how the robot would need to move within places with limited space, an omnidirectional wheel was deemed ideal for the robot's movement. A functionality distribution chart was also made, addressing the power supply, perception, processing, and monitoring process of both the robot and the patients in its care. In the following steps, the printed circuit board will be fabricated, the sensors and actuators will be connected, and the robot structure will be built. Some parts will be fabricated through 3D printing. Finally, the parts will be assembled and integrated to implement the logic developed in the simulation environment and the first tests with the physical prototype.

Acknowledgments

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SECI Model Guides the Generation and Diffusion of Knowledge in the Developing of an Innovative Product at a Small Science and Technology Institute

Amanda da Costa Marques^{1*}, Gláucio Bessa Oliveira¹, Meire Jane Lima de Oliveira¹, Renelson R. Sampaio¹ ¹SENAI CIMATEC University Center; Salvador, Bahia, Brazil

This research presents a case study about knowledge management at the Plasma Dental Pen project, in its stages of prototyping, conducted by the Núcleo Avançado de Inovação Tecnológica (NAVI) from Rio Grande do Norte. It applies the SECI theoretical-practical model by Nonaka & Takeuchi (1997) to analyze the dialectic of creating organizational knowledge to generate solutions related to the lack of experience with additive manufacturing in this project. For information acquisition, semi-structured interviews were carried out with the coordinator and a researcher from the organization and then compared with the proposed theory of the seminal authors and recent literature about it. We concluded that adapted applications of the SECI model contribute to the generation and diffusion of knowledge in the institution and its innovation process.

Keywords: Knowledge Management. SECI Model. New Product Development. Small Organizations. Organizational Knowledge.

Introduction

In recent decades, the globalized context of the market has increased pressure on companies to innovate, placing innovation, and therefore knowledge, at a level of differential resource in this competitive scenario. This fact brought the need to incorporate knowledge into productive activities. However, as knowledge is an intangible resource, its management within the organization can be complex and challenging, especially considering the context of minor Science and Technology Institutions (STI) [1].

In the book Creation of Knowledge in the Company (1997) [2], the authors Nonaka and Takeuchi present a study on the capacity of Japanese companies to create knowledge and propagate it within the productive scope, called organizational knowledge. According to the authors, the ability of these companies to create and manage organizational knowledge is why they boosted their innovation

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process and achieved such success in a short period. In the study, the authors present a theory about the creation and diffusion of knowledge within large organizations and demonstrate this process in the SECI model, which will be exposed ahead. Several organizations work to generate innovation, so they need to manage knowledge. Among them are the Science and Technology Institutions (STI), which, in general, are institutions to create and encourage scientific and technological research to translate them into innovative solutions that meet the needs of society. However, researchers often conduct projects within research development but with no experience in managing complex projects in research, development, and innovation (RD&I). Moreover, these projects sometimes have more academic aspects. Therefore, they sometimes are developed in environments that could be better in terms of technological infrastructure. So, there is a distance between the SECI model proposed [2] and the context of these institutions. As mentioned earlier, this study aims to analyze the model acting on a project carried out by NAVI, a small STI that works with technological innovation in Rio Grande do Norte, Brazil. The analysis is made from a case study about the prototyping stage of the Plasma Dental Pen project, focusing on the generation and dissemination of knowledge related to additive manufacturing, a new resource there.

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Materials and Methods

The study applied the theory of dynamic knowledge management in a small organization, interviewing the coordinator and a researcher of the investigated STI. Finally, according to bibliographic research, we did a comparative analysis between the Plasma Dental Pen prototyping process and the knowledge management theory. Evaluating how the SECI model, initially proposed for large corporations [2], we have applied the model in a small research institution to bring solutions to practical problems [3].

Theoretical Reference

The ability to create organizational knowledge represents the primary competitive advantage for companies, as it enables the generation and diffusion of innovations. Thus, the knowledge created in organizations represents one of their main assets that impact economic, financial, and social indicators [4]. Likewise, Sanjay Dhir [5] claims that integrating knowledge, organizational learning, technological capabilities, and technical adherence are vectors for organizational development in competitive contexts.

Nonaka and Toyama [6] explain that organizational knowledge arises from a dynamic, two-dimensional process - epistemological and ontological - originating in individuals with the potential to expand throughout the organization and beyond. This idea is opposed to the static view of the firm, presented in neoclassical theory and transaction cost theory. Each organization's strategy, structure, and culture influences knowledge creation.

The epistemological dimension includes two types of knowledge: tacit, inherent to the individual and context, difficult to be formulated and communicated, and explicit, encoded, which allows its transmission in formal and systematic language. The interaction between tacit and explicit knowledge is fundamental to creating and propagating organizational knowledge. Figure 1 illustrates this dynamic process, relating four chaining modes of knowledge to five phases.

As stated, the process takes place in a dynamic system. Nonaka and Takeuchi [2] highlight the importance of adding external knowledge to organizations to promote the exchange of information so that the system is open. Furthermore, Nonaka and Takeuchi [2] explain that to generate and share knowledge; there must be a specific context, the "ba." In organizations, the "ba" can arise in individuals, work groups, informal circles, meetings, virtual spaces, and front-line customer contact [7]. A company is a collection of "ba" from different ontological levels, interacting with each other organically and dynamically. Thus, the "ba" amplifies the knowledge creation process [6], providing the energy, quality, and places to

TACIT TACIT epistemological Socialization Externalization individual tacit knowledge generates in other individuals new tacit knowledge is externilazed in explicit knowledge, through methaphors tacit knowledge - shared experience. analogies, concepts, hyphothesis or models - conceptual knowledge. PHASE: TACIT KNOWLEDGE SHARING PHASE: CONCEPT CREATION Internalization Combination explicit knowledge is converted into tacit knowledge - operational explicit knowledge generates new explicit knowledge - systemic knowledge. EXP knowledge about production, project, processes and product PHASE: CONCEPT JUSTIFICATION management and policy implementation. PHASE: ARCHETYPE CONSTRUCTION PHASE: INTERACTIVE KNOWLEDGE DIFUSION \prec EXPLICIT 🗲 🗲 EXPLICIT 🗲

Figure 1. SECI Model.

Source: Nonaka and Takeuchi [2].

carry out individual knowledge conversions and their movement along the knowledge spiral [7]. According to Nonaka and Takeuchi [2], there must be so-called enabling conditions to promote this process at the organizational level. They are:

- 1. Intent: Implemented by defining the organization's strategy, goals, and objectives to acquire, create, accumulate and exploit knowledge;
- 2. Autonomy: At an individual level, it stimulates the generation of new ideas and self-motivation, enabling the creation of knowledge;
- 3. Fluctuation and Creative Chaos: The collapse of routines, habits, or cognitive structures in organization's members to stimulate the creation of new concepts and knowledge;
- 4. Redundancy: Intentional superposition of information about their activities, promoting the sharing of tacit knowledge; and
- 5. Variety of requirements: When the necessary information is diverse and accessible, helping to solve problems.

Study Execution

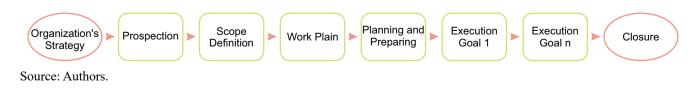
The study carried out in this article involves a small STI localized in Rio Grande do Norte, Brazil, named Núcleo Avançado de Inovação Tecnológica, or NAVI. NAVI has a team of about forty, including professors, students, and technicians. The project team acts as a researcher and seeks to develop innovative products and systems to meet demands, especially in health. Therefore, creating knowledge is essential to the organization's performance. The interviews were carried out with representatives of NAVI (the coordinator and a researcher) to understand the dynamics of knowledge creation and management. According to Robert Yin [8],

the interview is essential to evidence the case study better. In addition, the interview allows the interviewee to contribute in ways that provide unverified information in documents or reports [9]. We asked about NAVI's strategic planning to verify if its intention is formalized in a document. We understood that the design process follows a work plan and seeks to achieve goals and objectives in the time given. However, there needs to be indepth detailing in the planning that makes up the project since there is no systematic procedural method established in the STI. As a result, there is a certain informality between the processes, tasks, and relationships, making the adaptations carried out by the researchers recurring to find alternative solutions to solve the demands. Furthermore, it reinforces the creative character of the process, which is related to fluctuation and creative chaos. Thus, it was possible to understand the proposal development process until the prototype (Figure 2).

Since knowledge is an asset of great value, NAVI requests that every new researcher sign a term of secrecy and confidentiality to avoid the exposure of industrial secrets. In addition, if applicable, every new product has its patent and software registration. The STI is also concerned with complying with the General Data Protection Law - LGPD.

Qualitative data analysis of the captured data was carried out, specifically about the Plasma Dental Pen project, in its prototyping stage, to understand the dynamics of processes and project development. The research and development team had to learn additive manufacturing to prototype the product. In this process, it was possible to see the creation of tacit knowledge and its interaction throughout the phases of the SECI model to create organizational knowledge.

Figure 2. The design process for proposal development.



Results and Discussion

NAVI researchers interact with each other and with other research groups, characterizing a favorable "ba" for creating knowledge and, therefore, the generation of innovations. When a team struggles with an issue, it is possible to discuss it with other teams with expertise in the subject, analyzing the problem to find a solution. In addition to internal experiences of creating knowledge at NAVI, one can cite those carried out with research groups from other institutions, sometimes from other countries. As informed, this sharing can generate exchanges that improve the research, resulting in the internalization of new knowledge by the team. At these times, there is an exchange of experiences between researchers from different contexts, bringing other perspectives to the study. Therefore, contact with external data causes the socialization and the externalization foreseen in the SECI model. Furthermore, the research results are published in scientific articles, sharing the knowledge generated in the STI, which allows its systematization, and, therefore, its combination with other knowledge.

The activities carried out by the STI were organized in the SECI model proposed by the authors (Figure 3). In addition, using a product developed by NAVI, a plasma-based dental pen currently undergoing testing and improvements, as a reference to verify the dynamics of generation and diffusion of knowledge in the project, we found an adapted practice of the flow proposed by the SECI model.

The main difference between the foreseen practice presented by the SECI model initially proposed for large corporations, and this adapted practice in the STI, is that it occurs in a non-linear way between the stages, sometimes in a chaotic way, since there is low formalization between the processes. So the theory was visualized working inside but guided intuitively and maybe unconsciously, which corroborates with Menezes and Olave's [10] apud. Scarabelli and colleagues[4]. They emphasized that it is wrong to think that knowledge management practices work only for large corporations since such practices can lead organizations of any segment or size to better performance.

As the lack of a more deep structured development process, as indicated in the interview, the very act of innovating is risky and with many uncertains, which makes it difficult to plan every detail. However, with research development, tests are being carried out, theories and possibilities are being proven, and the project is taking a path that is not always as initially planned.

According to the interviewees, the researchers have autonomy in carrying out their work and exploring solutions as they come across problems, which is an essential stimulus to the creation of knowledge [8]. Furthermore, the uncertainty

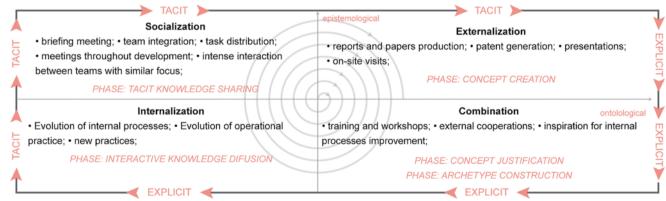


Figure 3. SECI model on course in the STI.

Source: Nonaka and Takeuchi [2].

regarding the demands they may face, the risk inherent to innovation projects, and the informality between processes give the course the enabling conditions of fluctuation and chaos. It requires a propensity and motivation from researchers to create new knowledge and adaptations that can become innovative and benefit society.

Considering the phases of the knowledge creation process and the analysis of the plasma-based dental pen development process, we found that the project is currently in the phase of construction of an archetype. To create the archetype, the team set up a prototyping group, a "ba," where they freely exchanged tacit and explicit knowledge about the process. Several adaptations to use available materials and knowledge were made to generate and later improve the Minimum Viable Product (MVP). In a few months, from constant exchanges and practical experiments, the team evolved the functional prototype and developed new knowledge, generating innovation in confluence with the SECI model. Soon, an intense process of knowledge socialization took place.

A research group was created focusing on prototyping and additive manufacturing to solve problems about knowledge the team had not mastered. Another "ba" performed a series of actions with satisfactory results for the organization. The researchers began a process of training in 3D printing, meeting regularly in physical and virtual spaces. Figure 4 demonstrates how the "ba" created in the STI intensified the generation and socialization of knowledge about additive manufacturing, evolving a process that had been paralyzed for some time.

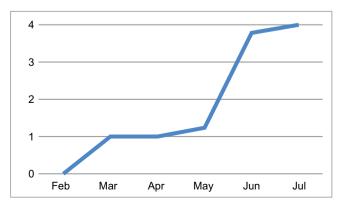
Figure 4 demonstrates the evolution of the tacit knowledge exchange between NAVI researchers during the implementation of an additive manufacturing process in a few months. The turning point, starting in May, demonstrates the effect of training made with a specialist in the area, where tacit knowledge was exchanged over two days. This fact exponentially boosted the curve in an upward movement, intensifying face-to-face meetings and the quick generation of prototypes and tests. Chiambareto and colleagues [1] said that the interactive and dynamic process of knowledge production applied to the development of the plasma-based dental pen resulted in a model of internal and external cooperation in "ba". It offers a case study of a small STI that becomes more competitive in its proposition to meet the demands of society by developing finalistic technological solutions.

Conclusion

This article aimed to explore and analyze the dynamics of knowledge generation and diffusion in a small-size STI, seeking to describe the development dynamics of a product based on the SECI model.

We verified a connection between the proposed theory and the actual practice of generating and

Figure 4. Relation between socialization and the generation of knowledge at the STI.



Kickoff meetings		
Group creation		
Group interactions online		
Training workshop		
Intensification of meetings		
Intense physical socialization		
Online meetings		

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spreading organizational knowledge in the project's phase analyzed. The main difference is that the practice works in a non-linear way, sometimes with chaotic processes due to low formalization between phases. The theory was seen acting on the project's stages but intuitively or unconsciously. It was possible to perceive the direct relationship between knowledge management at NAVI, and the generation of innovation, as proposed by the model mentioned above. This interrelation was dynamic in an organization's knowledge's epistemological and ontological dimensions.

Moreover, it occurs internally and externally with other organizations and society. Regarding the social dimension, it is relevant to highlight it as the origin and end of NAVI's effort to generate knowledge and innovation, as well as in this study. In addition, the findings of the seminal authors stand out as current. We also observed the lack of studies that deal with the creation of knowledge in STIs characterized as small organizations from SECI's approach, which opens the possibility of deepening this topic in future research.

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Ethanol Extract of *Passiflora cincinnata* Seeds Posses Antidiabetic, Antiglycant, and Antioxidant Activities *in vitro*

Flávia Adaís Rocha dos Santos¹, Elaine Luiza Santos Soares de Mendonça¹, Felipe Cabral da Silva¹, Jadriane de

Almeida Xavier^{1*}, J. P. Jose Merlin², Marília Oliveira Fonseca Goulart¹, H. P. Vasantha Rupasinghe^{2*} ¹Institute of Chemistry and Biotechnology, Federal University of Alagoas; Alagoas, Maceió, Brazil; ²Department of Plant, Food, and Environmental Sciences, Faculty of Agriculture, Dalhousie University; Truro, New Scotland, Canada

This work aimed to investigate the antidiabetic, antiglycation, and antioxidant potentials of the ethanol extract of seeds of Passiflora cincinnata (EPCIN) in vitro. The EPCIN was evaluated from the following assays: total phenolic content (TPC - mg of Gallic Acid Equivalents (GAE)/g of dry extract), Radical Scavenging Assays (DPPH•, HOCI-scavenging assay), and protective effects against glycation of bovine serum albumin (BSA) with methylglyoxal (MGO) or a mixture of reducing sugars, fructose and glucose, as well as the potential for MGO capture by derivatization with ortho-phenylenediamine (OPD). To evaluate the antidiabetic activity of EPCIN in vitro, we used the assays of enzymes a-amylase (4 U/mL), a-glucosidase (0.25 U/mL), and dipeptidyl peptidase-4 (DPP-4-3.125 mU). The cell viability of EPCIN-pretreated normal human bronchial epithelial cells (BEAS-2B) alone or in the presence of the carcinogen 4-[(acetoxymethyl)nitrosamine]-1-(3-pyridyl)-1-butanone (NNKOAc) was measured using MTS assay. Quercetin (QCT), piceatannol (PIC), acarbose (ACB), and sitagliptin (STG) were used for comparison purposes. EPCIN had an average of TPC 157.0 ± 1.5 mg of GAE/g of dry extract, exhibited IC₅₀ for DPPH• and HOCl of $11.9 \pm 1.8 \mu g/mL$ and $6.9 \pm 0.9 \mu g/mL$, respectively. EPCIN and AMG inhibited the formation of advanced glycation end-products (AGE) with IC₅₀ of 574 \pm 8.7 and 31.9 \pm 2.7 µg/mL for the initial stage and 542.6 \pm 2.7 and 52.8 \pm 8.1 μ g/mL for the intermediate stage of glycation, respectively. EPCIN showed IC₅₀ for α -amylase and α -glucosidase of 218.2 ± 15.9 µg/mL (p<0,05) and 242.0 ± 25 µg/mL (p<0,05), respectively. EPCIN did not show cytotoxicity for BEAS-2B cells at 10 and 50 µg/mL concentrations. In addition, it was also able to protect cultured human cells from oxidative stress caused by the NNKOAc at 100 µM. The in vitro evidence of the potential antioxidant, antiglycant, and antidiabetic effects warrants further investigation of the antidiabetic potential of Passiflora cincinnata seeds.

Keywords: Passion Fruit. Phytochemicals. Oxidative Stress. Type 2 Diabetes. Cytotoxicity.

Introduction

Since ancient times, phytochemicals have been used worldwide as alternative/complementary therapies to treat several pathologies due to the presence of biologically active compounds secondary metabolites, sometimes biosynthesized, in plants, after some chemical, physical or biological injuries [1]. Among them, polyphenols

J Bioeng. Tech. Health 2022;5(4):224-231 © 2022 by SENAI CIMATEC. All rights reserved. have been highlighted, mainly regarding their antioxidant activity. These compounds, among other mechanisms of molecular action, have decreased NF-kB expression pathways, attenuating the excessive production of reactive oxygen species (ROS) and decreasing lipoperoxidation and damage of biomacromolecules. Additionally, they stimulate the NRF2 signaling pathway, which leads to an increase of antioxidant enzymes, such as superoxide dismutase (SOD), glutathione peroxidase (GPx), and catalase (CAT) [2].

Although polyphenols have well-established antioxidant activity, a particular group of nonflavonoid compounds, the stilbenes, has increased interest in the scientific community. Among the stilbenes - resveratrol, piceatannol (PIC), hesperidin, hesperetin, pterostilbene, polidatin, stilbestrol, and pinosylvine have shown multiple spectra of biological activities, with a special emphasis in PIC. PIC's relevance is probably

Received on 17 September 2022; revised 24 November 2022. Address for correspondence: Jadriane Almeida Xavier. Institute of Chemistry and Biotechnology, Federal University of Alagoas, Maceio, Zip code: 57072-970, Brazil. E-mail: jadrianexavier@iqb.ufal.br. H.P. Vasantha Rupasinghe. Department of Plant, Food, and Environmental Sciences, Faculty of Agriculture, Dalhousie University, 50 Pictou Road, Truro, NS B2N 5E3, Canada, e-mail: vrupasinghe@dal.ca. DOI 10.34178/jbth.v5i4.243.

related to the presence of the catechol moiety [3-5]. In addition, researchers have identified the presence of PIC in the genus *Passiflorae*, which comprises more than 500 species, found predominantly in tropical and subtropical regions of the world [6-8].

In northeastern Brazil, the species Passiflora cincinnata, popularly known as "wild passion fruit" or "passion fruit of the Caatinga", has been less explored compared to other species because it has a specific sensory analysis, with unusual organoleptic characteristics, mainly regarding the pulp of its fruits, being considered to have a stronger flavor than the other species. However, it is worth mentioning the natural beauty of its flowers and its resistance to pests and hydric deficit [8]. In addition, the literature is scarce regarding their chemical composition and biological profile.

In this context, the objective of the present work was to evaluate the *in vitro* antioxidant, antiglycant, and antidiabetic activities of the ethanol extract of the seeds of *Passiflora cincinnata* (EPCIN). To the best of our knowledge, no study has been conducted so far reported concerning the seeds of Brazilian *P. cincinnata* as an antidiabetic agent through the association of α -glucosidase and DPP-4 inhibition mechanisms, not even as an antiglycant in the initial and intermediate stages of glycation. In addition, the cytotoxicity of EPCIN was studied in BEAS-2B cell lines, with and without the oxidative stress-causative carcinogen NNKOAc.

Materials and Methods

Preparation of the Ethanol Extracts of Passiflora cincinnata Seeds

We collected the unripe fruits of *Passiflora cincinnata* in November 2019 in a native forest in Olho d'Água do Casado, Alagoas. The seeds were separated from the fruit pulp, washed with distilled water, and dried in an oven at 50 °C for 48 h. The ethanol extract of *Passiflora cincinnata* seeds (EPCIN) was obtained according to the method described by Xavier and colleagues [6].

Total Phenolic Content (TPC)

The TPC was estimated using the Folin– Ciocalteu (FC) method, as described by Cicco [9], with some modifications. Briefly, 180 μ L of deionized water, 300 μ L of FC reagent, and 2.4 mL of 5% sodium carbonate (w/v) were added to 120 μ L of diluted samples. After incubation in a water bath at 40 °C in the dark for 20 min, the absorbance of the resulting mixture was measured at 760 nm using a UV–Vis spectrophotometer (Agilent 8453). The results were expressed as milligrams of gallic acid equivalents (mg GAE) per gram of dry extract.

Radical Scavenging Assay DPPH•

The antioxidant activity of EPCIN was determined using the DPPH• method [10]. Briefly, aliquots of 0.30 mL of sample dissolved in ethanol (5–25 μ g/mL) were mixed with 2.70 mL of DPPH• solution (40 μ g/mL in methanol). After incubation in the dark for 30 min, the absorbance was read at 516 nm, using a UV–Vis spectrophotometer (Agilent Technologies, Santa Clara, CA, USA). Results were expressed as the half-maximal inhibitory concentration (IC₅₀) in μ g/mL.

Hypochlorous Acid (HOCl) Elimination Assay

The HOCl elimination activity of EPCIN and was determined using the previously described method [11]. Briefly, a new HOCl solution (30 µM) was prepared in 100 mM phosphate buffer (pH 7.4). Then, in a 96-well plate, the following reagents were added at the indicated final concentrations: buffer solution (100 mM, pH 7.4), EPCIN (1, 5, 10, 25, 50, 100, 200, and 300 µg/ mL), dihydrorodamine (DHR) (5 µM) and HOCl (5 µM). QCT and PIC were used for comparison purposes. The fluorescence measurements were performed in a microplate reader (Infinite® 200 PRO, TECAN, Männedorf, Switzerland), at 37 °C, at wavelengths of 505 ± 10 nm and 530 ± 10 nm, for excitation and emission, respectively. The results were expressed as IC₅₀ in µg/mL.

Measurement of Intracellular ROS Level

The generation of intracellular ROS in BEAS-2B after treatments with EPCIN was measured as described previously [12]. The cells, pretreated with EPCIN for 3 h, were exposed to the carcinogen NNKOAc, for 3 h or alone in different experimental groups. DMSO (0.5%) was utilized as a control. ROS was quantified after treatments using the 2',7'-dichlorofluorescein diacetate dye (DCFH-DA) at a final concentration of 5 μ M followed by 40 min incubation at dark. Fluorescence measurements were performed in a microplate reader (Infinite® 200 PRO, TECAN, Männedorf, Switzerland), at 37 °C, at wavelengths of 485 nm and 535 nm, for excitation and emission, respectively.

Cell Cultures and Cell Viability Assay

BEAS-2B cells were cultured with LHC-9 media at 37 °C in an incubator with CO₂ (5%). Culture flasks (polystyrene T75) were pre-coated with a mixture of fibronectin (0.01 mg/mL), bovine collagen type I (0.03 mg/mL), and bovine serum albumin (0.01 mg/mL) dissolved in the LHC-9 medium overnight. The MTS assay was used to perform the cell viability assay [13]. For 24 hours, different concentrations of EPCIN were used to examine the viability of the cells. Next, an MTS reagent was applied, and the cells were incubated for 3 hours in the dark. A microplate reader (Infinite® 200 PRO, TECAN, Männedorf, Switzerland) was used, and the absorbance was recorded at 490 nm.

<u>α-Amylase Inhibition Assay</u>

The α -amylase inhibition assay was performed using a previously described method [14] with minor modifications. EPCIN and PIC, in different concentrations, were prepared in 0.01 M potassium phosphate buffer (pH 6.8) containing 8% ethanol. All other solutions were prepared in buffer only. ACB was used as a positive control. The reaction system consisted of adding the samples, α -amylase from porcine pancreas (4 U/mL), and after 10 min of incubation at 37 °C, the substrate 2-chloro-4nitrophenyl- α -D-maltotrioside (5 mM) was added and then incubated for more 30 min. The reaction was terminated by adding a trisodium phosphate solution of pH 11 (1%, w/v). The amount of 2-chloro-4-nitrophenol released was measured spectrophotometrically at 405 nm in a microplate reader (Infinite® 200 PRO, TECAN, Männedorf, Switzerland).

<u>α-Glucosidase Inhibition Assay</u>

The α -glucosidase inhibition assay was performed using a previously described method [15] with minor modifications. EPCIN and PIC, in different concentrations, were prepared in 0.01 M potassium phosphate buffer (pH 6.8) containing 2.5% ethanol. All other solutions were formulated in buffer only. The reaction system consisted of adding a sample, alpha-glucosidase enzyme (0.25 U/mL), and 4-nitrophenyl-α-D-glucopyranoside (5 mM) substrate. The mixture was then incubated at 37 °C for 15 min, and the reaction was stopped by adding sodium carbonate solution (0.2 M). Acarbose (ACB) was used for comparison purposes. The amount of p-nitrophenol (PNP) released was measured spectrophotometrically at 405 nm in a microplate reader (Infinite® 200 PRO, TECAN, Männedorf, Switzerland).

Dipeptidyl Dipeptidase Enzyme (DPP-4) Inhibition Assay

The DPP-4 inhibition assay was performed according to an established method [14]. STG, a standard DPP-4 inhibitor, was used to compare the effectiveness of PESE and PIC. Briefly, In a 96-well plate, the following reagents were added at the indicated final concentrations: the sample at different concentrations, DPP-4 human recombinant enzyme solution (3.125 mU), and Gly-Pro-7-amido-4-methylcoumarin hydrobromide substrate (2.5 μ M). The reaction mixture was incubated for

30 min in the dark at 37 °C. Then, the fluorescent product was recorded using the microplate reader (Infinite® 200 PRO, TECAN, Männedorf, Switzerland) at wavelengths of 350 nm and 450 nm for excitation and emission, respectively.

Inhibition of Advanced Glycation End Products (AGE) Formation

The formation of AGEs was evaluated in the initial (BSA, glucose, and fructose) and final stages of glycation (system containing BSA and MGO). This assay was based on previous methods [6]. Aminoguanidine (AMG) was used as a positive control. We used a mixture of fructose and glucose-reducing sugars to evaluate the initial stage. The reaction system consisted of the addition of adequate volumes of EPCIN or AMG solutions (at different concentrations), D-fructose (200 mM), D-glucose (200 mM), and bovine serum albumin (BSA, 3 mg/mL) in a total volume of 1.5 mL. EPCIN was dissolved in ethanol. All other solutions were dissolved in 0.05 M potassium phosphate buffer (pH 7.4) containing NaCl (100 mM) and NaN3 (0.02% w/v). The reaction system was incubated in the dark at 37 °C for 7 days with constant stirring. For the evaluation of the intermediate stage, the same procedure was followed; however, MGO was used instead of the mixture of reducing sugars. The fluorescent AGEs were measured using a microplate reader (Infinite® 200 PRO, TECAN, Männedorf, Switzerland) at $hat{kex} = 360$ and $hat{kem} =$ 440 nm. AMG, a known AGE formation inhibitor, was used as a standard.

Methylglyoxal Capture Potential

MGO capture was evaluated by derivatization with o-phenylenediamine (OPD) using a previously described procedure [6]. The reaction system was composed of MGO, phosphate buffer (negative control), or EPCIN (2 mg/mL) or AMG (2 mM, positive control) incubated at 37 °C for 1 h. After incubation, the OPD solution (4 mM) was added, and the tubes were kept for 30 min for the derivatization reaction between MGO and OPD to complete. Then, the formation of the derived product 2-methylquinoxyline (2-MQ) was monitored by high-performance liquid chromatography (HPLC) and detected at 315 nm. Formic acid (0.1% v/v, solvent A) and methanol (solvent B) were used as a mobile phase, with a flow rate of 1.0 mL/min. The linear gradient for elution was starting at 5% of solvent B, 0-3 min, 5 to 50% B; 3-16 min, isocratic in 50% B; 16-17 min, 50-90% B; 17-19 min, isocratic in 90% B and 19-19.5 min, 90-5% B. The percentage of MGO capture was calculated concerning the peak area corresponding to the 2-MQ product in the systems with and without treatment.

Statistical Analysis

All analyses were performed in triplicate (n = 3) using Graph-Pad Prism software (GraphPad Software Inc., San Diego, CA, USA). Data were presented as the mean \pm standard deviation (SD), and analyses of variance, one-way ANOVA, followed by Tukey test, and $p \le 0.05$ were considered significant between experimental groups.

Results and Discussion

The EPCIN yield was 1.9% from 12 g of dried and ground seeds. Extraction of extract yields is crucial in assessing the cost and benefits associated with potential nutraceutical development. Xavier and colleagues [7], when studying the ethanol extraction of the seeds of *Passiflora edulis*, obtained 4 times higher yields (7.9%). The degree of maturation of the fruit seems to be a factor that could influence the composition of the seeds.

Table 1 shows the levels of total phenols and antioxidant activity of EPCIN compared to QCT. Particularly concerning the DPPH• and HOCl elimination assays, we observed that although the antioxidant capacity of EPCIN was lower than that presented by the QCT (control), the IC₅₀ values are close to those proposed by the standard.

Table 1. Total phenol content (TPC) and	antioxidant]	potential	of the	ethanolic	extract	of se	eds of
Passiflora cincinnata in comparison to quere	cetin (QCT).						

Sample	TPC dry extract of EAG (mg/g)	DPPH• IC50 (µg/mL)	HOCl IC50 (µg/mL)	
EPC	157.0 ± 1.5	11.9 ± 1.8	6.9 ± 0.9	
QCT	-	$5.5 \pm 0.6 \ (18.1)$	2.2 ± 0.3 (7.2)	

EPCIN: ethanolic extract of seeds of *Passiflora cincinnata*; QCT: Quercetin; DPPH•: 1,1-Diphenyl-2-Picrylhydrazyl; GAE: Gallic Acid Equivalents. Results in Parentheses (μM).

Table 2. *In vitro* antidiabetic activity of ethanol extracts from seeds of *Passiflora cincinnata* and Piceatannol (PIC), in comparison with acarbose (ACB) and sitagliptin.

Sample	a- Amylase - IC50	α- Glucosidase - IC50	DPP-4 - IC50
	(μg/mL)	(µg/mL)	(µg/mL)
EPCIN	$218.2\pm15.9^{\circ}$	$242.0\pm25.1^{\text{b}}$	NA
PIC	$85.9 \pm 1.8 \; (339.4)^{\text{b}}$	$21.5\pm 8.3\;(88.0)$	$1,\!300.3\pm20.0(5,\!323.9)$
ACB	$0.6 \pm 0.1 \; (0.9)^{a}$	$251.6 \pm 4.5 \; (389.7)$	-
STG	-	-	$0.005 \pm 0.0005 \; (0.01)$

EPCIN: ethanol extract of seeds of *Passiflora cincinnata;* PIC: Piceatannol; ACB: acarbose; STG: sitagliptin; NA, it was not possible to calculate the IC_{so} ; Data in parentheses (μ M).

Santos and colleagues [6], when evaluating the antioxidant activity of the ethanol extract of *Passiflora edulis* seeds, observed a TPC of 227 ± 3.9 mg of GAE/g, approximately 2x that observed in the present study, which was reflected in the antioxidant activity in scavenging DPPH• (20.4 \pm 2.1 µg/mL), with lower activity than EPCIN; however, the antioxidant activity, obtained through the ability to eliminate HOCl, of *Passiflora edulis* (1.7 \pm 0.3 µg/mL) was approximately 4 times superior to that of EPCIN. The results suggest that EPCIN may be an essential source of phenolic compounds and that EPCIN has antioxidant activity, decreasing the formation of ROS and other metabolites.

The antidiabetic potential of EPCIN can be analyzed through the ability to inhibit α -amylase and α -glucosidase, in addition to the DPP-4 enzyme. This study used acarbose (ACB) and sitagliptin (STG) for comparison purposes. EPCIN showed a concentration-dependent activity against α -amylase and α -glucosidase inhibition, and the IC₅₀ values are shown in Table 2. EPCIN and PIC, one of the compounds present in the seeds of *Passiflora cincinnata*, showed higher potential towards α -glucosidase than α -amylase. We noted that EPCIN showed toward α -glucosidase an IC₅₀ value equivalent to that presented by ACB. However, it caused a low α -amylase inhibition. On the other hand, PIC showed excellent α -glucosidase inhibition potential, with IC₅₀ about 4.5 times lower than ACB, suggesting that PIC plays an essential role in the antidiabetic potential of EPCIN.

BSA glycation was performed in the presence and absence of EPCIN. In the initial stage, IC₅₀ values presented by EPCIN and AMG were 574.4 \pm 8.7 and 31.9 \pm 2.7 µg/mL, respectively. For the intermediate stage, where BSA was treated with MGO, the IC₅₀ values were 542.6 \pm 2.7 and 52.8 \pm 8.1 µg/mL, respectively. EPCIN inhibited the formation of fluorescent AGEs; however, AMG showed higher activity when compared to EPCIN. Gomes and colleagues [16] evaluated the hydroethanolic extract of *P. cincinnata* aerial parts. They observed a 68.17% inhibition of AGEs formation for a concentration of 10 mg/mL, while Santos and colleagues [6] found an IC₅₀ of 360 μ g/mL for the ethanol extract of *P. edulis* seeds.

When investigating the MGO capture potential in the reaction system, after 1 h incubation, EPCIN could capture 47.9% of the MGO present in the solution, while AMG presented 89.2% of MGO capture. The results show that EPCIN may act in the intermediate step of the glycation reaction, stabilizing the dicarbonyl species and thus inhibiting the response with amino groups of biomolecules through the formation of AGEs [17].

It has been recognized that when the cell viability is greater than 90%, the sample is considered non-toxic at a given dose. Figure 1A shows a dose-responsive decline in cultured BEAS-2B cells with increasing concentrations of EPCIN ($p \le 0.05$). EPCIN did not alter cell viability up to a concentration of 50 µg/mL.

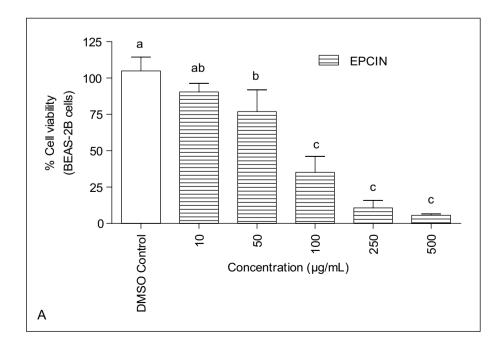
Xavier and colleagues [7], when testing the cell viability (human placental HTR-8/SVneo) in the presence of the ethanol extract of *Passiflora edulis* seed, observed that there was no reduction in cell viability, even at the concentration used of 100 μ g/mL.

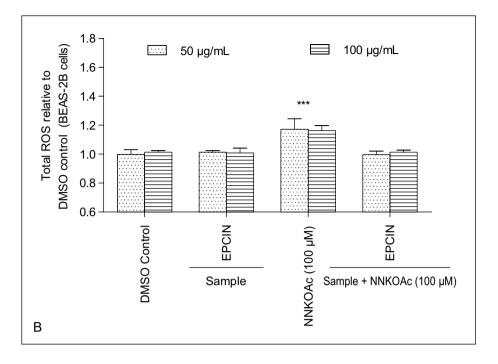
Additionally, Figure 1B shows the effects of EPCIN on the BEAS-2B cells exposed to NNKOAc (100 μ M), evidencing that the carcinogen was able to stimulate the production of ROS and that the pre-treatment with EPCIN was able to protect cultured BEAS-2B cells against oxidative stress. EPCIN was also added to cells in the absence of NNKOAc, and again no increase in ROS production was observed when compared to the control.

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Figure 1. Dose-dependent effects of the ethanol extract of seeds of *Passiflora cincinnata* (EPCIN) on the viability of normal human bronchial epithelial cells (BEAS-2B) (A). The relative amount of ROS evaluated in normal human bronchial epithelial cells (BEAS-2B), after exposure to carcinogen alone or with pre-treatment of ethanol extract of seeds of Passiflora cincinnata (B) at concentrations of 50 and 100 μ g/mL.





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Conclusion

EPCIN showed potential antioxidant, antiglycant, and antidiabetic effects. Furthermore, EPCIN was shown to be non-toxic to BEAS-2B cells at the concentration effective to exhibit antidiabetic and antioxidant activities, in addition to protecting the BEAS-2B cells from oxidative stress caused by NNKOAc. Based on this study, further studies need to be conducted using experimental animal models to assess the extract's safety and confirm its antioxidant, antiglycant, and antidiabetic activities. In conclusion, EPCIN has the potential to be used as an alternative therapy for managing type 2 diabetes mellitus.

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Carbon Footprint of Hydrothermal Liquefaction of Microalgae Biomass Cultivated in Availability and Limitation of Nutrients

Lorena Rodrigues Cunha^{1*}, Diego Lima Medeiros², Ícaro Thiago Andrade Moreira^{1,2}

¹Chemical Engineering Graduate Program (PPEQ), Federal University of Bahia (UFBA); ²Clean Technologies Network (TECLIM), Federal University of Bahia (UFBA); Salvador, Bahia, Brazil

This work aimed to assess the carbon footprint of microalgae biomass processing in hydrothermal liquefaction (HTL) to produce biopetroleum and co-products. The foreground inventory covered the cultivation in open ponds with availability (C1) and limitation (C2) of nutrients, followed by harvesting and processing in HTL for 1 kg of microalgae biomass in total solids. The ecoinvent[™] 3.6 databases and IPCC- 2021 GWP 100 years method were used for background inventory and impact indicator in openLCA® 1.11.0. The carbon footprint of C1 (1.1 kg CO_{2eq}) was more significant than that of C2 (0.7 kg CO_{2eq}). The most considerable carbon footprint contribution per stage was the Production stage (cultivation and harvesting), with 64%-88%, in the evaluated scenarios. In comparison, this per process was the fertilizer (71%) in C1 and the heat (32%) in C2. Keywords: Biotechnology. Environmental Performance. Life Cycle Assessment (LCA). Greenhouse Gases (GHG). Microalgae Bioproducts.

Introduction

Society industrialization contributed to the expansion of fossil energy consumption, which increased greenhouse gas (GHG) emissions. Therefore, several countries worldwide are committed to adopting measures to mitigate GHG emissions, such as replacing fossil resources with renewable resources [1-3]. In this context, fuels from renewable and carbon-neutral sources promise to replace the fossil fuel. However, substitutes, as first and second-generation biofuel production, demand fertile soils, which is associated with rising food costs. In this way, microalgae-based biofuels have advantages compared to first and second-generation biofuels due to their ability to grow in unsuitable land for agriculture, more significant photosynthetic activity compared to terrestrial plants, and potential to use inputs from residual sources such as gaseous and aqueous effluents [4,5].

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Microalgae biomass can be converted into bioproducts using varied processes such as the thermochemical routes. Hydrothermal liquefaction (HTL) is a promising technology for converting wet biomass into biopetroleum [6]. Thus, HTL reduces energy consumption, environmental burdens, and financial costs associated with biomass drying [6,7]. In this regard, Life Cycle Assessment (LCA) is used to quantify the carbon footprint of a product system and support decision-making for GHG emission reduction. Thus, the carbon footprint is widely used in energy policy and practices such as the Brazilian Biofuel Policy (RenovaBio). Therefore, this study aims to quantify the carbon footprint of biomass processing in HTL from microalgae cultivation in availability (C1) and limitation (C2) of nutrients.

Materials and Methods

The attributional LCA method based on ISO-14044 [8] was used in this study to quantify the carbon footprint in the evaluated scenarios. The reference flow and functional unit combined in this study was 1 kg microalgae biomass processing in total solids (TS). The product system covered the operation phase of the following processes in the foreground inventory: cultivation in open raceway ponds with availability (C1) and limitation (C2)

Received on 25 September 2022; revised 20 November 2022. Address for correspondence: Lorena Rodrigues Cunha. Alameda Zulmira Ferreira, 42 - Saboeiro, Salvador - BA -Brazil. Zipcode: 41180-335. E-mail: lorenarccunha@gmail. com. DOI 10.34178/jbth.v5i4.244.

of nutrients, followed by harvesting within the Production stage and conversion of microalgal biomass into biopetroleum and co-products in HTL in the Processing stage (Figure 1). In this regard, the evaluated scenarios consist of a product system of microalgae biomass processing in C1, a high-protein content in C1 and a highcarbohydrate content in C2.

The production stage consists of the cultivation in open raceway ponds with annual average productivity of 18 g $(m^2 day)^{-1}$ in TS. It is supplied by nitrogen and phosphorus nutrients from synthetic fertilizers, saline water from a local source, and high-purity carbon dioxide from a residual source, followed by harvesting with settling, filtration, and centrifugation processes to achieve a 20% concentration in TS [9]. The Processing in HTL lasts 30 min at 350 °C and 20 MPa. The operation phase of the Production and Processing stages of microalgae-based biopetroleum and co-products were assessed in this study. In contrast, the construction, decommissioning, and downstream stages, such as refining, delivery, use, and post-use, were disregarded. The foreground inventory of the Production stage was obtained from estimations, laboratory analysis, and field experiments in Medeiros and Moreira [10]. In contrast, Jones and colleagues obtained that of the Processing stage was obtained from estimations, laboratory analysis and field experiments [11] (Table 1).

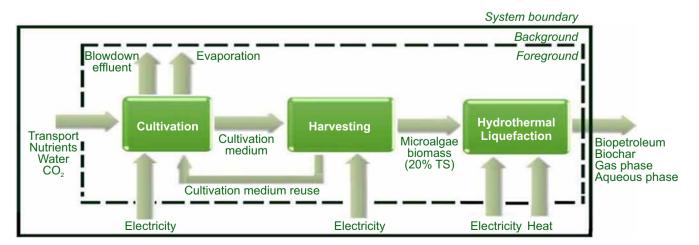
The openLCA® software version 1.11.0 with the background inventory from the ecoinventTM database version 3.6 for an allocation procedure of process subdivision (cutoff criteria) was used in this study. The assessed category for environmental performance was the carbon footprint from the IPCC-2021 method with the global warming potential indicator (GWP) for 100 years in a kilogram of carbon dioxide equivalent (kg CO_{2eq}).

Results and Discussion

The carbon footprint of microalgae biomass processing in HTL was more prominent in the scenario with nutrient availability (1.1 kg CO_{2eq} in C1) compared to that with nutrient limitation (0.7 kg CO_{2eq} in C2). The most significant carbon footprint contribution per stage was the Production stage (cultivation and harvesting), with 88 % in C1 and 64% in C2 (Figure 2).

Table 2 presents the carbon footprint contribution per process for C1 and Table 3 shows it for C2. The most considerable carbon footprint contribution per process was the fertilizer (71%) in the Production stage of C1 and the heat (32%) in the Processing stage of C2. Even though C2 had a greater electricity demand, its smaller nutrient demand

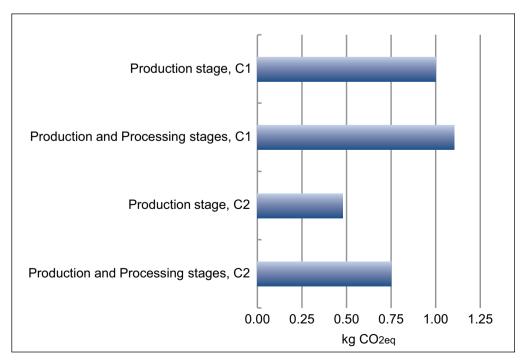
Figure 1. Product system of microalgae biomass processing in hydrothermal liquefaction.



Parameters	Unit	C1	C2
Cultivation and Harvesting			
Occupied area	m² year	0.15	0.16
Water, saline	L	32	34
Carbon dioxide, CO2	kg	1.9	2.1
Ammonia, liquid	kg	0.10	0.019
Nitrogen, N	kg	0.085	0.016
Diammonium phosphate	kg	0.046	0.009
Nitrogen, N	kg	0.010	0.002
Phosphorus, P2O5	kg	0.025	0.005
Transport of fertilizer, truck	t km	0.30	0.056
Electricity	kWh	0.48	0.52
Water, air	L	22	24
CO2, loss, air	kg	0.19	0.21
Water, blowdown effluent	L	5.9	6.7
Biomass, loss	kg	3x10 ⁻⁴	3x10 ⁻⁴
Hydrothermal Liquefaction			
Electricity	kWh	0.36	0.36
Heat	MJ	5.9	5.9

Table 1. Foreground inventory of the Production and Processing stages of 1 kg microalgal biomass processing in total solids.

Figure 2. The carbon footprint of 1 kg microalgae biomass processing in the evaluated scenarios.



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Table 2. Carbon footprint contribution per process of 1 kg microalgae biomass processing in C1.

		•		
Contribution	Process		Amount	Unit
✓ 100.00%	P Hydrothermal liquefaction, C1	-	1.16993	kg CO2 eq
✓ 88.27%	P Microalgae biomass production, C1	-		kg CO2 eq
> 54.89%	P market for nitrogen fertiliser, as N nitrogen fertiliser, as N Cutoff, U - GLO			kg CO2 eg
> 12.48%	P market for ammonia, liquid ammonia, liquid Cutoff, U - RoW	i		kg CO2 eq
> 07.29%	P Carbon dioxide supply, residual source, high-purity	i		kg CO2 eq
> 07.05%	P market group for electricity, low voltage electricity, low voltage Cutoff, U - BR	i		kg CO2 eq
> 04.20%	P market for phosphate fertiliser, as P2O5 phosphate fertiliser, as P2O5 Cutoff, U - GLO	i		kg CO2 eq
> 02.37%	P market for transport, freight, lorry, unspecified transport, freight, lorry, unspecified Cutoff, U - GLO	i		kg CO2 eq
✓ 10.26%	P market for heat, district or industrial, natural gas heat, district or industrial, natural gas Cutoff, U - GLO	÷		kg CO2 eg
> 04.41%	P heat and power co-generation, natural gas, 200kW electrical, lean burn heat, district or industrial, natural gas Cutoff			kg CO2 eq
> 03.53%	P heat and power co-generation, natural gas, 1MW electrical, lean burn heat, district or industrial, natural gas Cutoff			kg CO2 eg
> 02.32%	P heat and power co-generation, natural gas, 500kW electrical, lean burn heat, district or industrial, natural gas Cutoff			kg CO2 eq
✓ 01.47%	P market group for electricity, low voltage electricity, low voltage Cutoff, U - BR			kg CO2 eq
> 00.74%	P market for electricity, low voltage electricity, low voltage Cutoff, U - BR, South-eastern grid			kg CO2 eq
> 00.41%	P market for electricity, low voltage electricity, low voltage Cutoff, U - BR-North-eastern grid			kg CO2 eq
> 00.16%	P market for electricity, low voltage electricity, low voltage Cutoff, U - BR-Southern grid			kg CO2 eq
	P market for electricity, low voltage electricity, low voltage Cutoff, U - BR-Northern grid			kg CO2 eq
	P market for electricity, low voltage electricity, low voltage Cutoff, U - BR, Mid-western grid			kg CO2 eq
			0.00009	ky COZ EQ

Table 3. Carbon footprint contribution per process of 1 kg microalgae biomass processing in C2.

Contribution	Process		Amount	Unit
✓ 100.00%	P Hydrothermal liquefaction, C2	-	0.74484	kg CO2 eq
✓ 64.73%	P Microalgae biomass production, C2		0.48217	kg CO2 eq
> 22.70%	P market for nitrogen fertiliser, as N nitrogen fertiliser, as N Cutoff, U - GLO	r,	0.16910	kg CO2 eq
> 18.13%	P Carbon dioxide supply, residual source, high-purity	r,	0.13502	kg CO2 eq
> 16.88%	P market group for electricity, low voltage electricity, low voltage Cutoff, U - BR	1	0.12570	kg CO2 eq
> 05.06%	P market for ammonia, liquid ammonia, liquid Cutoff, U - RoW	1	0.03767	kg CO2 eq
> 00.99%	P market group for transport, freight, lorry, unspecified transport, freight, lorry, unspecified Cutoff, U - GLO		0.00735	kg CO2 eq
> 00.98%	P market for phosphate fertiliser, as P2O5 phosphate fertiliser, as P2O5 Cutoff, U - GLO		0.00732	kg CO2 eq
✓ 32.04%	P market group for heat, district or industrial, natural gas heat, district or industrial, natural gas Cutoff, U - GLO	•	0.23863	kg CO2 eq
> 19.81%	P market for heat, district or industrial, natural gas heat, district or industrial, natural gas Cutoff, U - RoW	۰.	0.14758	kg CO2 eq
> 11.44%	P market group for heat, district or industrial, natural gas heat, district or industrial, natural gas Cutoff, U - GLO	1	0.08520	kg CO2 eq
> 00.79%	P market for heat, district or industrial, natural gas heat, district or industrial, natural gas Cutoff, U - CA-QC		0.00586	kg CO2 eq
✓ 03.23%	P market group for electricity, low voltage electricity, low voltage Cutoff, U - BR	r,	0.02403	kg CO2 eq
> 01.63%	P market for electricity, low voltage electricity, low voltage Cutoff, U - BR, South-eastern grid		0.01211	kg CO2 eq
> 00.91%	P market for electricity, low voltage electricity, low voltage Cutoff, U - BR-North-eastern grid		0.00676	kg CO2 eq
> 00.34%	P market for electricity, low voltage electricity, low voltage Cutoff, U - BR-Southern grid		0.00257	kg CO2 eq
> 00.18%	P market for electricity, low voltage electricity, low voltage Cutoff, U - BR-Northern grid		0.00135	kg CO2 eq
> 00.17%	P market for electricity, low voltage electricity, low voltage Cutoff, U - BR, Mid-western grid		0.00125	kg CO2 eq

reduced the total carbon footprint compared to C1. The fertilizer supply from residual sources such as wastewater should be prioritized in microalgae cultivation to minimize the use of synthetic fertilizers. In addition, catalysts can be applied in HTL to reduce the reaction time and energy demand. Therefore, different optimization strategies are required to improve microalgae bioproducts' technical, environmental, and economic performance.

Conclusion

Life cycle assessment (LCA) was used to quantify the carbon footprint of microalgae biomass production from cultivation in availability (C1) and limitation (C2) of nutrients and their processing in hydrothermal liquefaction (HTL). Even though C2 had a greater electricity demand compared to that C1, the carbon footprint of C1 was larger than C2 due to its greater synthetic fertilizer demand. Therefore, this work supports decision-making to reduce greenhouse gas (GHG) emissions in producing microalgae bioproducts such as biopetroleum and biochar.

Acknowledgments

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Temperature Effect in the Babassu (Orbignya speciosa) Oil: A Physico-Chemical Study

Rebecca da Silva Andrade^{1*}, Marta Andrade Pires², Miguel Angel Iglesias Duro³

¹Universidade Federal do Recôncavo da Bahia; Feira de Santana, Bahia ²Universidade Maurício de Nassau; ³Universidade Federal da Bahia; Salvador, Bahia, Brazil

Babassu (*Orbignya speciosa*) is a Brazilian palm with extraordinary importance in socioeconomic and ecologic terms. It is found in humid tropical areas, especially in degraded landscapes. There are several uses for babassu coconut and babassu oil. However, their immense potential for large-scale providing other industrial products still needs to be explored due to the necessity for modern scale planning and deep knowledge of vast spectrum thermodynamic properties. This paper gathers a new experimental physico-chemical study of the temperature effect on two critical properties, density and ultrasonic velocity for babassu oil, due to its rising economic significance and a high potential for intensive farming in regions with low economic resources. We consider how accurately different theoretical prediction methods work due to modern processes, design, and algorithm simulations being strongly computer-oriented. The Agrawal-Thodos equation for density and Collision Factor Theory for ultrasonic velocity was selected, mainly attending to ease of use and range of application. We observed a good response at the studied conditions, despite geometrical simplifications into triglyceride molecules and using estimated critical magnitudes by molecular group contribution approach. A broad comparison was made with disposable open literature thermodynamic data, showing an essential dispersion of data, and highlighting the quality of the experimental data presented in this work.

Keywords: Babassu Oil. Density. Ultrasonic Velocity. Prediction. Theoretical Models. Molecular Group Contribution Approach. Surrogate Oil.

Introduction

The babassu coconut palm is of Brazilian origin, found in the Amazon basin and nearby humid tropical regions, especially in degraded landscapes. It is a typical transition plant from the region of the Cerrado biome, the Amazon rainforest, and the Brazilian semiarid northeast. The *Arecaceae* family records approximately 240 genera and 2,700 species worldwide [1-4], existing 146 species in different Brazilian ecosystems, standing out in terms of economic, social, and ecological potential. Mainly species of the genera *Attalea, Orbygnia, Syagrus, Acrocomia,* and *Mauritia*, are often sold at popular markets in Brazil [5-8] for the traditional use of fruit and heart of palm in fresh food or processed as sweets,

J Bioeng. Tech. Health 2022;5(4):237-249 © 2022 by SENAI CIMATEC. All rights reserved. and drinks, oils, and crafts. In the *Orbygnia* genus, the babassu (*Orbignya speciosa*) stands out, an isolated robust palm tree of 10-30 meters high and 30-60 centimeters in diameter, with 7 to 22 pinnate leaves, measuring 4-8 meters in length [9].

Babassu (Babaçu in Portuguese) is one of the Brazilian palm trees with greater significance in terms of ecology, and society, with economic relevance for the Brazilian states of Bahia, Maranhão, Piauí, and Tocantins [10]. It shows excellent relevance for the subsistence of many traditional communities since the whole plant can be used. The leaves are used to cover traditional houses, in crafts, the stipe as a building element of the civil structure, the fruits as a source of energy (coal), almonds as food, and the manufacture of cosmetics [7-8,10-12]. The palm tree produces coconuts arranged in different separated clusters. Four main structures characterize these fruits: mesocarp, endocarp, epicarp. and internal almonds. The epicarp is formed by resistant fibers, mainly in manufacturing brushes and carpets. The mesocarp contains 20%-25% starch and is used in foods such as flour and a drink similar to chocolate. The endocarp is a raw material for the

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manufacture of insulators and the production of different materials such as methanol, acetic acid, tar, and coal. The internal almonds are inside the endocarp, and more than 60% of the almond is oil. The residual pie, after oil extraction, is usually applied for final compost and supplementary animal feed [13-18].

The fatty acid profile of babassu oil has been evaluated by different researchers[19-23], demonstrating the high content of acid lauric. The oil from babassu coconut is rich in this fatty acid, with a concentration above 40% [24,25]. The lauric fats, like babassu oil, are essential in the fats and oils industry. They are resistant to non-enzymatic oxidation, and unlike other saturated fats, they show low melting temperatures. So, depending on their physical properties and resistance to oxidation, the food industry uses them to prepare special fats for ice cream, margarine, and cocoa butter substitutes. They are also used in the cosmetics industry.

Coconuts and palm kernel oils are the principal sources of lauric fats. These fats' primary sources in Brazil are coconut, palm kernel, and babassu. In the extraction of babassu coconut oil, firstly it is used a cold pressing procedure to reduce the oil content in the almond pie up to 12-15%. Then, the dry residue is extracted by solvent, leaving a residual oil content in the solid phase lesser than 1%. The presence of lipase enzymes in vegetable oils is the catalyst for enzymatic hydrolysis and, then, rancor taste, mainly when the unsaturated fatty acids profile is high, which is not in this case. In Brazil, babassu oil is used almost exclusively in cleaning and personal-care products. Its use in food technology is still secondary, appearing only in margarine production. There is, however, a rising interest in developing new markets for the use of babassu. Nevertheless, its potential for providing other industrial products remains unexploited due to the lack of scale, adequate production structure, and deep scientific investigation [26-30].

In present times where global warming poses a severe threat, alternate sources for attending ever increasing energy demands are strongly necessary.

Green fuels, non-dependent on non-sustainable wellsprings such as biodiesel and bioethanol, are promising, and efforts have been made to develop and optimize technology production and blends. Biodiesel production is one such method that is an excellent alternative source of energy. The principal concern about using edible vegetable oils for biodiesel production is that they might add problems in terms of already occurring food shortages and price levels. The solution should be on diverse sources of biodiesel production as non-edible oil and fats and waste oil from food processing. Compared to petrodiesels, biodiesel has poor low-temperature properties, low oxidative stability, high density, and lower compressibility. Alternative vegetable oils such as babassu is a non-edible oil with low cost. It contains significant amounts of shorter chain saturated acids into triglyceride, gathers low free fatty acid value, and shows a higher cetane number with better oxidative stability.

Thermodynamic properties are the most critical parameters required in equipment design and processes. Physico-chemical properties of biodiesel or petrodiesel blends, such as density, ultrasonic velocity, and compressibility, depend on the dissimilar chemical composition of the fuels. These magnitudes influence combustion, quality of gas emission, and injection timing [31-34]. Density is one of the most crucial properties of the fuel due to pumps and injectors must deliver an amount of finely adjusted fuel precisely for adequate internal combustion [35]. Compressibility defines spray characteristics upon injection. Since biodiesel's compressibility is lower than petrodiesel, the injection timing can cause different gas emissions performances [36]. The fuel injection process occurs almost in the isentropic condition in the combustion device. Then, isentropic compressibility is the most appropriate magnitude to estimate the fuel injection timing. The experimental procedure to obtain direct isentropic compressibility measurements is acoustic. Ultrasonic velocity measurements are simple experimental procedures with accurate

results and wide acceptance for any blends [37-40].

Concerning the physical properties related to oils and fats industry equipment design [41-46], we present the temperature dependence (288.15-323.15 K) of density and ultrasonic velocity for babassu oil (*Orbignya speciosa*). We fitted the temperature-dependent polynomials from the experimental data, and the corresponding parameters were gathered. The current process design is strongly computer-oriented, so we considered how accurately different prediction methods work.

It is possible to find many chemicals in vegetable oils, such as free fatty acids, phenols, peroxide, monoacylglycerols, diacylglycerols, flavonoid polyphenols, polycyclic aromatic hydrocarbons, and many other complex substances. However, the triacylglycerol molecule is often considered the main chemical structure of vegetable oils. Therefore, to develop calculations using mathematical models, we consider a surrogate oil simulating that a single triglyceride molecule can adequately describe babassu oil with a fatty acid content proportional to its analytic composition (Table 1).

The Agrawal-Thodos (AT) equation [47] for density and the Collision Factor Theory (CFT) procedure [48] for ultrasonic velocity were selected for prediction, attending to ease of use and range of application. A good response at the studied conditions was observed, despite geometrical simplifications into triglyceride molecules and using estimated critical magnitudes by Joback's molecular group contribution approach [49]. An exhaustive comparison was made with disposable open literature thermodynamic data, showing an essential dispersion of data, and highlighting the quality of the experimental data presented in this work.

Materials and Methods

Materials and Measurement Devices

The oil, supplied by usual local providers (Cocal Maranhense, Itapecuru-Mirim, Maranhão-Brazil), was stored in sunlight-protected form and constant humidity and temperature in our laboratory. The provider analyzed it to determine its fatty acid compositions and the standard applied procedure described earlier [50]. The average molar mass was computed as follows:

$$M_{oil} = 3 \cdot \left(\sum_{i=1}^{N} x_i \cdot M_i \right) + 2 \cdot M_{CH_2} + M_{CH}$$
(1)

being x_i molar fraction and M_i the molar mass of each fatty acid without a proton, N the number of fatty acids found by analysis and M_{CH2} and M_{CH} are the molar mass contributions of glycerin molecule residue. The variation in the composition

Table 1. Molar mass and fatty acids composition of babassu oil.

Compound	Molar Mass (gmol ⁻¹)	Fatty Acids Composition (mass%)
Babassu oil	676.278	Caprylic (8:0) 4.74
(Orbignya speciosa)		Capric (10:0) 5.17
		Lauric (12:0) 50.46
		Myristic (14:0) 13.91
		Palmitic (16:0) 9.70
		Stearic (18:0) 8.94
		Oleic (18:1) 5.16
		Linoleic (18:2) 1.92

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between different samples mainly affects mono and polyunsaturated fatty acids, the change in molar mass being lower than ± 1 g mol⁻¹. Table 1 shows the molar mass and fatty acids composition of babassu oil. The obtained results are similar to those observed in the disposable open literature [21,51].

Densities and ultrasonic velocities were measured by an Anton Paar DSA-5000M vibrational tube densimeter and sound analyzer, with a resolution of 10^{-5} gcm⁻³ and 1 ms⁻¹. Apparatus calibration was performed periodically by vendor instructions using Millipore quality water and ambient air at each temperature. Accuracy in the measurement temperature was better than $\pm 10^{-2}$ K. The obtained measurements were coincident, in general terms, with earlier published data (Table 2) [51-79].

Data Treatment

The measured physical properties were correlated as a function of temperature using the Equation 2:

$$P = \sum_{i=0}^{N} A_i T^i$$
⁽²⁾

where P is density (gcm^{-3}) or ultrasonic velocity (ms^{-1}) , T is the absolute temperature in Kelvin, and A_i is fitting parameters. N is the extension of the mathematical series optimized using the Bevington test. The unweighted least squared method obtained the fitting parameters by applying a fitting Marquardt algorithm. The root means square deviations were computed using the Equation 3, where z is the property's value, and nDAT is the number of experimental data.

$$\sigma = \left(\frac{\sum_{i=1}^{n_{DAT}} (z_{exp} - z_{pred})^2}{n_{DAT}}\right)^{1/2}$$
(3)

Fitting parameters of the Equation 2 and the root mean square deviations, attending to Equation 3, are gathered in Table 3. Figures 1 and 2 present the temperature trend of density,

Table 2. Expe	erimental/literature	density and	d ultrasonic	velocity for	r babassu oi	il at 298.15 K.

Compound		ρ/(gcm ⁻³)	u/(ms	s ⁻¹)
	Exptl.	Lit.	Exptl.	Lit.
Babassu oil	0.91886	0.9140 [53]	1411.35	NA
(Orbignya speciosa)		0.9047 [54]		
		0.923 [55]		
		0.920 [56]		
		0.9151 [57]		
		0.929 [61]		
		0.9202-0.9204 [62]		
		0.9169 [63]		
		0.956 [66]		
		0.914-0.917 [67]		
		0.923 [68]		
		0.9137-0.9171 [70]		
		0.9122-0.9152 [78]		

NA: Non Available.

ultrasonic velocity, and isentropic compressibility, computed by means Newton-Laplace equation from density and ultrasonic velocity experimental measurements. These figures show a progressive diminution of density and ultrasonic velocity when the temperature rises due to a sharp diminution of packing efficiency of the enclosed macromolecules into the bulk phase. Both combined effects, higher molecular kinetics by rising temperatures and steric hindrance of heavy molecular structures, produce a growing difficulty in packing molecules. Figure 1B shows a zoom of density trend into Figure 1A around the 288.15-298.15 K range, in which a higher number of earlier literature data were found. Figure 2 presents the inverse relation of isentropic compressibility and density and ultrasonic velocity by Laplace-Newton equation, showing an inverse relationship with temperature.

Results and Discussion

Isobaric Compressibility

A frequently applied derived quantity is the temperature dependence of volumetric properties, which is expressed as isobaric expansibility or thermal expansion coefficient (α), obtained from accurate isobaric experimental data of volumetric trend at a specific range of temperature. The data reported in the literature usually show only values of the thermal expansion coefficients of pure compounds and their mixtures, showing the

relative changes in density, calculated by $(-\Delta \rho / \rho)$ as a function of temperature, and assuming that a remains constant over the temperature range. In the case of pure chemicals, these oils can be computed by the Equation 4:

$$\alpha = -\left(\frac{\partial \ln \rho}{\partial T}\right)_{P,x} \tag{4}$$

taking into account the strong temperature dependence of density (Figure 1A). Attending to this relation, Figure 3 shows the isobaric expansibility of babassu (*Orbignya speciosa*) oil. Only two previously published collections of isobaric expansibilities were found. As observed, our experimental values gather decreasing negative values for rising temperatures, showing a similar trend to Barañano and colleagues (2019) [52] but different from those data obtained from Ceriani and colleagues (2008) [73].

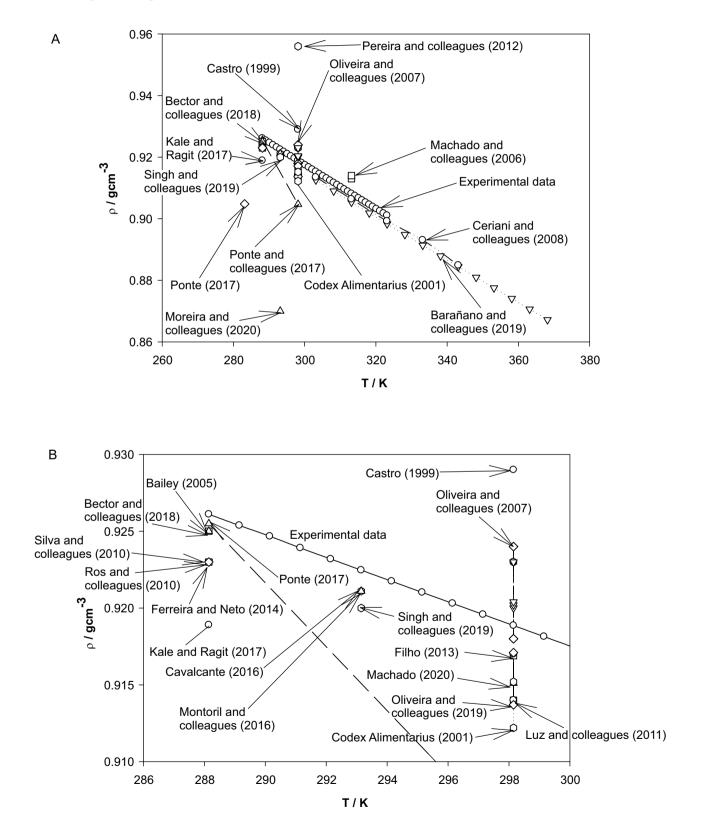
Critical Point Prediction

The basis for the design and theoretical estimation work into chemical processes is a collection of data related to the thermodynamic trend of the compounds evolved. However, many times is not possible to find open literature with reasonable values of properties compounds. So, theoretical estimation methods are generally employed. Group-contribution methods have been used, and in the last few years, a vast collection

Table 3. Fitting parameters of Equation 2 for 288.15-323.15 K and the corresponding root mean square deviations (Equation 3).

ρ/(gcm ⁻³)							
Compound	A0	A1	A2	A3	σ		
Babassu oil	1.257755E+00	-1.853207E-03	3.410485E-06	-3.377978E-09	5.203964E-06		
	u/(ms ⁻¹)						
Compound	A0	A1	A2	A3	σ		
Babassu oil	1285.76	8.971444	-0.044655	53.586930E-06	6.062544E-02]		

Figure 1. (A) Density values, (B) zoom of density values figure, and (C) ultrasonic velocity for babassu oil at a range of temperature (288.15-323.15 K).



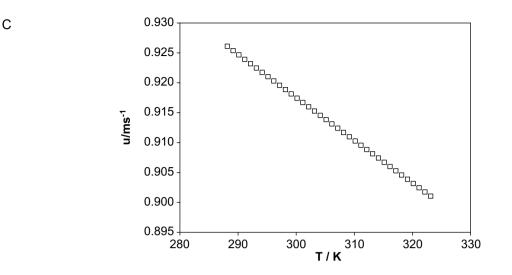


Figure 2. Isentropic compressibility (TPa⁻¹) for babassu oil at a range of temperature (288.15-323.15 K).

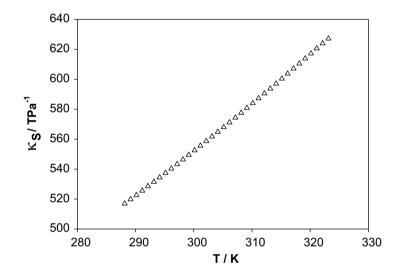
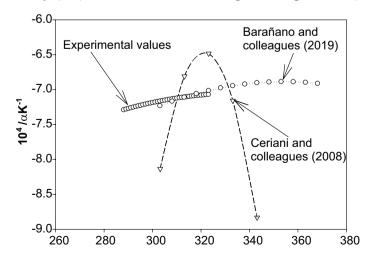


Figure 3. Isobaric expansibility (K⁻¹) for babassu oil at a range of temperature (288.15-323.15 K).



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of methods have been proposed [49,80]. In these methods, the property of a compound is a function of different structurally-dependent parameters, which are determined by summing the frequency of each molecular group enclosed into the molecule and its particular contribution. Marrero-Gani [81] developed an advanced group contribution method for critical point estimation of covalent molecules based on the UNIFAC molecular group conception. The application of three different sets of functional groups, one for a first-order approximation and the other two sets for refining the estimations for complex compounds, providing additional structural information, has led to an advanced and robust group-contribution method for the estimation of acute thermodynamic properties. It overcomes the limitation of traditional group contribution models that cannot adequately distinguish isomers or resonance structures. This method was applied to obtain the critical point of the surrogate triglyceride of babassu oil for use in density estimation. Compared with database information on different oils, the observed deviations are negligible. Table 4 gathers the computed critical point for the studied oil.

Prediction of Densities

The physical property packages used in chemical simulators typically rely on generalized equations for predicting properties as a function of temperature, and pressure, among others. Despite the success of developing several procedures of density estimation for pure compounds or mixtures, only a few of them may be of the actual application for fats and oils. One proposed correlation that holds promise for application to oils is the Agrawal-Thodos (AT) (Equation 5) [47]:

$$\rho = 1 + k \cdot \left(1 - \frac{T}{T_{\rm C}}\right)^{\beta} \tag{5}$$

where T and T_c are work temperature and critical temperature, respectively. This relationship requires that parameters k and β be established to define the density of a saturated liquid for temperatures extending up to the critical point of this fluid. The k and β parameters were proposed in the original paper. Initially, this equation was developed for simple covalent cryogenic fluids. So, this model should be applied because babassu oil is a surrogate oil composed of a unique triglyceride molecule (Table 1). Table 5 presents the deviations of this model gathered at the studied temperature range.

Prediction of Ultrasonic Velocities

There has been an increasing interest in ultrasound low/high-frequency techniques for industrial engineering in the last few decades. Then, ultrasonic velocity has been systematically measured. However. the literature needs to be more comprehensive regarding the range of work conditions or complex mixtures such as natural fats and oils. Moreover, the data about substances' ultrasonic measurements are insufficient in databases. The DIPPR database (DIPPR, Design Institute for Physical Properties) is an extensive physical data source on chemical compounds. It gathers rigorously evaluated results of experimental measurements and high-accuracy correlations for computation as functions of the temperature at saturated conditions. However, despite this extensive compilation of high-quality data,

Table 4. Critical properties for surrogate triglyceride molecule of babassu oil by Marrero-Gani group contribution method [81].

Compound	Pc (bar)	Tc (K)	Vc (cm ³ mol ⁻¹)
Babassu oil (Orbignya speciosa)	8.139	965.962	2436.212

Table 5. Root mean square deviations (gcm⁻³) for AT density prediction for babassu oil at the studied temperature range.

Compound	k	β	σ
Babassu oil (Orbignya phalerata Mart.)	-10.80012E-3	-5.511988E+0	3.663758E-4

ultrasonic velocity needs to be gathered among the variety of thermodynamic magnitudes enclosed in this database. In the last few years, a necessity for ultrasonic data was noticed in the open literature, mainly for complex mixtures and biological nature compounds. The Collision Factor Theory (CFT) [48] computes the isentropic compressibility using collision factors parameters, which are a function of temperature in pure solvent or mixture. The Equation 6 could express this model:

$$\kappa_{\rm S} = \rho^{-1} \cdot \left(\frac{\mathbf{u}_{\infty} \cdot \mathbf{S} \cdot \mathbf{B}}{\rm V} \right)^{-2} \tag{6}$$

where u_{∞} is 1600 m/s, S is the collision factor, B is the actual molecule volume per mole, and V is the molar volume. The collision factors (S) of the pure solvents (the fatty acids as explained in Table 1) used in the CFT calculations were estimated by using the ultrasonic velocities of each fatty acid using Wada's group contribution method previously proposed by Freitas and colleagues 2013) [82]. The characteristic molar volumes were calculated by the group contribution method of Bondi. The experimental data for the babassu oil studied here were compared with the obtained values as surrogate oil by CFT procedure. Table 6 gathered the deviation for ultrasonic velocity estimation by the CFT method.

Comparison with Open Literature Data

In the last decades, it has boosted the use of natural oils, different from those usually applied for vast food stock production, searching for low cost, green procedures, and circularity in new business opportunities. Despite the commercial interest of these oils, the open scientific literature contains few physicochemical data, which are essential for the design of equipment and processes. Valuable collections of accurate data and information as a function of temperature into a wide range are scarce for complex fluids such as oils. It is often not easy to identify the final quality of the data because the purification process of the solvents, the device calibration, or the accuracy of the measurements needs to be commented upon in original published papers. Only a few collections of density data for the studied oil are disposable, as earlier commented [51-79]. As expected, information related to ultrasonic measurements is mainly more dispersed and scarce. As far as we know, no disposable data for this oil are available for ultrasonic velocity. Figures 1a and 1b show a comparison between our experimental measurements and that data from open literature as a function of temperature. Relative agreement is verified for a few collections of density data [52, 60, 65, 69, 77] observed substantial deviations for many works containing data on this oil.

Table 6. Collision factor, molecular volume (cm3), and percentage error for CFT ultrasonic velocity prediction for babassu oil at 298.15K.

Compound	S (cm ⁻³)	В	% Error
Babassu oil (Orbignya phalerata Mart.)	1.0850	218.88	7.602

Conclusions

Babassu is one of the Brazilian palm trees with greater significance in terms of ecology, society, and economic relevance. The fatty acid profile of babassu oil has been evaluated by different researchers, demonstrating the high content of acid lauric, being these lauric fats of high importance for the fats/oils industry with core applications in the cosmetic, food industry, and confectionery. However, despite their interest and rising new markets for the use of babassu, its potential for providing other industrial products remains unexploited due to the lack of mainly adequate scientific characterization and physico-chemical investigation, as explained earlier [51-79].

This work gathers an extensive collection of density and ultrasonic velocity at the temperature range 288.15-323.15 K. Prediction methods for density and ultrasonic velocity worked well in terms of accuracy, despite introduced approximations and group contribution procedures used to analyze critical points of evolved fatty acids. A broad comparison was made with disposable open literature thermodynamic data, showing a vital dispersion of values. As previously commented, disposable open literature offers only a few collections of density data for babassu oil and invalid previously measured data for ultrasonic velocity. Although, in general terms, a relative agreement is observed for a few collections of density data [52, 60, 65, 69, 77] observed solid deviations for many works containing data on this oil, highlighting the quality of the experimental data presented in this work.

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Study of the Photophysical Properties of Carbon Dots Derived from Banana Peels From Different Cities Used to Produce Ink and Film Fluorescence

Livia E. da Silva ^{1*}, Orlando Lucas de L. Calado¹, Cintya D. A. do E. S. Barbosa¹

¹Institute of Chemistry and Biotechnology, Federal University of Alagoas, Campus A.C. Simões, Tabuleiro dos Martins; Maceió, Alagoas, Brazil

In this study, carbon dots (CDs) were synthesized via microwave, using precursor banana peel extract from different cities (Maceió and Aracaju) to evaluate their optical and structural properties. In addition, the volumes of the extract were varied for laboratory scale-up tests. DLS analyses showed that the most significant size frequencies for all CDs were less than 10 nm. UV-Vis and FTIR absorption spectra indicated the presence of aromatic groups and heteroatoms. In addition, the CDs showed excitation wavelength-dependent emission, with maximum intensities at 457 nm. The results indicate the high robustness of the method and its potential application in the production of fluorescent films and inks.

Keywords: Nanoparticle. Carbon Dots. Green Synthesis. Reproducibility.

Introduction

Carbon dots (CDs) are luminescent carbon nanoparticles that exhibit sizes smaller than 10 nm and physicochemical properties, good dispersion in water, biocompatibility, photostability, low toxicity, and vast emission range in the visible region [1].Morphologically, CDs are formed by a core containing functional groups on the surface, composed of sp² and sp³ hybridized carbons, respectively. In turn, the literature suggests that the groups present on the surface of these nanoparticles are responsible for their optical properties, such as excitation wavelength-dependent/independent emission [2]. Therefore, many efforts have been employed to synthesize CDs due to their various applications, which stand out in their use in optoelectronic devices and invisible inks in anticounterfeiting processes [3]. However, after its accidental discovery by Xu and colleagues in 2004, the methods for obtaining CDs were limited to onerous processes, referred to as laser ablation and electrochemical oxidation, in addition to

using expensive materials [4]. However, simpler processes have been adopted since 2010 to reduce environmental impacts and facilitate the synthetic routes of CDs, such as using precursors from renewable sources [5].

In 2020, researchers synthesized carbon dots by hydrothermal method using banana peels and obtained CDs with emissions in the blue, producing fluorescent ink [6]. However, the work has a long synthesis time and needs to present reproducibility tests since the composition of the residue may change due to different species and climatic conditions. In this regard, a study conducted in 2015 by Zhang and colleagues used pollens from different flowers (colza, camellia, and lotus) to analyze the reproducible nature of CDs through their optical and structural properties [7]. Meiling and colleagues (2016) conducted a similar study using different types of starches as precursors [8]. Both works have highlighted the importance of reproducibility testing to ensure that the properties of carbon dots remain similar, even if the same biomass is from different species and/or localities.

In this study, we extracted banana peels from the cities of Maceió and Aracaju to prepare CDs with different volumes via microwave. This process ensured the material's reproducibility and scaling to be evaluated through photophysical properties and applied as inks and fluorescent films.

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Materials and Methods

Materials

The banana peels were obtained from supermarkets in Maceió and Aracaju's cities. The solution of sodium hydroxide (NaOH) 5 mol/L was prepared in the laboratory, and distillate water was used during synthesis, purification, and characterization.

Synthesis and Purification of Carbon Dots (CDs) (Figure 1)

Banana peels from the city of Maceió were triturated in a food processor with 1 L of distilled water to prepare 25 mL, 50 mL, and 100 mL samples. All were filtered using a plastic sieve to remove residues, and every sample was added 1 mL, 2 mL, and 4 mL of sodium hydroxide, respectively. The extracts were then submitted in microwave reaction for 2 mins at 630 W. The resultants supernatants were centrifuged at 13000 rpm for 10 min and filtered on 0.22 μ m membranes to remove larger particles. The CDS procured from the 25 mL (CDS-M25), 50 mL (CDS-M50), and 100 mL (CDS-M100) volumes were stored in a refrigerator. The method was reproduced for banana peels from the city of Aracaju, named CDS-A25, CDS-A50, and CDS-A100, for 25 mL, 50 mL, and 100 mL, respectively.

Preparation of Fluorescent Film

150 mg of PVA [Poly(polyvinyl alcohol)] were dissolved in 5 mL of water under stirring at 85° C on the heating plate for 3 min. After cooling, 60 μ L of glycerol (plasticizing agent) was added to the solution. Then, 100 μ L of the CDs were added to the mixture, which was transferred to the plastic petri dish (35mm x 10mm). Finally, the film solution remained in the oven at 50 °C for 30 h for drying. The method was applied separately for each CD.

Preparation of Fluorescent Ink

The fluorescent inks were prepared using the solutions of the CDs (0.01 g/mL). The solutions were employed in the brush pen for writing on commercial filter paper, which was subjected to UV light under 360 nm radiation to visualize the words.

Characterizations Techniques

The quantity of light absorbed by the samples, diluted at 25µL/2mL, was measured by UV-VIS spectroscopy. In addition, the dynamic light scattering (DLS) technique was used to evaluate the dimensions of the nanoparticles in suspension. Additionally, in order to characterize the functional and bonding groups present in the CDs, 10µL of each solution were dripped separately onto approximately 50 mg of KBr and subjected to heating in the oven (around 90 °C, for 4h), obtaining the dry samples in which tablets were prepared for the acquisition of Fourier Transform Infrared Spectroscopy (FTIR) observations. Finally, the photostability and fluorescence of the CDs were analyzed using a spectrofluorometer with the samples diluted to 25µL/2mL. For this study, the photostability was analyzed for 60 min, and the emission spectra obtained were excited in the 300 nm to 440 nm wavelength.

Results and Discussion

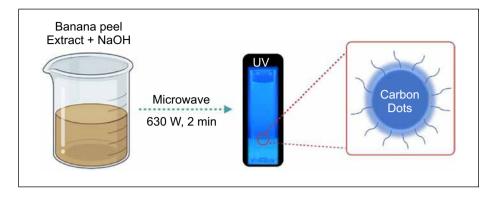
Figure 2A/B shows the dynamic light scattering (DLS) histograms of CDS-M25 and CDS-A25, in which the nanoparticles of CDS-M25 are mainly distributed in the range of 3.8 - 9.0 nm with an average diameter of 5.33 ± 0.12 nm. The distribution of CDS-A25 is in the same range, but its average diameter is 6.22 ± 0.22 nm. Both sizes are similar to works in the literature that used banana peel as precursor material [6,9].

The chemical compositions of the CDS from the different cities were characterized by FTIR spectra (Figure 3A). Broadbands are visualized around 3450 cm⁻¹, assigned to O-H/N-H stretching vibrations,

CDS-A25

6.22 + 0.22 nm

9.6 11.2 12.8 14.4 16.0



35

30

25

20

15

10

5

0

3.2

4.8

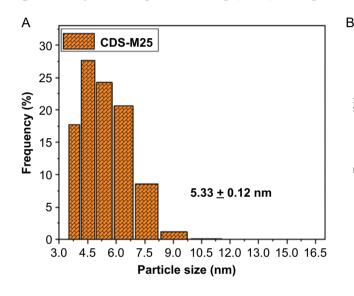
6.4

8.0

Frequency (%)

Figure 1. Schematic representation of carbon dots synthesis.

Figure 2. Dynamic light scattering (DLS) histogram of carbon dots.



and C=O and aromatic ring (C=C) groups are identified at 1646 cm⁻¹ and 1585 cm⁻¹, respectively, indicating the sp³ and sp² hybridizations of the CDS. C-N, C-O bonds, and S=O vibrations are found at 1340 cm⁻¹, 1085 cm⁻¹, and 1043 cm⁻¹, respectively, revealing the presence of nitrogen, oxygen, and sulfur, which may have been derived from the amino acid tryptophan, vitamin B6 and B2 found in the precursor [6,9,10]. Oxygen on the surface groups favors the hydrophilic behavior of these nanoparticles, facilitating their applications due to high dispersion in water. Figure 3B shows the UV-VIS absorption plots of the CDS obtained from both cities (Maceió and Aracaju), with absorption peaks centered at 266 nm and 327 nm. The highest energy

peak, visualized around 266 nm, is characteristic of the π - π * bond of C=C associated with the aromatic ring (sp2). The second peak, at around 327 nm, is attributed to the n - π * transition referring to groups present on the surface, convenient of the C=O and C=N of sp³ carbon [10].

Particle size (nm)

The photoluminescence of CDS-M25 and CDS-A25 was analyzed at different excitation wavelengths ranging from 300 to 440 nm. The fluorescence spectra demonstrate that the carbon dots' emission depends on the excitation wavelength and most of the works reported in the literature [9] (Figure 4A/C). Upon increasing the excitation wavelength, the emission is shifted from blue to green due to the different energy levels on

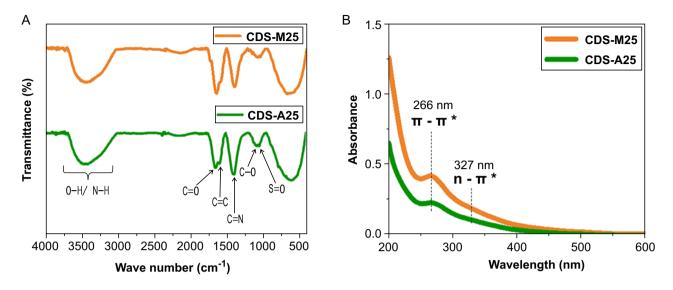
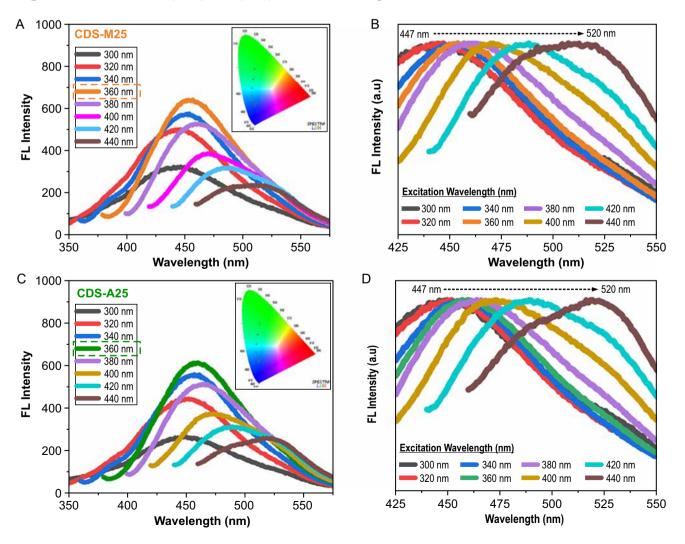


Figure 3. FTIR (A) and UV-vis (B) spectra of carbon dots.

Figure 4. Fluorescence (A,C) and (B,D) emission shift spectra of carbon dots.



the surface of the CDs (Figure 4 B/D). In addition, the CDs showed excellent photostability. Scalable synthesis was an essential and rarely-reported aspect in the literature approached in this study. Using the banana peel extract from different cities as a precursor, we prepared six carbon dots by gradually increasing the reaction volume, de 25, 50, and 100 mL, which were denoted CDS-M25, CDS-M50, and CDS-M100 and CDS-A25, CDS-A50 and CDS-A100 for the cities of Maceió and Aracaju, respectively. Under natural light and 360 nm UV light, it is possible to visualize no difference in the coloration and fluorescence of the nanoparticles, The absorption plots of the CDs exhibited peaks at around 266 nm and 327 nm, independent of the synthesized volume (Figure 5 A/B). Also, they demonstrated emissions with maximum intensities located at 457 nm when excited at 360 nm Figure 5C). These results indicate that obtaining carbon dots from banana peels via microwave promotes a sustainable and reproducible method for CD fabrication. The strong fluorescence of carbon dots in the visible region and their unique properties, such as biocompatibility, photostability, and good dispersion in water, make these nanoparticles excellent candidates for fluorescent ink application [3]. For this study, the aqueous solutions of CDs were employed in sketch pens for writing on commercial filter papers. Under daylight, the inks are colorless and cannot identify the words. However, under UV light with excitation at 360 nm, the words are visualized, and even after months of storage under ambient conditions, the fluorescence on the papers remains constant (Figure 6A). Complementarily, the inks have a good potential to be used in covert and anti-counterfeiting communications since they have clear, long-lasting colorations and do not cause environmental damage. They can be great alternatives to traditional inks. The solid-state carbon dots emission usually suffers self-quenching due to the aggregation of the CDS. The particles close to the CDS are at minimal distances from each other, which causes the energy transfer between them to be excessive, leading to

a decrease in the fluorescence of the carbon dots [11]. Some organic matrices are employed to avoid these effects and preserve the optical properties of solid CDS because their chains form obstacles and increase the distance between the particles adjacent to the CDS. In this work, the CDs are incorporated into PVA, which has excellent filmmaking properties, to maximize its applicability and analyze possible optical similarities between the CDS from the cities of Maceió and Aracaju. Figure 6B presents that the films are highly transparent under natural light, while under UV light, under excitation of 360 nm, they show bright blue fluorescence. All other carbon dots exhibited the same profile as CDs-M25 as luminescent ink and film.

Since this is a study rarely reported in the literature, this work is important because it allows the scale-up of CDs using a unique residue from different localities. Furthermore, it is interesting because it ensures that the optical properties of these nanoparticles derived from biomass will not be significantly modified and can range their localities and applications. In addition, the films produced here can minimize the problems associated with the aggregation effect generally characteristic of these solid-state nanoparticles.

Conclusion

CDs-derived banana peel extract from different cities (Maceió and Aracaju) was successfully synthesized by a simple microwave method, with excellent luminescence in the blue. Finally, all CDs exhibited an expressive similarity of their photophysical properties and promising application as ink and film fluorescent.

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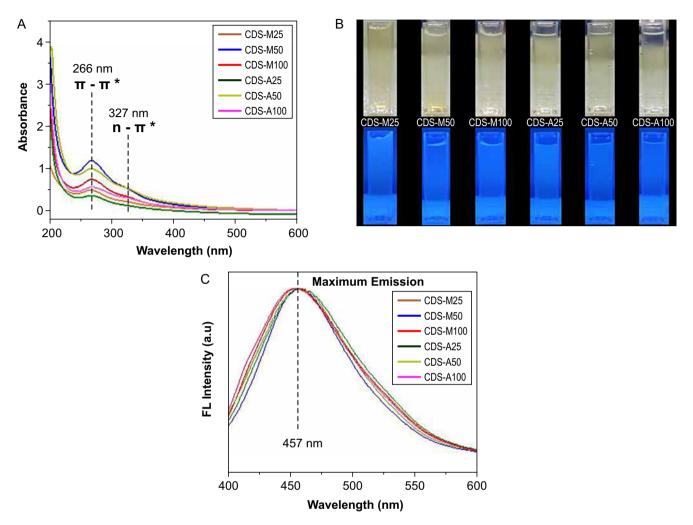
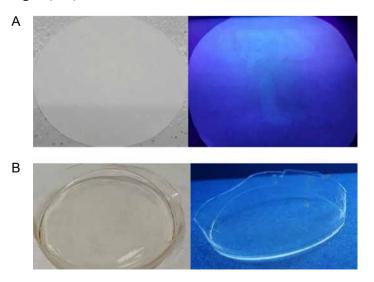


Figure 6. Photos on paper of CDS-M25 under sunlight (left) and UV irradiation (A) and (B) film fluorescent of CDS-M25 under sunlight (left) and UV irradiation.



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Theobroma Cacao: An Evaluation of Enzyme Treatment with Pectin in the Pulping of Cocoa

Pedro Henrique Cruz de Souza^{1*}, Gabriele de Abreu Barreto¹, Ingrid Lessa Leal²,

Letícia de Alencar Pereira Rodrigues¹

¹SENAI CIMATEC University Center, SENAI Institute for Advanced Health Systems Innovation (ISI SAS); ²SENAI CIMATEC University Center, Food & Beverage Department; Salvador, Bahia Brazil

Cocoa (*Theobroma cacao L.*) in Brazil has a notable social and economic influence. However, when processed, cocoa generates byproducts that are discarded, including its pulp. This study aimed to evaluate the influence of the enzymatic treatment with pectinase on the physical-chemical properties of the extracted cocoa pulp. Untreated pulps obtained a lower yield (T1: 1.40% and T2: 4.4%) than those receiving treatment (T3: 15.62% and T4: 19.47%). Comparing the processes, the pH values remained close between 3.49 to 3.41, the soluble solids content between 16 and 19 °Brix and the colorimetric analysis reporting L* 27.22 to 27.49; a* 11.35 to 11.59 and b* 0.26 to 0.51. The results demonstrated that the enzymatic treatment is a viable and expressive alternative in the pulping of cocoa beans, contributing mainly to the final or intermediate product desired yield. Keywords: Cocoa Pulp. Pectinase. Agro-Industrial Residue.

Introduction

Due to its high volume, cocoa pulp became an agro-industrial residue, and the search for its applicability has been growing considerably [1]. From some studies, we observed the use of cocoa pulp for several products, such as cocoa jellies, fine and fermented beverages, alcohol, vinegar, yogurts, ice cream, juices, and even pulp in its natural form [2]. Another considerable residue in the cocoa industry is the shell of this fruit since it makes up approximately 70% of it [3].

Although it is considered a waste product, cocoa pulp is a raw material with great potential for application in the industry [1]. Its composition is formed by water (approximately 85%), sugar (12.5%), and other compounds in small quantities, such as proteins and citric acid [4]. The chemical composition of cocoa is directly related to numerous factors, and the main one is the type of cocoa.

Cocoa (*Theobroma cacao L*.) is a tropical species spontaneously found in the humid lowland

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forests of South and Central America [5]. It is one of the cultures capable of keeping the man in the countryside, thus having high social and economic importance in several tropical regions worldwide [6]. However, a series of byproducts need to be generated to obtain the final product to be commercialized, among them cocoa pulp and honey, which are still little used for commerce, being generally consumed *in natura* due to their perishability [7].

Knowing the characteristics of the pulp varieties currently planted in Brazil is necessary to allocate part of the pulp for producing new products. Cocoa pulp is characterized by the presence of fibers, pectin, and insoluble fibers, giving the product high viscosity with the pasty aspect of non-Newtonian fluid. These characteristics are ideal for producing alcoholic beverages such as wine and some foods such as jams, marmalades, and syrup [8]. Owing to the substantial presence of pectin, which plays an essential role in food projects due to its ability to modulate the response of humans to inhibitory effects on lipid intake and absorption in food [9], pectinase aims to perform pectin hydrolysis and clarification of fruit juices by dehydration. Pectinases are frequently used in the fruit juice industry and winemaking, with the filamentous fungus Aspergillus niger as the primary source [9]. Adding pectinases in juice processing reduces

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viscosity and increases the number of soluble solids in the final product [9].

Materials and Methods

Sample Selection

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The cocoa (*Theobroma cacao L*.) samples were of a foreign variety and were purchased in Salvador, Bahia, Brazil. They were kept at room temperature until the moment of processing.

Pulp Extraction

For extracting the pulp, the fully ripe pulps were first selected. While still in the shell, they were sanitized with a chlorine solution (100 ppm) for 15 minutes. After rinsing, the cocoa samples were opened, and the pulp was removed. In a beaker, 25g of pulp, 125μ L of Pectinex® Ultra Tropical enzyme (Novozymes) (mixture of pectinases, cellulases, hemicellulases, and beta-glucanases), and 50mL of water were homogenized, and the enzyme action time was counted (Figure 1). For this assay, two blanks were evaluated (T1 and T2).

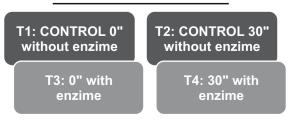
After the system-resting period, the yield was calculated, and the physico-chemical analyses were performed (in duplicate).

<u>Yield</u>

The yield consisted of the pulp released from the seeds and was calculated using the masses obtained

Figure 1. Enzymatic treatment conditions for cocoa pulp at 0 and 30 minutes.

CONDITIONS OF TREATMENT



according to Equation 1, in which SW - starting weight and FW - final weight.

Equation 1

Yield (%) =
$$\left[\frac{SW(g) - FW(g)}{SW(g)}\right] * 100$$
 (1)

pH Determination

The pH was measured with a bench pHmenter, previously calibrated according to the manufacturer's standards, in which 10mL of the sample were analyzed following the method described by Adolfo Lutz [10].

Determination of Total Titratable Acidity

Based on the method described by Adolfo Lutz, 10mL of the sample was set aside and titrated with an aqueous solution of NaOH (0.1M). The result was expressed as % (v/v) [10].

Soluble Solids Determination

The Adolfo Lutz method was used, and the total soluble solids content was determined using a portable digital refractometer (Portable Digital Refractometer - BZW65). Appropriate calibrations of the refractometer were made using water at 20°C according to the manufacturer's instructions. An aliquot of the sample was added to the refractometer prism, and the scale read directly in Brix [10].

Colorimetric Analysis

A colorimeter (CR 10, Konica Minolta) was used to analyze the color of the cocoa pulp, selecting the CIELAB color space and using 3 repetitions per plate. In this color system, L* represents brightness (L*=0 - black and L*=100 - white), and a* and b* are the color coordinates responsible for chromaticity: (+a* = red and - a* is green, +b* is yellow and -b* is blue) [11].

Results and Discussion

The enzyme used to make the extraction of cocoa pulp aims to perform the hydrolysis of pectin, bringing benefits such as increased yield and clarification of the pulp. When comparing the physical-chemical analysis of the fruit pulp in question (Table 1) with the literature values, it was observed that the average pH of the sample had a value close to that found by Santos [8] in his test of characterization of cocoa honey for the production of jelly without added sugar.

The titratable acidity of the cocoa pulp had a value close to that of Silva and colleagues [12], who observed 1.16% in their analyses. All the results found after the analyses follow what is established by the current Brazilian legislation [13]. The soluble solids content meets the content reported in cocoa pulp by Pettipher [14], whose soluble solids concentrations ranged between 16.55 and 19.90 °Brix. When comparing samples T1 and T2, there was an increase in yield from 1.401% to 4.413%. However, the other parameters do not indicate expressive changes; when comparing T3 and T4, there is also an increase in yield of more than 4%. Regarding yield, sample T3 (with treatment at 0 minutes) compared to T1 (no treatment at 0 minutes) yield was about 11 times higher when compared to T2 (no treatment at 30 minutes) to T4 (with treatment at 30 minutes) yield that increased about 4 times. However, pH, titratable acidity, Brix, and density, remained close. Table 2 presents the colorimetric analysis parameters of the cocoa pulp after enzymatic treatment. The L* parameter expresses the luminosity or clarity of the sample and varies from 0 to 100, so the closer to 100, the lighter the sample, and the further away, the darker. More positive a* values indicate a tendency towards red color and more negative towards green color. The more positive b* values express a higher yellow intensity, and the more negative ones have a higher blue intensity.

Therefore, the analyzed samples show higher turbidity, average L* at 27, with a reddish (average a* of 11.5) yellowish (average b* 0.3) tendency. The present study's results indicate no expressive variation in the parameters of colorimetric analysis for samples with and without enzymatic treatment.

Conclusion

We demonstrated in this study that the yield in diluted pulp submitted to enzymatic treatment was 11 times higher when compared to the treatment without enzyme. It shows that the application of the pectinex ultra tropical enzymatic complex is a good alternative for pulping cocoa seeds since this diluted pulp can serve as a basis for the elaboration of cocoa nectar, with greater use of this fruit, generating labor savings and without specific utensils/equipment. However, further studies are needed to evaluate other dosages and combinations with other enzymes and the application of other effects, such as temperature and agitation.

Table 1. Physical-chemical analyses of cocoa pulp with and without enzymatic treatment.

Analyses		Samples				
	T1	T2	Т3	T4		
Yield (%)	1.40±0.53	4.41±0.10	15.62±9.22	19.47±2.75		
pH	3.49±0.01	3.49 ± 0.02	3.41 ± 0.01	$3.42{\pm}1.98$		
Total titratable acidity (%)	0.99 ± 0.99	0.99 ± 0.86	1.10 ± 0.66	1.11 ± 1.54		
°Brix	$18,70\pm0.01$	16.55 ± 0.01	17.40 ± 0.01	19.90 ± 0.01		
Density (g/mL)	$0.96{\pm}0.02$	$1.00{\pm}0.01$	0.99 ± 0.05	0.99 ± 0.02		
Comment Andhoustin						

Source: Authorship.

Parameters	Samples					
	T1	T2	T3	T4		
L*	27.49±0.02	$27.46{\pm}~0.05$	$27.33{\pm}0.10$	$27.22{\pm}0.06$		
a*	$11.41{\pm}0.04$	$11.35{\pm}~0.023$	$11.59{\pm}~0.03$	$11.56{\pm}~0.04$		
b*	0.26 ± 0.02	$0.29{\pm}~0.02$	$0.30{\pm}~0.04$	$0.51{\pm}~0.07$		

 Table 2. Colorimetric analysis of cocoa pulp with and without enzymatic treatment.

Source: Authorship.

Acknowledgments

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Rainwater Reuse at the Gonçalo Moniz Institute - FIOCRUZ-BA

Carlos Letácio S.L. da Silva1*, Roni Dias Vinhas¹, Edna dos Santos Almeida¹, Bruna Aparecida Souza Machado¹

¹SENAI CIMATEC University Center, Postgraduate Program in Management and Technology, SENAI CIMATEC;

Salvador, Bahia, Brazil

This work aims to evaluate the reduction in water consumption at the IGM/FIOCRUZ-BA facilities, evaluating the potential for rainwater harvesting. To this end, the areas of roofs with the potential for reuse of rainwater were surveyed, their capture capacities considering rainfall data, in addition to a survey of the institution's water consumption. We observed significant results in percentages of reduction in water consumption in the case of rainwater reuse and the potential savings generated when compared with the data effectively spent on the water in the IGM. We observed that the capture capacities of the roofs and the pluviometric indices of Salvador can provide potential savings to the Instituto Gonçalo Moniz (IGM).

Keywords: Rainwater. Precipitation. Reuse.

Introduction

The intended use and consumption of fresh water is one of humanity's most significant challenges and is essential to continue to live sustainably and maintain life on Earth. Water is essential for human existence and the planet's most valuable asset. Approximately 70% of its entire surface is covered with water, with 97% formed by seas and oceans consisting of salt water and only 3% corresponding to fresh water, which can be found in underground reservoirs, rivers, and lakes, and in the humidity of the air [1].

According to the International Water Management Institute [2], the rational use of water and the fight against its waste today is worldwide concerning. The problems associated with water are its uneven geographical distribution, the disorderly population increase, and resource misuse. Studies carried out by the institute estimate that about 1/3 of the world's population will experience extreme effects of water scarcity by the year 2025 [3].

It is also noteworthy that water scarcity in the not-so-distant future causes concern. In debates, when the subject is the environment, a concern to preserve this resource gains strength, emphasizing the importance of water and the sustainability of this water resource for nature [4].

In this context, the SDGs (Sustainable Development Goals) relevant to the 2030 agenda bring within their scope an invitation to the planet to produce actions that will minimize or mitigate poverty and protect the environment to ensure that people can enjoy peace., prosperity, and a more sustainable planet. Within the SDGs, SDG6 has as its premises to ensure the availability and sustainable management of water and sanitation for all [5].

Reusing rainwater is an alternative to the sustainable use of this resource. Rainwater harvesting aims to collect and store rainwater through roofs, gutters, and conduits used for its collection and transport to supply reservoirs that serve applications that do not require drinking water [6]. Thus, this article aims to analyze the rainwater reuse through the roofs of the Instituto Gonçalo Moniz (IGM). We will capture the water and store it to reduce drinking water consumption in activities that allow using non-potable water. Furthermore, as most of the rainwater harvesting will take place through the roofs, it is intended to reduce expenses on the invoices of the concessionaire that supplies water and sewage services, prioritizing so that this whole process occurs by gravity. Thus, they are not necessary for other expenses with electricity

Received on 20 September 2022; revised 18 November 2022. Address for correspondence: Carlos Letácio S.L. da Silva. Av. Orlando Gomes, 1845 - Piatã, Salvador - BA- Brazil. Zipcode: 41650-010. E-mail: carlos.lessa@fiocruz.br. DOI 10.34178/ jbth.v5i4.249.

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supply, preserving environmental sustainability characteristics.

Materials and Methods

The IGM/FIOCRUZ-BA is an Institute for the production of science, technological development, and training of human resources in the health area. It is an integral part of the Sistema Único de Saúde (SUS). Therefore, it has socio-environmental obligations that tend to a collective conscience for improving the health and well-being of society.

This work evaluated the reduction of water consumption in its facilities, identifying the potential for capturing rainwater for reuse, its possible use in flushing toilets and urinals, and gardening and maintenance activities. From the methodology used, it was possible to identify alternatives for rainwater harvesting, propose improvements in actions that are already carried out, and suggest their expansion.

To this end, the areas of roofs with the potential for reuse of rainwater were surveyed, their capture capacities considering rainfall data, in addition to a survey of the institute's water consumption through consultations on monthly invoices from the concessionaire providing the service (EMBASA) in the period between November 2020 and October 2021, in order to compare the institution's funding capacity and consumption needs.

Important Considerations

The capture of rainwater in the IGM is intended to be one of the measures taken to reduce water consumption to contribute to the sustainability of the environment, collaborating to maintain this finite natural resource. Furthermore, the environmental theme brings society an understanding of environmental sustainability to enable new ways and solutions to save natural resources that can improve comfort to a more satisfactory level 2.

The significant point is to examine the constitution of the roof's material to verify the

fluidity coefficient and prevent the material from contaminating the water captured and stored. Mechanisms such as filters and screens should also be created to avoid clogging through branches and leaves and to facilitate the cleaning of the capture system.

The use of rainwater is an option that can prove to be very attractive for minimizing the effects of water scarcity in large urban centers and the costs generated by the consumption of water obtained from traditional sources [7].

The rainwater harvesting system benefits everybody, bringing advantages through the capture of rainwater to reduce water consumption from the public concessionaire and remove it from public roads since that water could form floods and bring public and private damage [8].

Water conservation can be defined as any action that: reduces water abstraction from springs, reduces consumptive uses, reduces waste or losses, increases use efficiency, increases recycling or reuse, and prevents water pollution [9].

Calculation of the Volume of Water

To calculate the volume of rainwater captured by the roofs and stored in reservoirs, we used the formula of the ABNT Standard, NBR 15527:2019 (below), which depends on the surface runoff coefficient of the roof and the efficiency of the initial runoff average rainfall and roof areas disposal system.

$\mathbf{V} = \mathbf{P} \mathbf{x} \mathbf{A} \mathbf{x} \mathbf{C} \mathbf{x}^{\eta}$

In which:

V is the annual, monthly, or daily volume of usable rainwater in liters;

P is the average annual, monthly, or daily rainfall in mm; **A** is the collection area in m²;

C is the surface runoff coefficient of the roof (0.92);

uptake factor is the catchment system's efficiency, considering the solids disposal device and initial flow diversion if the latter is used [10].
 0.85 (recommended by Standard 15527:2019, in case of missing data).

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The average monthly precipitation data for the city of Salvador, where the IGM is located, were obtained from the Climatempo website.

Results and Discussion

Potential Areas for Rainwater Collection

To calculate the area of rainwater caught, we inspected the roofs to identify building coverings that allow safe access for frequent inspections and cleaning of the tiles so that the water is collected with as few impurities as possible. The conditions for installing reservoirs were also considered so that they can store water in a place that allows supply through gravity. The architectural projects of the pavilions' roofs were consulted with the unit infrastructure service. We obtained 2.516 m² as the potential area for capture the water (Table 1).

Survey of Rainfall Data

Figure 1 shows the average monthly rainfall for Salvador based on constant rainfall.

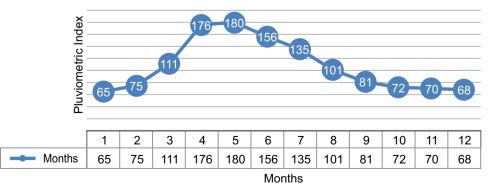
The data presented represent the behavior of rainfall throughout the year. Climatological averages are values calculated from a 30-year observed data series. The monthly volumes of usable rainwater were calculated with the data in hand (Table 2). This information can estimate the amount of non-potable water that can be collected for reuse and consequent reduction of water consumption in the IGM.

Table 2 also shows the amounts in m³ of drinking water consumed and the respective amounts paid that were taken from the invoices of the concessionaire responsible (EMBASA) for the water and sewage supply of the IGM in the period of one year, counted from November 2020 to October 2021. Finally, it is possible to observe very significant

Pavilions	Roof's Area (m ²)
Silver Aluizio	350
Italo Sherlock (Central)	425
Lain Carvalho (NEB)	260
Zilton Andrade	798
LASP 6	83

 Table 1. IGM roof areas.

Figure 1. Average rainfall in Salvador.



Source: Climatempo.

www.jbth.com.br

Period	P (mm)	Rainwater (m³)	Drinking water consumed (m ³)	Amount paid for drinking water consumed	% of the potential reduction in water consumption with rainwater reuse
Nov/20	70	137.73	277	BRL 10,444.01	49.72
Dec/20	68	133.79	317	BRL 12,066.56	42.20
Jan/21	65	127.89	639	BRL 24,881.60	20.01
Feb/21	75	147.56	308	BRL 11,675.18	47.91
Mar/21	111	218.39	339	BRL 12,918.65	64.42
Apr/21	176	346.28	389	BRL 14,822.18	89.01
May/21	180	354.15	432	BRL 16,516.73	81.97
Jun/21	156	306.93	252	BRL 9,592.46	121.79
Jul/21	135	265.61	298	BRL 11,249.52	89.13
Aug/21	101	198.72	313	BRL 11,886.45	63.48
Sep/21	81	159.37	310	BRL 11,765.22	51.40
Oct/21	72	141.66	365	BRL 13,920.07	38.81
		2,538.09	4,239.00	BRL 161,738.64	59.74

Table 2. Calculation of rainwater harvesting value for non-potable use.

numbers of percentages of reduction in water consumption in the case of the reuse of rainwater and the potential savings generated when compared to the data effectively spent on the water in the IGM. Another possibility to be evaluated in a later study is its use for drinkable purposes. In a preliminary search in the literature, we identified two evaluations on the subject that show possibilities of using water for this purpose, provided that ways to improve its quality are verified. In an evaluation presented by Hagemann [11], rainwater proved suitable for use in the state in which it was collected. However, eventually, some parameters were exceeded when compared to the legislation. Regarding exceeded values, turbidity and Escherichia coli were mentioned, but which, if reduced, would improve the potential for using rainwater. However, the analyses indicated relatively close data when evaluating parameters for collecting water directly from the atmosphere and comparing it with the water collected from roofs. Pereira [12] performed microbiological analyses in another evaluation that showed similar

performances. Both rainwater and water from the supply network showed no contamination for the parameters evaluated. However, compared with the legislation on drinking water, it was found necessary to carry out treatment to remove organic matter and eliminate microorganisms.

Conclusion

The capacity of collecting the roofs and the rainfall in Salvador can save 59.74% of the costs paid by the institution for water supply, provided that the water collected can be stored and used for purposes that do not require drinking water. This good economy, in financial terms, can generate reductions of approximately one hundred thousand reais per year in the invoices to be paid by the institution. In view of the perspective of cost reduction, the amount to be saved can be directed to investment in implementing facilities for reusing rainwater on the roofs of buildings, the object of this study. In addition, reusing rainwater is an

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outstanding contribution to preserving this essential natural resource and the environment. The next phase of the study will be to evaluate the costs for the implantation of the reservoirs and hydraulic installations and the analysis of the quality of it for drinking and other purposes.

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A Multi-Layer Perceptron Model for Underwater Object Recognition

Igor Vilas-Bôas Silveira^{1*}, Roberto Monteiro², Oberdan Pinheiro Rocha², Alex Álisson Bandeira Santos² ¹Marinha do Brasil; Rio de Janeiro, RJ; ²SENAI CIMATEC University Center; Salvador, Bahia Brazil

The more human gets interested in sea exploration, the more research to detect objects under the water is done. Therefore, the ability to detect, classify, recognize and track all kinds of objects is evolving daily. This paper aims to introduce a computer model for underwater object classification and recognition based on a Multilayer Perceptron network. The model was constructed with a mixed dataset for the training phase, combining artificial and natural objects, and it reached approximately 99.97% classifying accuracy.

Keywords: Computer Model. Underwater Objects. Classification. Recognition. Accuracy.

Introduction

Underwater target (object) recognition has a great variety of research purposes: monitoring underwater life sustainability, underwater gas pipeline leak detection as an industrial or environmental prevention application, identifying the presence of manufactured archeological objects for archeological research, underwater detection for mineral exploration, among others [1-4]. In addition, military activities such as Mine Counter Measures (MCM) [5] and Search and Rescue (SAR) operations [6] may also take advantage of this capability.

Also known as target detection, target recognition is a kind of computer vision task that aims to identify specific types of visual objects [7]. A system able to perform this task may have at least three essential elements: a sensor, a vehicle, and a data processing unit. The sensor is responsible for collecting data from the environment, codifying and sending it as an electrical signal to the data processing unit. The vehicle carries one or more sensors that can either be attached or tugged. Finally, the processing unit is responsible for interpreting the data collected by the sensor. As the element that decodes the electrical signal sent by the sensor, the processing unit is the 'brain' that makes all the necessary calculations to identify, classify, and, therefore, recognize one or more targets.

A generic diagram (Figure 1) describes the process that occurs since the very beginning: when the sensor captures information from the environment (data carried either by acoustic or visible light waves), passing through the transmission of this information to the processing unit, and reaching, at last, the signal interpretation and object recognition stage.

The recognition task finds its way in several algorithms and techniques developed and improved through the last years, and it is the core of this paper. This paper is divided as follows: Section 2 will give an insight into some of these techniques in use nowadays; section 3 will explain the methodology applied for the computer modeling; section 4 will discuss the results acquired by the model.

Related Works

From conventional signal processing methods using Fourier Transform to modern Machine Learning (ML) algorithms [8], many techniques and methods were developed and improved to perform accurate target recognition, as well as Automatic Target Recognition (ATR).

Image classification based on Deep Learning (DL) algorithms has been actively studied in recent years [9]. Indeed, as Teng and Zhao [10] has highlighted, significant improvements in the digital

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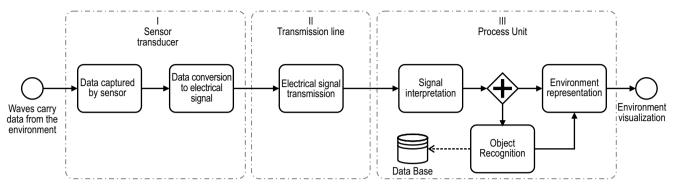


Figure 1. Environment representation process diagram.

Source: Authors

image for target recognition and classification were reached by using DL.

While traditional object detection methods' performance quickly stagnated, DL developed powerful tools that can learn semantic, high-level, and deeper features [11].

According to Neupane and Seok [8], conventional signal processing and ML algorithms come up with some limitations that deep learning algorithms can overcome. Considered a subset of ML, DL works based on the Artificial Neural Networks (ANNs) concept, especially with multiple layers. For example, the Multi-Layer Perceptron (MLP) is a kind of Artificial Neural Network (ANN) with at least three layers: the input, the output, and a hidden layer. Another important DL method to be mentioned is the Convolutional Neural Network (CNN), which has become a modern approach for object detection and classification. For example, Makantasis and colleagues [12] developed an accurate and automated manufactured object detection approach using a CNN to encode spectral information and an MLP for the classification task. Jin and colleagues [13] proposed a method for ATR using a forward-looking sonar based on Deep Convolutional Neural Networks (DCNNs). Girshick and colleagues [14] developed a new approach that combines region proposals with CNNs. Thus this method was called Regions with CNN, or simply, R-CNN. Later, the same author developed the Fast R-CNN by improving the previous approach.

R-CNN and Faster CNN explore the idea that an image may contain multiple objects, and they use regions to find a particular object. The first one to present a different approach was Redmon and colleagues [15], called You Only Look Once (YOLO). The idea is to divide the image into an $S \times S$ grid, and for each grid cell, predict B bounding boxes and C class probabilities. A further version of YOLO, called YOLOv4, was tested for underwater target recognition by Chen and colleagues [16], achieving improvements in recognition accuracy and speed and reducing hardware requirements.

Materials and Methods

Computer Modeling

In order to build the proposed computer model, six components were taken into account as the essential ones: image acquisition, preprocessing, feature extraction, training, classifying, and application. Figure 2 depicts these six components as six blocks and the modeling procedure.

The first step of the modeling procedure, the image acquisition, consists of reading and converting the original dataset images into a bidimensional matrix so that each pixel on the original image corresponds to an RGB value. After that, at the preprocessing stage, a Sobel filter is applied to the data matrix, generating a binary

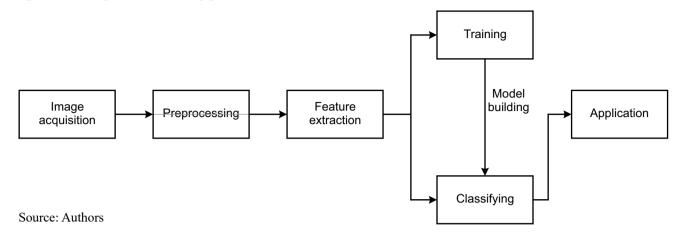


Figure 2. computer modelling procedure.

matrix and making easier the identification of image contours.

Once the image is filtered, it is possible to calculate(statistically) the attributes that contain the input patterns for the features vector. This process is performed during the feature extraction stage, which transforms the binary matrix into a features vector matrix containing input patterns for training and classifying. Four attributes were defined to compound the features vector: areaFraction (percentage of non-zero pixels), mean, stdDev (standard deviation), and area (in pixels). These attributes are represented in the figure 3 as the inputs of an MLP.

The classifying process is performed in two phases: training (learning phase) and data classification (test). In the training phase, the classifying model is built by describing a set of the following classes: pipe, turtle, and shark. Hence the model extracts the attributes from the features vector to perform the training by using the training dataset. The training elements are associated with the class labels to which each belongs. Since the class label of each element is provided to the classifier, this step is known as supervised learning. The output of the classifier will indicate a command for an application.

Network Architecture

An MLP was the ANN chosen to perform the computer modeling of the object recognition

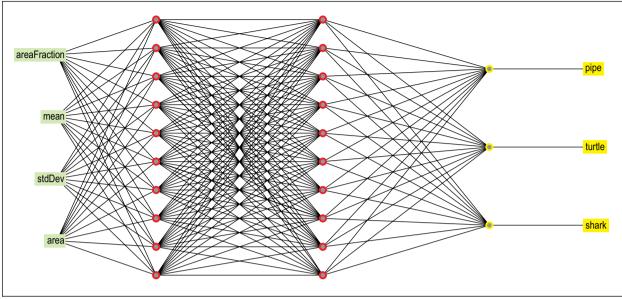
algorithm. Figure 3 shows the architecture of the network used. In the first layer, green-colored nodes represent the described input layers. Right after, two hidden layers are represented by red-colored nodes, each containing ten nodes. The output layer, at last, is composed of three yellow nodes so that each one equals a class.

Table 1 describes the network in terms of its hyperparameters.

Dataset

A dataset was built by combining two other existing datasets: MARIS and UOT-100. The MARIS dataset originates in the Italian national Project MARIS (Marine Autonomous Robotics for InterventionS), whose goal is the development of beneficial technologies for underwater intervention in the offshore industry [17]. It contains 9600 stereo images of both single and multiple pipes with different colors ranging from 5 to 6 cm. Oleari and colleagues [18] and Kallasi and colleagues [19] are some of the many works unfolded by Project MARIS. The UOT-100 (Underwater Object Tracking) dataset was created to facilitate the developing of tracking algorithms well-suited for underwater environments. It contains 104 underwater video sequences and more than 74,000 annotated frames from natural and artificial underwater videos. Panetta and colleagues [20] and Kezebou and colleagues [21] are some essential papers

Figure 3. MLP architecture.



Source: Authors

Table 1. Network hyperparameters.

Hyperparameter	Value
Number of layers	4
Number of hidden layers	2
Number of hidden units (for each hidden layer)	10/10
Batch size	100
Epochs	1000
Activation function	Sigmoid
Learning rate	0.03
Momentum	0.2

about object tracking and the UOT dataset. The resultant dataset used for this paper contains 150 images and three classes: a class 'pipe' from MARIS and the classes 'shark' and 'turtle' from UOT-100.

Results and Discussions

In order to analyze the network performance, the following metrics were used:

- Mean absolute error (MAE): computes the mean absolute error between the labels and predictions;
- Root mean squared error (RMSE): computes root mean squared error metric between y_true and y_pred;
- Relative absolute error (RAE): computes the ratio of the absolute error of the measurement to the actual measurement;

• Root relative squared error (RRSE): computes the square root of the sum of squared errors.

For the 150 images selected to compound the training dataset, the model could classify 145 instances correctly, achieving an accuracy of approximately 96,667%. Therefore, 5 of the 150 images, i.e., only 3,33%, were incorrectly classified. The confusion matrix shown in FIgure 4 might shed some light on these incorrect instances. As revealed, three turtles were classified as sharks; two were classified as turtles.

Table 2 shows the returned values for each mentioned metric.

Figure 4. Confusion matrix.

a	b	с		< classified as
50	0	0	I	a = pipe
0	47	3	I	b = turtle
0	2	48	I	<pre>< classified as a = pipe b = turtle c = shark</pre>

Source: Authors.

Conclusion

Many kinds of research and developments in underwater object detection have recently appeared. The advances in deep learning methods brought a new perspective on the recognition modeling process. This work created a computer model for underwater object detection based on an MLP through a supervised learning DL process and using a mixed dataset. The results returned by the model, as presented in section 4, were above the expectations,

Table 2. Performance metrics.

Metric	Value
MAE	0.0308
RMSE	0.1388
RAE	6,9191%
RRSE	29.4353%

with the classifying accuracy reaching about 96,97%. Further studies may be done by exploring other techniques, such as CNN, R-CNN, or even YOLO, as well as other combinations of datasets.

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Jabuti Project: Maze Solver Micromouse Robot

Ana Luiza Cantharino Maciel^{1,2*}, Maria Eduarda Benfica Gonçalves^{1,2}, Vítor YanMiranda Basañez^{1,2},

João Vitor Silva Mendes^{1,2}

¹SENAI CIMATEC University Center; ²Researcher at IEEE RAS CIMATEC; Salvador, Bahia, Brazil

The present article discusses the development of the Jabuti Project, which consists of a micromouse, a maze solver robot. The project mainly aims to build a low-cost robot and to assist university students in the practical study of robotics. To solve the maze, a wall-follower algorithm was implemented for anarduino, and stepper motors constituted a PCB of the project to provide more stability to the robot, infrared sensors for area recognition, and a caster wheel to direct it. In conclusion, the circuit parts will be estimated to be assembled and integrated to implement the developed logic with tests in the physical prototype.

Keywords: Robot. Wall-Follower. Infrared Sensor. Labyrinth.

Introduction

In the last decades, robots have taken an active part in human lives, such as in industrial environments or in a regular daily routine; that became possible over time due to the Industrial Revolutions, mainly the Second, and intensified with the advent of IoT(Internet of things), Machine learning and AI (Artificial intelligence)technologies. There upon to innovations, it is possible to understand how to create and control robots in their most diverse applications in the technology field. Then, seeing the world's current pace, university students must have more than just theoretical studies about robotics. However, practical simulations with simple robots such as a micromouse, give them motivation and interest in this kind of development. Therefore, this educational topic was discussed at the 2016 International Conference on Advanced Robotics and Intelligent Systems and stated, "It is found that the micromouse is an excellent topic for students to learn the implementation of mobile robots because it contains multidisciplinary knowledge and skills."[1].

Micromouse History

The inspiration for Micromouses began in 1977 when Donald Christiansen [2] challenged his readers to design and build a robot called "micromouse": an autonomous robot that finds a path from a start cell to the end of every simple and unknown maze based on a variety of algorithms guided by sensors. The Institute of Electrical and Electronics Engineers (IEEE) Spectrum magazine announced as 'Amazing Micromouse Competition', which was first held in New York in 1979 [2,3]. The events are held worldwide and are most popular in the United Kingdom, United States, Japan, Singapore, India, and South Korea and becoming popular in subcontinent countries such as Sri Lanka (Figure 1A/B).

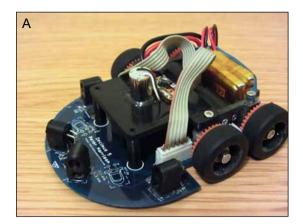
Building the Robot

According to the article "The development of a half-size micromouse and its application in mobile robot education" [1], the challenge is not only to build a robot that resolves mazes but one that move more efficiently and is smaller and lighter as possible. Therefore following the Harvardrobotics team in the 2016 Brown IEEE Micromouse Competition [4], this kind of robot is usually integrated by: 3 IR distance sensors and 2 Hall Effect motor encoders to determine the robot's position and orientation as well as for detecting walls; powered by 2 DC motors, controlled through

Received on 12 September 2022; revised 21 November 2022. Address for correspondence: Ana Luiza Cantharino Maciel. Av. Orlando Gomes, 1845 - Piatã, Salvador - BA, Brazil | Zipcode: 41650-010. E-mail:ana.maciel@aln.senaicimatec. edu.br. DOI 10.34178/jbth.v5i4.251.

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Figure 1A/B. Competitor Micromouse robot and competition of Taiwan Micromouse Contest 2017 [3].





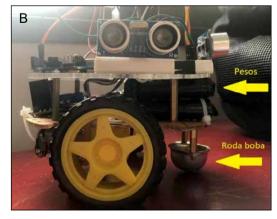
an H-bridge motor controller via a pulse-width modulated signal; using an Arduino micro that Integrates the information from onboard sensors into a flood-fill maze navigation algorithm; using a simple design of a rectangular and small chassis with two regular wheels and a caster wheel.

Jabuti Robot

The Jabuti project is a practical implementation of the micromouse robot with the primary goal of encouraging students of SENAI CIMATEC in the technology field to learn and adapt to the robotics scenario, stimulating them to participate and feel included in the modern world of innovation. Considering the context and needs of the project, we decided to create a robot using four infrared sensors to send information to the arduino by jumpers. So, through that, determine the robot's movement according to each situation by a wall follower algorithm with 2 regular wheels and a caster wheel (Figure 2A/B)) obemen. Then, developing a program that allows the robot to choose an exit autonomously was necessary. Then, the main idea was to map the maze while researchers for the exit.

It makes students develop skills like 3D modeling structures, programming problemsolving, algorithms, sensor reading and understanding microcontrollers, circuit boards, and mechanical parts. It also stimulates the will to innovate and be creative in future works. This article describes the production and development process of a Micromouse robot.





Figures 2A/B. Robot model [5].

Materials and Methods

<u>Algorithm</u>

The programming aimed to solve the maze through the C language based on a wall-follower system that consists in prioritizing turning to the right, with the second option to follow the front and the third option turning left [6,7]. This criterion will be used to map the maze to find the way out of it. So, we formulated a flowchart (Figure 3).

Infrared Sensor

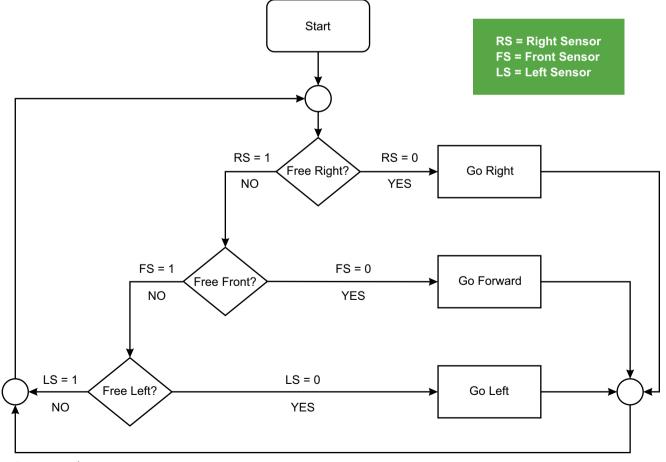
Micromouse is formed by 4 distance sensors: two for the front, one for the left, and one for the right. They give the robot direction robot in the maze, so if the robot detects a presence by any sensor, the

Figure 3. Flowchart of the algorithm.

robot goes in another direction. The infrared sensor, widely used in robotics to detect the presence, was selected to perform this task. The handicap of this sensor compared to the ultrasonic is its lack of liability, as it is more sensitive to interference such as sunlight. The choice of the IR sensor was due to its low cost and the micromouse's environmental factor, which would be indoors, such as in colleges and laboratories. (Figure 4A/B).

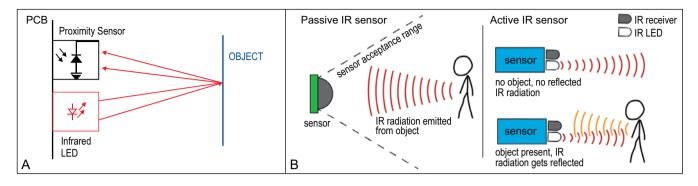
Printed Circuit Board (PCB)

After researching the algorithm and infrared sensor functions, we developed the PCB project. Therefore, the PCB is constituted of 2 Stepper motors, controlled by an H-Bridge, 4 connectors to the 4 Infrared sensors, and a caster wheel attached to the structure (Figure 5).



Source: Authors.

Figures 4A/B. IR sensor operation [10,11].



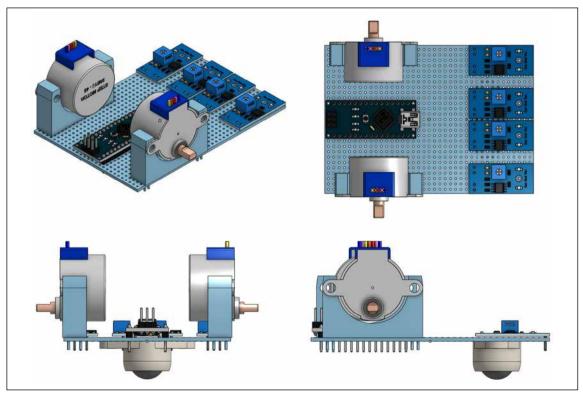
3D Chassis's Model

According to the PCB model and components needed for the robot, we made a 3D model of the chassis (Figures 6 and 7). It includes battery support, 2 stepper motors support, a designated space to fit the PCB and some screw holes to the IR sensors, and the support for the caster wheel.

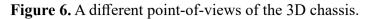
Results and Discussions

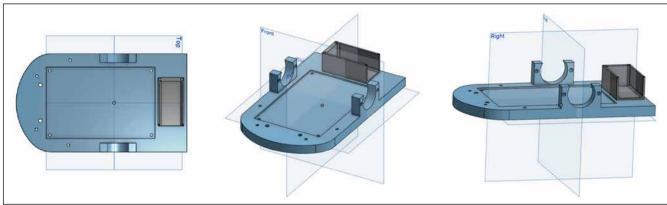
As a result of this paper and studies, a diagram of the sensor arrangement, a wall follower algorithm, a PCB (Printed Circuit Board) model, and a project simulation in the Webots software, and a Workshop about this study has been developed and presented.

Figure 5. Different point of views for the PCB layout.

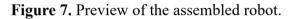


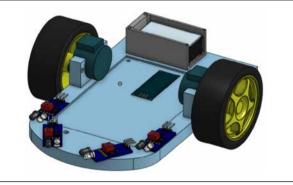
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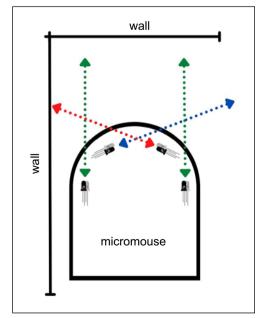
Sensor Arrangement

The sensor arrangement (2 facing the front and two on diagonal to each side-Figure 8) was thought to make the most precise and economical collection of information for the robot to move and map the maze. That makes better modeling of surroundings than the traditional way to use 3 sensors (1 in the front and one on each side) like the Harvard robotics team in the 2016 Brown IEEE MicromouseCompetition [4], or save to use 8 IR sensors like the model of Lunghwa University of Science and Technology in Taiwan [1].

<u>Algorithm</u>

To initialize the algorithm, the Stepper.h library was added, which includes specific functions for the stepper motor in the arduino IDE. After that, the

Figure 8. Diagram of the sensor arrangement.



Source: Authors.

motor's number of steps per revolution was defined as equal to 32, with 2048 revolutions per revolution. Next, the variables for the sensors and stepper motors were declared, along with their inputs. The functions of sensors and motors were also created; the first was to read and display the distances detected by the sensors, and the second was to determine the motor speed and its pin configuration on the board. In the loop function, if and else conditionals were used to relate the information received by the sensors (Presence or not of a wall) with the respective desired motor outputs. Lastly, a repository was created in GitHub to keep the code (Figure 9) [12].

<u>PCB</u>

The Jabuti robot uses stepper motors, unlike conventional micromouses that use DC motors with encoder, because the stepper motor united to the information of the active infrared sensors gives the robot more control, avoiding crashing into the walls. As a result, it improves the ability to map the maze without the high cost of an encoder.



<u>Workshop</u>

Considering the knowledge we acquired during research, the Jabuti team, united with colleagues of IEEE CIMATEC, promoted a workshop about the need for maze-solving robots and programming logic and developed two small robots with the same principles as the one presented in this article (Figure 10). Therefore, it was an excellent experience that showed us the importance of this project and how it activates creativity and presents it from an educational perspective.

Conclusion

In this paper, we presented the current situation of an autonomous robot's development and assembly processes and the understanding of its programming and its application. In addition, we showed how sensors would be used to assist in autonomous movement.

The current progress of the electronic design and simulation of the Jabutiproject was also shown,

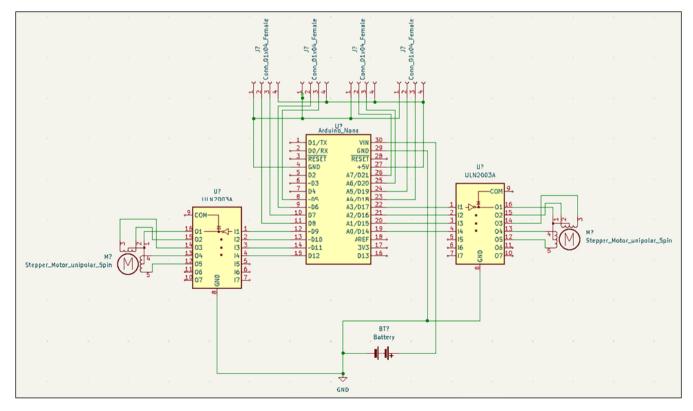
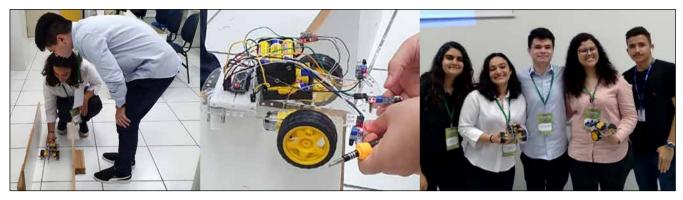


Figure 10. Workshop.



taking into account how the robot would need to move in places that could have more than one exit in the maze and the need to install a caster wheel to assist in moving the robot. The PCB model was also made, showing the connections between the arduino nano, the chip, and the stepper motors.

For the next steps, the ideal robot proposed in the article will be assembled with the PCB and the chassis designed alongside the studies of the sensors. In consequence, the project will be continued and has the goal to be applied in schools and other universities events

Therefore, the goal of building a low-cost robot was achieved by being a compact structure with simplified and amplified use of the components, like the disposition of the sensors to cover more area. Through that, the secondary objective was also achieved, leading the students to study and put into practice the concepts needed for project construction.

Acknowledgments

We thank to IEEE RAS CIMATEC and CIMATEC LAB MAKER.

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Statistical Study of Eco-Efficiency in Compact and Average Cars (Chevrolet, Ford, VW, Fiat, Renault) in Brazil Based on the Metro Table in 2019

André Luis Pires Wenceslau Soares^{1*}, Adrian Widmer¹, Gabriel Souza Dunkel¹, Joseph Samuel Neiva¹, Orlando Mota Pires¹, Aloisio Santos Nascimento Filho²

¹Computer Engineering, SENAI CIMATEC University Center; ²Department of Statistical, SENAI CIMATEC University Center; Salvador, Bahia, Brazil

This article aimed to identify the most efficient and ecological car models. Based on the analysis of cars classified as "light vehicles" in 2019 by INMETRO data in Brazil. A program in C helped analyze the frequency distribution of the variables of CO₂ emission and mileage per liter, allowing us to evaluate the efficiency of the compact and medium models of the "light" class. At the end of the study, there was an emphasis on the eco-efficiency of the vehicle assemblers Fiat and Renault.

Keywords: INMETRO. Program in C. CO2 Emission. Eco-Efficiency. Vehicle Assemblers.

Introduction

The environment and sustainability are themes widely discussed nowadays. In that regard, the discussion about the use of fossil fuels becomes relevant to the current reality. Major international bodies and nations around the globe, like Germany, are already alert to the weakening of this market in the long term since they depend on finite and polluting resources. On the other hand, using electric vehicles has become popular, and great business people like Elon Musk have increasingly invested in the area.

Bringing this discussion to the Brazilian scenario, replacing vehicles powered by fossil fuels with electric cars is still a distant reality. The need for more public policy and government relaxation in the face of environmental problems, for example, delay the adoption of this international trend by decades. According to the Greenhouse Gas Emission System, in 2019, Brazil emitted more than 2 billion tons of CO_2 into the atmosphere.

That number could be reduced by using green technologies in vehicles [1].

J Bioeng. Tech. Health 2022;5(4):279-285 © 2022 by SENAI CIMATEC. All rights reserved. With that in mind and the reading of the article "*Carros menos poluidores e Mais econômicos, escolha*" by João Mesquita [2], the team came up with the conclusion that it is possible to determine which vehicles are running in the national territory can be considered more "ecological". Therefore, the INMETRO's [3] light vehicle table, with manufactured automobiles and their configurations, was essential for the execution of this study. Furthermore, the data collected was used to continue the primary research, generating tables and statistical figures about which brands, engines, and cars show better results in the face of sustainability.

Many discoveries were made in the development of this article, going even beyond what had been planned. The in-depth analysis proved efficient and brought curious information about the automakers operating in the country. The conclusions will be discussed in this document, supported by the data collected, and available for consultation.

Materials and Methods

In the Methos, an audit trail was initially carried out, where two Renault models that did not fit the data standards were excluded from the analysis. After processing the data, the team created a program in C, taking advantage of their knowledge of Computer Engineering and

Received on 15 September 2022; revised 24 November 2022. Address for correspondence: André Luis Pires Wenceslau Soares. Rua Acácia Amarela, 353 – BL B apto 003 - Salvador - BA, Brazil | Zipcode: 41502-310. E-mail:andre.wenceslau@ yahoo.com.br. DOI 10.34178/jbth.v5i4.252.

gathering data more reliably. We used concepts learned in the classroom and mathematical models to add class, amplitude, and types of frequency to these values.

In the Methods, the type of study, site, population (in case of field research), period, technique, and data analysis, as well as ethical standards followed (in case of human research), should be explained. In short, describe all the method(s) used to perform the study.

The code can be explained. First, the user is asked to impute the number of elements or terms he will work with (n). The entire program used this integer value, from which the class number calculation is generated, which is also an integer. After obtaining the class, the user is asked to put all the values that can be decimals, ending with the number zero. Then these numbers are put into a vector (A variable that has a specific number of empty spaces that can store multiple values). Working with vectors, we can make calculations and comparisons for all numbers and generate tables with a large amount of data without much effort. The Figures present some steps of this creation. An example is where the program compares three vectors that have all the values(n) and the two that delimit the beginning and end of each class, adding one more to "phi", which determines the absolute frequency value in each class.

This program evaluates the question related to the proximity of the amplitude. One of the formulas used in statistics to verify if the amplitude is correct to aggregate all classes is that we must add 1 to the amplitude if the product between the number of classes and the value of amplitude added to the number of the smallest value is less than the most significant value.

We generated a standardized table with the final result of obtaining data for one of the tables, in the code, with the approximation of one decimal place based on the output formatting. This table only needs to be copied to Excel without the necessity to do any calculations by hand or format the program's cells with different formulas.

Results and Discussion

The following statistical step was the presentation of the data. We used "pseudo tables" created previously by programming in compilers to generate the frequency tables of the CO₂ emission of the Compact and Medium cars and their respective mileage per liter in the Chevrolet, Ford, VW, Fiat, and Renault brands (Tables 1-4). These were useful in allowing a more excellent perception of group discussion and the creation of the figures illustrated in this article.

Data Presentation and Debates

The boxplot model chart was chosen based on the team's previous knowledge acquired in class and on the recommendation of teachers Aloísio Santos and Roberto Coelho. This model allowed for better analysis and more accurate conclusions from the data collected. Also, the model presents central tendency and dispersion measures clearly and precisely [4]. Figures 1 and 2 present the results of the graphs.

The graphs' analysis was obtained by verifying data from the tables of the National Institute of Metrology, Quality and Technology (INMETRO) and the Brazilian Labeling Program (PBE). We conclude that through the graph of fossil CO₂ emission (g/km) in compact cars of the brands: Chevrolet, Ford, VW, Fiat, and Renault in 2019. The Chevrolet cars automaker have the lowest average of fossil CO2 emission (g/km), but the automaker that has the car with the lowest emission rate is Fiat, which also has the car with the secondhighest emission rate analyzed. On the other hand, Renault has the car with the highest emission rate, in addition to having the highest average emission in its cars, among the analyzed automakers. When examining the same compact cars, this time by the mileage per liter graph in cars that use diesel or gasoline in the city, the automaker Renault has the cars with the highest and lowest mileage per liter of all the analyzed cars, revealing a trend of extreme variance. While the Chevrolet automaker's

g/km	Frequency	Cumulative frequency	fri.	Fri.
90 - 97	8	<u>8</u>	19.51%	19.51%
97	13	21	19.51%	51.22%
104 111	14	35	34.15%	85.37%
111 118	3	38	7.32%	92.68%
118 125	2	40	4.88%	97.56%
125 132	1	41	2.44%	100%
-	41	-	100%	-

Table 1. Frequency distribution of CO₂ emission (g/km) in compact cars of the brands: Chevrolet, Ford, VW, Fiat, and Renault.

Table 2. Frequency distribution of CO₂ emission (g/km) in medium cars of the brands: Chevrolet, Ford, VW, Fiat, and Renault.

km/L	Frequency	Cumulative frequency	fri	Fri.
91 99	14	14	26.92%	26.92%
99 107	16	30	30.77%	57.69%
107 115	17	47	32.69%	90.38%
115 123	3	50	5.77%	96.15%
123 131	1	51	1.92%	98.08%
131 139	0	51	0%	98.08%
139 147	1	52	1.92%	100%
-	52	-	100%	-

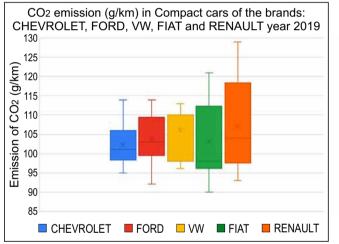
Table 3. Frequency distribution of km per liter in compact cars from brands that use diesel or gasoline in the city: Chevrolet, Ford, VW, Fiat, and Renault.

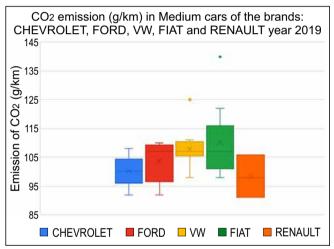
km/L	Frequency	Cumulative frequency	fri	Fri.
9.90 10.72	4	4	9.76%	9.76%
10.72 11.53	10	14	24.39%	34.15%
11.53 12.35	9	23	21.95%	56.10%
12.35 13.17	14	37	34.15%	90.24%
13.17 13.98	2	39	4.88%	95.12%
13.98 14.80	2	41	4.88%	100%
-	41	-	100%	-

g/km	Frequency	Cumulative frequency	fri	Fri.
9.30 10.07	2	2	3.85 %	3.85 %
10.07 10.84	6	8	11.54%	15.38%
10.84	19	27	36.54%	51.92%
11.61 12.39	10	37	19.23%	71.15%
12.39 13.16	12	49	23.08%	94.23%
13.16 13.93	2	51	3.85%	98.08%
13.93 14.70	1	52	1.92%	100%
-	-	52	-	100%

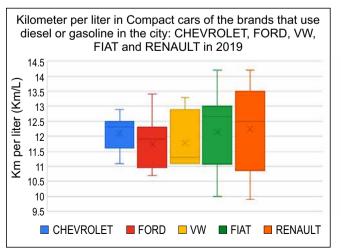
Table 4. Frequency distribution of CO₂ emission (g/km) in Medium cars of the brands: Chevrolet, Ford, VW, Fiat, and Renault.

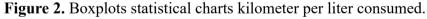
Figure 1. Boxplots statistical charts CO₂ emission.



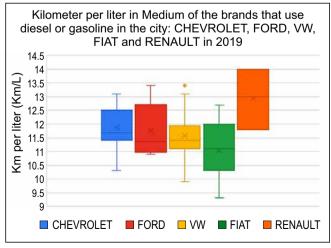


Source: Personal file created from INMETRO data year 2019.





Source: Personal file created from INMETRO data year 2019.



cars present a constant with average values, not presenting more economical cars or expensive cars.

However, when looking at the values of the fossil CO₂ emission graph (g/km) in average cars of the brands: Chevrolet, Ford, VW, Fiat, and Renault of the year 2019, the automaker Renault shows a predominance of cars that emit a low rate. of fossil CO₂ (g/km), while Fiat cars are the ones with the highest emission rates, among those analyzed, even showing cars that are significantly out of the curve. In congruence with the emission of fossil CO₂, the automakers that present a lower emission rate in their cars also present a higher mileage per liter in the city: like Renault, which has a predominance of more kilometers traveled per liter in its cars. Among the automaker, Fiat has the least economical cars of all the automakers analyzed.

Interpretation Measures of Central Tendency and Degree of Dispersion

One of the final steps of the research was to explore measures of central tendency and measures of dispersion. The expression of the arithmetic means of the classes in the frequency tables was used to produce the graphs, generating data on CO_2 emission and kilometers traveled per liter of Chevrolet, Fiat, Ford, and VW cars, in the compact and medium categories to obtain the averages totals, reaching the limits in the scatterplots.

The equation has been adapted so that \overline{x}_i is equal to Midpoint, f_i is equal to Absolute Frequency, and n is equal to the number of medium or compact cars.

$$\overline{X} = \frac{1}{n} \sum_{i=1}^{n} (\overline{X_i} \cdot f_i)$$
(1)

Scatterplots, widely used in statistics, are based on graphically representing an association of different measures for further analysis to find a connection between the data. For example, the same graphs might help obtain a possible answer to the initial question about the relationship between the kilometers per liter and the CO₂ emission of the automakers' vehicles in 2019. It was also possible to compare the disparities between compact and medium models by placing the data side by side. The scatterplots showed the averages for each automaker, with the orange line referring to compact cars and the yellow line the tendency per average moving, the light blue line and the green line are the averages among medium cars, and it is a Linear trend (Figures 3 and 4). In addition, an overall average was included in the graphs to improve the visualization of which vehicle assembles are the most eco-friendly.

We observed that among compact cars, the automaker FIAT has the most financially economical example, the ARGO model, DRIVE version, which runs 14.2(km/L) in the city, and it is also the car that emits less CO₂ fossil(g/km). On the other hand, as for the medium-sized cars, the most economical is the Renault, model Logan, Authentique / Expression version, which runs 14(km/L) in the city, and is also the one that emits less CO₂ fossil(g/km). With these observed data, it becomes clear that if someone is aiming to buy an economical way to transit in a city and at the same time pollute less, compact cars are a better option than medium cars.

Conclusion

In short, through research and analysis of the car proficiency study, it became possible to: raise frequency tables; analyze central and dispersion measures; generate different statistical structures, such as Boxplot and dispersion measurement graphs, through data provided by the National Institute of Metrology, Quality, and Technology (INMETRO), and together with the knowledge acquired in the classes, it was also possible to carry out an audit trail, facilitating the analysis of defects, which made it possible to discuss the results closer to reality. Finally, there is the possibility of using the knowledge in statistics added to the knowledge of programming, which is highly studied in Computer Engineering, serving in this way to optimize the works with large numbers of data, as the works in "BIG DATA" in the technology area portrayed.

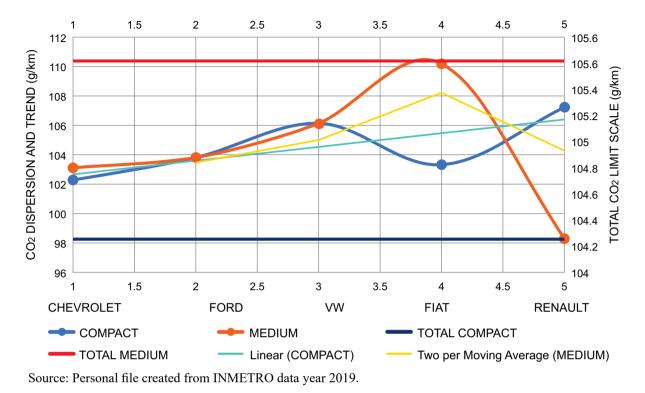
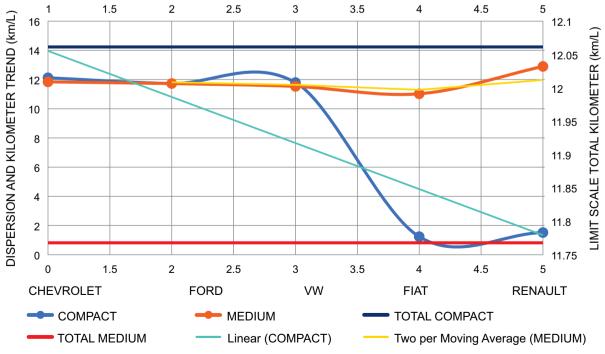


Figure 3. Dispersion measures in fossil CO₂ emission (g/km) between compact and medium cars in each brand:.Chevrolet, Ford, VW, Fiat, and Renault.

Figure 4. Dispersion measures of diesel/gasoline (km/L)by medium cars of each brand:.Chevrolet, Ford, VW, Fiat, and Renault.



Source: Personal file created from INMETRO data year 2019.

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We want to thank teachers Aloisio Santos Nascimento Filho e Roberto Costa for their assistance in developing this research.

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Signal Acquisition Methods for Vital and Nonvital Parameters in Electronic Health Devices: A Scoping Review

Thiago Cardoso Maia^{1*}, Maely Guilherme Botelho Coelho Filho¹, Yasmim Batista Oliveira², Luiza Zanoni Barbi², Thamiles Rodrigues de Melo¹, Valter Estevão Beal¹, Valéria Loureiro da Silva¹

¹SENAI CIMATEC University Center; Salvador, Bahia; ²Academic Association of Technology and Inovation; Vitória, Espírito Santo, Brazil

This paper presents the most common vital and nonvital parameters in current wearable electronic devices, describing the respective signal acquisition methods. We included complete studies in indexed sources and accessible online in the consulted databases between the years 2017 to 2022. Nine studies focused on capturing at least one vital sign. Five addressed HR, four FR, two BP, four SpO₂, and seven body temperature. As for nonvital parameters, half of the total sample approached gait analysis, while one-third addressed non-invasive blood glucose sensors. The preparation of this material aimed to aid the scientific community by summarizing essential information to foster the development of new technologies capable of improving health decisions. Keywords: Devices. Wearables. Sensory.

Introduction

The investment in wearables in the past few years has been increasing due to the growing unmet needs of health management, defined as the matching between available resources and optimal care. Wearables provide a suitable solution to the challenge of monitoring patients in varying systems of care, inpatient and outpatient, home or office.

Dias and Cunha (2018) [1] classified wearable electronic devices into two large groups: a) activity monitoring, which includes self-monitoring; and b) health-related, subdivided into three areas. The first area is prediction: It helps in clinical management, aiming at a better prognosis.The second area is anomaly detection, which identifies unusual patterns based on machine learning algorithms. Finally, the third area is diagnostic support, which sustains the diagnostic decision as informed by data from wearable devices.

Complementarily, El-Rashidy and colleagues (2021) [2] conceptualize remote monitoring

systems in three stages. The first stage is the data acquisition by extracted parameters.

The second defines data transmission and storage for analysis, classification, and processing. Finally, the third stage consists of back-end systems with real-time data that support medical decisions according to patients' status.

Three aspects of technology development can be highlighted in this context: long-term stability, resilience, and biocompatibility [3]. It is thus fundamental to understand the context of wearable electronic device insertion, recognizing that devices increasingly enable bidirectional feedback between healthcare professionals and patients. Such technological advance corresponds to a complementary approach to health systems, favorable to expanding preventive medicine and reinforcing patient-centeredness [4,5].

This scoping review aims to synthesize the current wearable technology literature, focusing on the frequency of distinct methods to acquire vital and nonvital data and on the frameworks that contextualize wearable electronic devices.

This review has four primary purposes:

- Specifying vital and nonvital parameters most used in wearables;
- Elucidating the respective methods of capturing data;
- Describing the respective validation

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experiments, including both positive and negative technological consequences

• Discussing the applications of wearables.

Materials and Methods

The scoping review was the chosen study design to clarify, group, and synthesize the most relevant current knowledge about wearable electronic devices. First, the population, concept, and context (PCC) strategy was defined: a) in terms of population as non-invasive wearable electronic devices; b) concerning the concept as categorically presenting the means of capturing the vital parameters processed by such wearables; c) regarding the context as health care at primary, secondary and tertiary levels. From this, the question was established: What is the most relevant scientific evidence for capturing vital parameters in wearable health sensors? To answer this question, different types of literature were searched, including qualitative and quantitative analysis, primary studies, systematic reviews and scope reviews, master's dissertations, or doctoral theses published in journals or scientific conferences, in English or Portuguese, in available indexed sources. Studies on augmented reality (absence of technology in Software\Hardware) were excluded, as well as those that could have presented the methods for capturing vital and nonvital parameters. Besides, documents that presented non-wearable or non-portable hardware or described transcutaneous data capture methods were excluded.

The databases used were: Virtual Health Library (VHL), EMBASE for Excerpta Medica dataBASE (EMBASE), Google Scholar, and Online System of Search and Analysis of Medical Literature (Medline). To search the databases, controlled descriptors referenced by DeCs/MeSH were established, crossed with keywords in English, using the Boolean operator "AND". The review was restricted to studies published between 2017 to 2022. Table 1 described the detailed search strategy.

Observing Table 1, the Google Scholar search was used to ensure the retrieval of current and potentially eligible studies for this review. For this reason, four independent searches were carried out in this database, combining the descriptors and keywords since the unified search was impossible due to the number of characters. Thus, the articles from the first ten pages of the first search were included (100 articles), in addition to the first page of 10 first articles from other searches (30 articles), resulting in a total of 130 articles. All articles from the search strategies were initially selected from the other databases.

The articles were independently selected by title and abstract by two reviewers to minimize the risk of selection bias. Disagreements during the inclusion process were discussed between the reviewers and a final agreement was reached. After this initial phase, the full-text version of included studies was retrieved and read by reviewers. Reviewers extracted the following parameters from the included studies: identification of the selected material; year of publication; authors; language; study design, and inferred results, enabling the identification of similarities, differences, and complementarities. The Flowchart (Figure 1) depicts details in the inclusion and exclusion process, consistent with the PRISMA Guidelines.

Results and Discussion

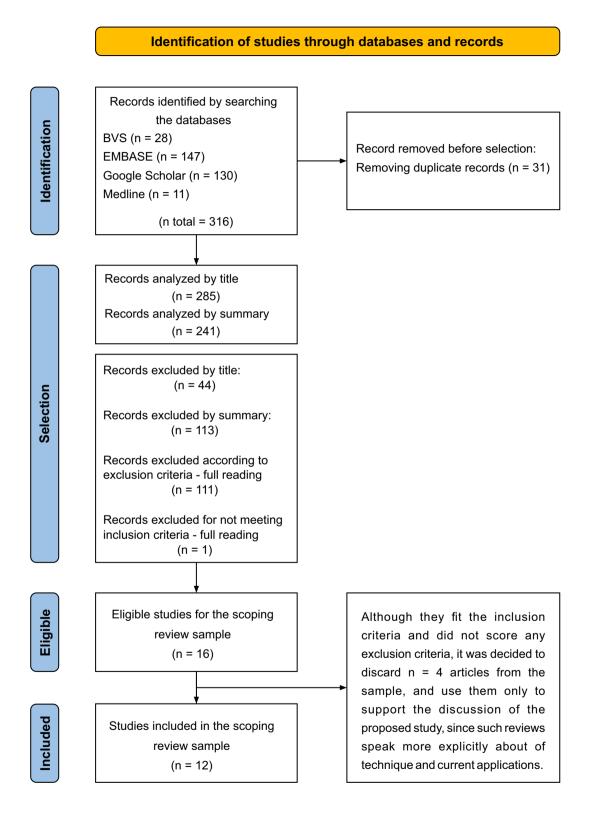
The search in the four databases resulted in 316 articles; of these, 12 we selected for the final sample. Table 2 describes the studies in English. There is also regularity in the frequency of publication of articles per year related to the theme in the last decade: 2017 (8.33%), 2018 (8.33%), 2019 (25.00%), 2020 (16.66%), 2021 (25.00%) and 2022 (16.66%). It confirms the significant investment in the development of wearable sensors for health in recent years.

Up to 75% of studies focused on capturing at least one vital sign. Of these, 5 described HR uptake (55.55%), 4 addressed RF (44.44%), 2 acquired BP measurement (22.22%), 4 had SpO₂ (44,44%),

Table 1. Search strategy in the databases used to survey the literature.

Database	Strategy	Articles
BVS	("Wearable Electronic Devices") AND ("Vital Signs" OR Glucose) AND ("Health care")	28
EMBASE	('wearable electronic devices' OR 'wearable sensors' OR 'health wearables') AND ('vital sign'/exp OR 'arterial oxygen saturation'/exp OR 'gait'/exp OR 'walking speed'/exp OR 'walking pace' OR 'glucose'/exp OR 'body equilibrium' exp OR 'body equilibrium' OR 'body sway' OR 'equilibrium, body' OR 'musculoskeletal equilibrium' OR 'postural balance' OR 'postural equilibrium') AND ('primary health care'/exp OR 'first line care' OR 'health care, primary' OR 'primary care nursing' OR 'primary health care' OR 'primary healthcare' OR 'primary nursing care' OR 'tertiary health care'/exp OR 'health care delivery'/exp OR 'community care'/exp OR 'hospitals, rehabilitation' OR 'health care' OR 'health care' OR 'health system' OR 'healthcare' OR 'long stay care') #1 AND (2017:py OR 2018:py OR 2019:py OR 2020:py OR 2021:py OR 2022:py)	147
Google Scholar	("Wearable Electronic Devices" OR "Wearable sensors" OR "Health wearables") AND ("Vital Signs") AND ("Health care") ("Wearable Electronic Devices" OR "Wearable sensors" OR "Health wearables") AND ("Gait Analysis" OR "Walking speed") AND ("Health care") ("Wearable Electronic Devices" OR "Wearable sensors" OR "Health wearables") AND (Glucose) AND ("Health care") ("Wearable Electronic Devices" OR "Wearable sensors" OR "Health wearables") AND (Glucose) AND ("Health care") ("Wearable Electronic Devices" OR "Wearable sensors" OR "Health wearables") AND ("Oxygen Saturation") AND ("Health care")	130
MedLine	Wearable Electronic Devices.mp. or Wearable Electronic Devices/ OR Wearable sensors.mp. OR Health wearables.mp. AND vital signs/ or blood pressure/ or body temperature/ or heart rate/ or respiratory rate/ OR Oxygen Saturation.mp. OR gait analysis/ or walking speed OR walking pace.mp. or Walking Speed/ OR Blood Glucose/ or Glucose.mp. OR Postural Balance.mp. or PosturalBalance/ AND Primary Health Care.mp. or Primary Health Care/ OR Tertiary Healthcare.mp. or Tertiary Healthcare/ OR Community Health Services.mp. or Community Health Services/ OR Hospitals, Rehabilitation.mp. or Hospitals, Rehabilitation/ OR Delivery of Health Care.mp. or "Delivery of Health Care"/	11

Figure 1. Prisma 2020 flow diagram (adapted) of the article selection process.



Author	Title	Publication	Language	Study Type
Majumder and colleagues [6]	Wearable sensors for remote health monitoring	2017	English	Narrative review
Siddiqui and colleagues [7]			English	Scope narrative
Yinji and colleagues [8]	Flexible hybrid electronics for digital healthcare	2019	English	Prospective observational
Weenk and colleagues [9]	Wireless and continuous monitoring of vital signs in patients at the general ward	2019	English	Randomized controlled trial
Witt and colleagues [10]	Windows into human health through wearables data analytics	2019	English	Literature review
Celik and colleagues [11]	Gait analysis in neurological populations: Progression in the use of wearables	2020	English	Scope narrative
Purohit and colleagues [12]	Smartphone-assisted personalized diagnostic devices and wearable sensors	2020	English	Scope narrative
Areia and colleagues [3]	A chest patch for continuous vital sign monitoring: Clinical validation study during movement and controlled hypoxia	2021	English	Prospective Cohort, observational cross-sectional
Haveman and colleagues [4]	Continuous monitoring of vital signs with the Everion biosensor on the surgical ward: A clinical validation study	2021	English	Prospective observational double-blind
Mejia Cruz and colleagues [13]	Walking Speed Measurement Technology: A Review of 2021	2021	English	Literature review
Haveman and colleagues [5]	Continuous monitoring of vital signs with wearable sensors during daily life activities: Validation study	2022	English	Validation study, Prospective observational
Yoon and colleagues [14]	Multifunctional hybrid skin patch for wearable smart healthcare applications	2022	English	Experimental

 Table 2. Simplified description of selected studies.

and 7 quantified body temperature (77.77%). In addition, one study analyzed the accuracy of detecting arrhythmias and normal cardiac rhythm. Regarding nonvital parameters, half of the total sample addressed, alone or not, wearables with a focus on gait analysis, while one-third addressed non-invasive blood glucose sensors.

Regarding body location chosen for wearable electronic devices, seven studies (31.81%) described bracelets, and three reported a chest patch (13.63%). The same proportion of studies described fingers, soles, and the hip (9.09%) as body location, whereas earlobe, spines, upper arm, lower limbs, and ring were described by 4.54% of the sample (i.e., one study each).

Based on the frequency of methods to capture vital and nonvital parameters, five categories were defined in this scoping review:

- 1. Types of sensors;
- 2. Acquisition methods covered in this scoping review;
- Preferred insertion body sites for each type of sensor;
- 4. Available wearable electronic devices found and health outcomes.

Five vital parameters were reported for continuous patient monitoring, which is associated with better health outcomes: heart rate (HR), respiratory rate (RR), blood pressure (BP), blood oxygen saturation (SpO₂), and body temperature [9]. Regarding nonvital parameters, published studies tended to report on gait analysis – including counting steps and detecting the risk of falls [13] – and non-invasive glucose monitoring [7]. As such, continuous and remote monitoring of vital parameters, added on-demand to nonvital parameters, are tools for healthcare professionals to foster better care.

Conclusion

This scoping review presents a survey of wearable continuous monitoring systems aimed at the health area, focusing on acquiring vital and nonvital signs. In addition, there is an essential search for increasingly portable and preferably multisensory technologies, culminating in savings in health resources and greater patient engagement. It is inferred that the purpose of using wearable electronic devices is to contribute to optimizing and complementingthehumanworkperformedbyhealth professionals, ensuring continuous surveillance and consequent improvement of patient care. It was found that continuous monitoring through including wearable sensors. data analysis and predictive algorithms, added to health interoperability. And it promotes better decisionmaking by professionals, greater assertiveness in decision-making and clinical outcome, better prognosis, and a shortening of the care journey time. Although not to exhaustion, the present study sought to provide a synthesized material capable of supporting the scientific community, encouraging the elaboration and development of new wearable technologies capable of facilitating and maximizing the improvement of decisionmaking in the health area.

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Renegotiations and Disallowances by Health Board for Medical-Hospital Care and High-Cost Procedures from Brazilian Army Health System in 2021

Wagner Elpídio do Nascimento^{1*}, Carlos César Ribeiro Santos¹, Letícia de Alencar Pereira Rodrigues¹, Jonata Souza dos Santos¹

¹SENAI CIMATEC University Center, Salvador, Bahia, Brazil

This article describes the worth of renegotiations and disallowances by the Health Board of the Brazilian Army for high-cost procedures in 2021 from all military regions. Its principal objective is to describe the economy resulting from the values renegotiated and/or disallowanced by the Board. The specific purposes are to describe the renegotiated and/or disallowanced values distinguished from each military region, to mention the primary medical specialties, and list the main reasons for renegotiations or disallowances, suggesting measures to outcome the Brazilian Army's health audit services. It is a retrospective, descriptive, qualitative, and quantitative study. In the results, the 11th, 7th, and 2nd Regions stand out with the highest total values in the authorizations, renegotiations, and denials of 2021. Cardiointervention and Neurosurgery/Neurointervention were the areas with the most significant prominence in values, followed by Orthopedics, Oncology, Urology, and home care. We suggested measures to improve the performance of the Brazilian Army's health audits teams, such as training and continuous education; elaboration and regular updating of the Standard Operating Procedures in audit processes; the exclusive dedication of audit team members, avoiding functional deviations; construction and updating of local market value indicators for orthoses, prostheses, and special materials; use and regular updating of the Brazilian Army's assistance protocols; closer communication between the Board of Health, Military Regions and Military Health Organizations. This article explored the theme; however, further research must deepen and corroborate our study.

Keywords: Health Audit. Medical Audit. Disallowances. High-Cost Procedures.

Introduction

The Brazilian Federal Constitution defines the Armed Forces in article 142 [1] as permanent and regular national institutions whose purpose is to defend the country and guarantee constitutional power, law, and order [1]. In this context, the Brazilian Army (BA) is permanently present in all states and the Federal District to fulfill its attributions. In addition, its contingent is distributed throughout the national territory in 12 Military Regions (MR), which are subordinated to 8 Military Area Commands (Figure 1).

Considering the national scope of BA, it is fundamental for military agents and their

J Bioeng. Tech. Health 2022;5(4):293-304 © 2022 by SENAI CIMATEC. All rights reserved. dependents to have an organizational structure for determined health care with outstanding coverage.

Within this scenario, there is the Army Health System (SSEx, *Sistema de Saúde do Exército*, in Portuguese), responsible for ensuring health care for hundreds of thousands of users, whether they are military (active or inactive), dependents, pensioners or civil servants connected to the Army and their dependents in all Federation units.

SSEx comprises Military Health Organizations (MHO), administratively subordinated to each MR. It is also technically subservient to the Health Board (DSau, *Diretoria de Saúde*, in Portuguese), a technical-normative and managing health support body of BA, located in Brasília - DF, which is subordinated to the Human Resources Department (DGP, *Departamento Geral de Pessoal*, in Portuguese) [2].

SSEx Management Units (SMU) are the Military Organizations (MO) and the MHO. They are responsible for registering expenses related to assistance provided to SSEx beneficiaries and for paying expenses of Civil Health Organizations

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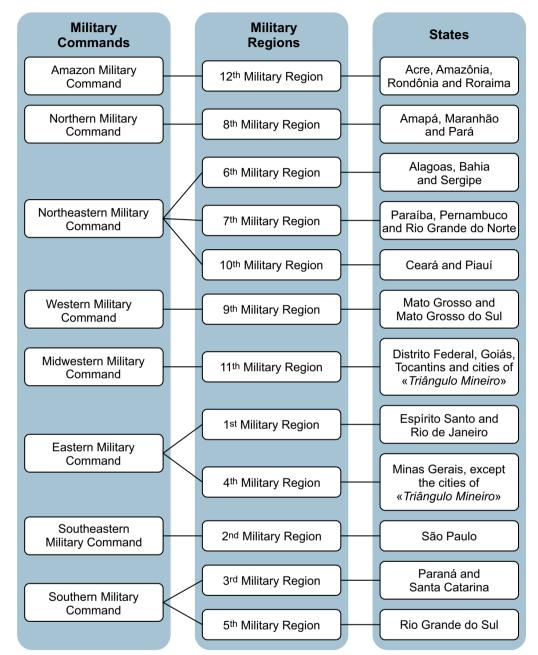


Figure 1. Distribution of the Brazilian army in the national territory.

Source: Lima (2021) [2].

(CHO) and Autonomous Health Professionals (AHP) [3].

The structure of SSEx is hierarchical and composed in increasing order of complexity:

- 1. Medical Posts;
- 2. Garrison Hospitals;
- 3. General Hospitals;
- 4. Region Military Hospitals;

5. Central Army Hospital (CAH) (the unit with the high complexity of the BA, in Rio de Janeiro – RJ).

Still, regarding the structure of the SSEx, there is the Military Hospital of Resende (which directly supports the "A*cademia Militar das Agulhas Negras*"), the Field Hospital, the Military Polyclinics, the Central Dental Clinic of the Army, the Army's Chemical-Pharmaceutical Laboratory and the Army Institute of Biology. Finally, each MO has its own Health Training (Health Section) for essential military assistance.

Figure 2 shows the distribution of MHO in the MRs. Despite BA's extensive MHO network, when the MHO assistance capacity is depleted, the assistance is extended to the network hired, insured, or regionally accredited CHO and AHP [2].

Investing resources in medical hospital care (MHC) in CHO and AHP is crucial for the sustainability of SSEx. Furthermore, the life expectancy increase in the Brazilian population, with a growth in the prevalence of chronic degenerative diseases, medical inflation, and the frequent emergence of new health technologies, leads to a significant challenge in managing the SSEx budget.

In this scenario, auditing health accounts assume fundamental importance for budget control and continuous search for improving SSEx.

The first health audit practices date back to the 1920s, through a retrospective analysis of medical records [4]. The audit concept was proposed in 1956 by Lambeck, who defined it as a mechanism for assessing the quality of care based on direct observation, records, and the patient's clinical history [5].

In Brazil, one of the first official health audit documents was a publication by the Regional Council of Medicine of Paraná in 1983 [6]. In the following years, with the ruling of the Federal Constitution of 1988 and the advent of the Unified Health System (SUS, *Sistema Único de Saúde*, in Portuguese), the audit became a tool used in health care by the SUS, through private health service providers and health insurance [2]. As a result, the law No. 8689, regulated by Decree No. 1651 of 1995, created the SUS National Audit System (NAS) [7].

Regarding BA, the regulation of auditing in health began with the Ordinance of the Army Commander nº 759 of December 20th, 2002, which approved the legal Norms for Implementation and Operation of Medical Ethics Commissions for Review of Medical Records, Medical Bills Compliance, and Hospital Infection Control at the Brazilian Army MHO [2]. Furthermore, article 20 describes the attributions of the commission for the fairness of medical bills [8]:

[...] carry out a technical, ethical, and accounting review of hospital and outpatient bills from providers contracted/accredited by SSEx, to avoid possible distortions, control the quality of services, and, above all, ensure the judicious use of financial resources.

The evolution of the auditing medical bills process in BA led to the publishing of the Technical Standard on Medical Auditing of the Brazilian Army (NTAUMEx in Portuguese) in 2017, which, in article I, guides the procedures of the external and internal medical audit services in MO or MHO under the responsibility of the Management Units [9]. In addition, this norm contains guidelines on the minimum composition of the MU audit teams and their attributions. However, a new NTAUMEX is being prepared, replacing the current one.

This study focused on the audit of BA medical bills, specifically on financial gain obtained by DSau from the renegotiations and the disallowances in the processes of pre- and postaudit for MHC; and high-cost elective procedures coming from all MRs in 2021.

However, considering DSau's renegotiations and disallowances for MHC and high-cost procedures could already be checked at MHO, what measures can be suggested to optimize health audit actions in BA to avoid rework, whether from MHO, MR, or DSau?

This question led us to the principal and specific objectives of this study. We structured this work into four sections:

- 1st Section: Theoretical reference to the theme;
- 2nd Section: Methods;
- 3rd Section: Data analysis with results and discussion;
- 4th Section: A brief conclusion.

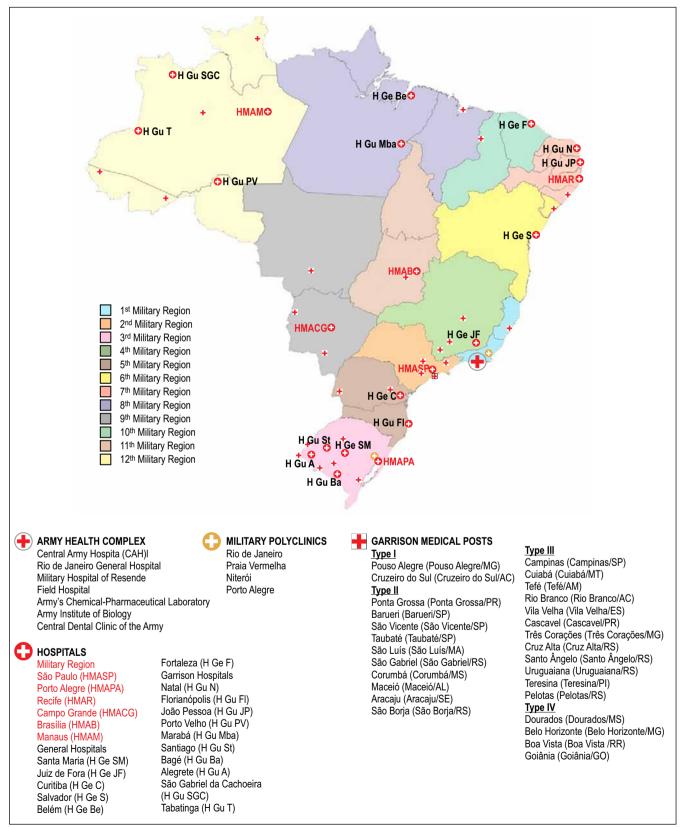


Figure 2. Distribution of Military Health Organizations (MHO) in the Military Regions (MR) in Brazil.

Source: DSau's website. < http://www.dsau.eb.mil.br/index.php/unidades-desaude>.

Theoric References

The work of the Brazilian Army's health auditor is crucial since it contributes to raising the level of user satisfaction, helps the rational and adequate allocation of resources in assistance, minimizes waste, and enhances the effectiveness and efficiency of the SSEx. Furthermore, it enables more investments in the MHO network, increasing its resolution and reducing the need for expenses with CHO and AHP.

Regarding the audit activity, Maia and Paes [10] mention, "The word Audit comes from the Latin AUDITORE, which means the listener who listens. It is the expert in charge of examining accounts. It is the independent assessment and advisory activity of the upper echelon in management [...] addressed to examining and analyzing adequacy, efficiency (the action), effectiveness (the result), effectiveness (the desire; cost/benefit), and quality in health actions, practiced by service providers, under the quantitative (production and productivity), qualitative and accounting (operating costs) aspects, in compliance with ethical and legal precepts.

Maia and Paes [10] also point out that auditing health services are one of the most relevant topics for nosocomial institutions, essential for maintaining the financial sustainability of such organizations.

More broadly, Morais and Burmester [6] argue that a good health audit system should be developed in three major segments:

Operational Audit: Focusing on control and execution of assistance.

Analytical Audit: Focusing on indicators of care processes.

Clinical Audit: Focusing on improving the quality of processes and care outcomes.

They also classified the audits within the operational aspect as follows:

Preventive: Pre-audit, clearance, or prospective audit. An audit that aims to analyze the adequacy of the diagnostic and therapeutic proposal for

each case, according to health guidelines and/or respective contracts for extra health care.

Concurrent: Operative, concurrent, or hospital bed audit. This audit occurs during the assistance and aims to evaluate and adjust the care plan. Retrospective: Post-event, review, or account audit. This audit occurs after a care event and seeks to analyze the adequacy of the care offered.

The Army Ordinance Commander nº 1.585 of October 2, 2019, approved the General Instructions for implementing PASAM [11]. The preface mentions [11]:

[...] The achievement of this Program involves a permanent process of evaluating and certifying the quality of health services, which promotes the continuous improvement of Military Health Organizations based on the priorities: the USER, ECONOMY, and LEGALITY of the actions. [...]

Accreditation is a voluntary process through which health institutions commit to improving the safety and quality of patient care and ensuring a safe environment, reducing risks to patients and professionals.

The constant evolution of techniques and the daily incorporation of new technologies into health services have made hospitals complex. Therefore, it is essential to highlight the constant search for service excellence, focusing on patient safety and administrative efficiency.

It is imperative to bring to the Army Health System these instruments that are being created to guarantee patient safety and quality in health care, strengthening the task of developing its health accreditation system for military assistance.

PASAM has been conducting diagnostic and follow-up visits to all MHOs at Garrison Hospital level or higher, with the perspective of accreditation by the program as of 2023.

After a quick explanation of the current status of the healthcare quality audit in BA, we return to the focus of this study. First, considering SSEx, NTAUMEx defines the stages of activities related to the BA's medical audit services (article 14 and paragraphs) [9]:

I - *Preliminary, Prior or Prospective Audit:* It concerns preliminary analyses and authorizations for requested exams or procedures following the coverage parameters provided in current legislation and Accreditation Terms. This step is essential for releasing exams/procedures of high-cost and elective-base hospitalizations [..].

II - Concurrent or Concomitant Audit: It is about the follow-up and development of hospitalization, involving timely authorizations by the Medical Auditor resulting from daily visits to patients hospitalized in CHO and follow-up of surgical procedures in loco by the auditor to qualitatively/quantitatively validate the OPME used.

III - Retrospective or Posterior Audit: It is about the information that will be analyzed after the presentation of the Invoices and that will allow the formal registration of nonconformities and the monthly entries of the used services in the systems developed or outsourced for this purpose by the Army.

NTAuMEx highlights the accounting of health auditing, especially about authorizations, monitoring, and verification of the assistance provided in the CHO and the resulting medical bills. Lima [2] summarizes it as follows:

[...] for Brazilian military organizations, health auditing is a management tool for contracts with private organizations that provide health services on a regional basis for monitoring and supervising their proper compliance.

It is crucial to know some points of the Brazilian legislation to understand the principal goals of this study.

Considering that the present study handles highcost medical procedures that occurred in 2021, it is opportune to address the rule in force since the definitions of values for high-cost procedures were determined by Ordinance No. 235-DGP of 10 October 2017, after revoked by Ordinance No. 372-DGP of February 14, 2022. Ordinance 235-DGP approved the Norms for Directing SSEx Beneficiaries to the Assistance Unit, CHO, or AHP of another MR or a garrison of the same MR. Figure 3 presents the authorization flowchart for highly complex elective procedures.

According to Ordinance No. 235 in its article 2^{nd} , SSEx beneficiaries may be referred to MHO or CHO from other garrisons or MR if the technical capacity in the garrison of origin is exhausted or when the cost of the procedure in another garrison or MR is lower than that of origin.

For example, the origin - MU FUSEx/MO - can forward high-complexity cases to the reference MU FUSEx/MHO or CHO. However, up to the limit of BRL 5,000.00, decision-making autonomy rests with the MU FUSEx.

For amounts from R\$ 5,000.01 to BRL 20,000.00, decision-making autonomy becomes to the MRs. However, it is still up to the reference MU/FUSEx MHO to quote the more complex procedure with local CHO, MHO, such as CAH, Military Forces Hospital (*Hospital das Forças Armadas* - HFA, in Portuguese), or Militar Hospital of São Paulo Region (*Hospital Militar da Área de São Paulo* - HMASP, in Portuguese).

The last one is for neurosurgical situations and the quotation with the Garrison Medical Center in Belo Horizonte, which has a proper table of values for an orthosis, prosthesis, or unique material – OPME (*órtose, prótese materiais especiais*, in Portuguese) – with better prices than other MRs). Such quotes will support MR's decision, which may handle the patient to another garrison or MR, request OPME renegotiation or authorize the procedure at a local CHO.

When amounts exceed BRL 20,000.00, MR delivers the authorization analysis to DSau, which, in turn, can conduct the patient to another garrison or MR, soliciting OPME renegotiation or authorizing the procedure at a local CHO. It is customary for cases evaluated by DSau to undergo analysis by the technical chamber of the specialty relevant to the requested procedure,

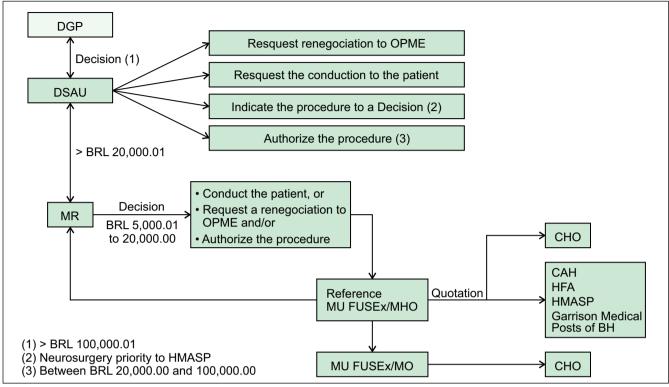


Figure 3. Flowchart for highly complex elective procedures.

Source: Brasil, Ministério da Defesa, Exército Brasileiro, [12].

when necessary, before the decision of the Board. It is essential to point out that, similarly to what happens in RM, the analysis of the DSau must be supported by quotations made previously by the reference MU/FUSEx MHO, responsible for the beneficiary.

Finally, for procedures with values greater than BRL 100,000.00, the decision is up to the DGP, always after listening to DSau, following the exact established quotation.

Materials and Methods

This research focuses on the renegotiations, and disallowances carried out by DSau in the pre- and post-audit processes for MHC and highcost elective procedures from all MRs in 2021. It is a retrospective, descriptive, quantitative, and qualitative research 13].

The data collected came from the control sheet for renegotiations and disallowances of MHC and high-cost procedures from the Regulation and Auditing Division in Health (DRAS, Divisão de Regulação e Auditoria em Saúde, in Portuguese) of DSau. Moreover, the time interval of the data was restricted to 2021.

The variables considered were the final total value of the procedures after renegotiations and/ or disallowances, with the respective returns (\$) obtained per MR and month, highlighting the medical specialties and the higher cost procedures and the principal reasons for savings in renegotiations.

Based on data analysis, this study suggested measures that may improve the audit process of accounts for MHC and costly procedures under SSEx.

Data Analysis

We started with the total amount of MHC and high-cost procedures that were renegotiated or disallowances when analyzed by DSau, and their respective MR of origin (Figure 4). Figure 4 shows the 12 MRs and the total costs for MHC and procedures greater than BRL 20,000.00 in 2021 that were subject to disallowance or renegotiation by DSau. The colorful blocks symbolize each month. We highlighted three RMs: the 11th RM, which had a total value of BRL 3,507,979.00 in 2021, followed by the 7th RM, whose value was BRL 3,468,163.00, and the 2nd MR, with BRL 2,037,886.00.

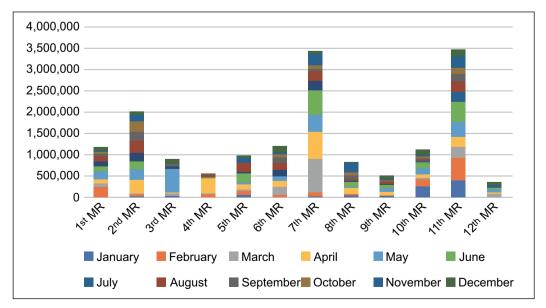
Figure 5 shows the total savings from D Sau's renegotiations and disallowances from MHC and high-cost procedures in 2021 and their respective MRs. The colorful blocks symbolize each month. The first three places are the same compared to Figure 4. However, there is an inversion between the first and second places, in which the 7th MR leads with a value of BRL 906,314.70, followed by the 11th MR with BRL 792,842.60, and the third position goes to the 2nd MR, with BRL 394,102.50.

Figure 6 identifies the MHC or the individual procedure at the highest cost each month of 2021. In April, the 4th RM was the highest value, with a total cost final amount of BRL 334,507.10, resulting from a vascular surgery procedure to correct an aneurysm. This value was the final amount after the disallowance of BRL 50,102.72, referring to

OPME. The 2nd place among the highest costs for single-user MHC came from the 3rd MR, BRL 322,192.60, after savings of BRL 42,498.77 due to adjustments in the billing. It occurred in May 2021 for oncological chemotherapy treatment. The 3rd position of the year came from the 7th MR, in March, BRL 249,297.00, after savings of BRL 42,990.04 in renegotiation, due to a heart valve replacement.

Figure 6 also presents in January 2021, 10th MR, a percutaneous implantation of the aortic valve, BRL 145,727.32, after a disallowance of BRL 38,732.00 in OPME; February 1st, MR, a spinal cord neurostimulator implantation, BRL 168,573.35, after savings of BRL 32,544.00 in the OPME renegotiation; June, 7th, MR, a percutaneous implantation of the aortic valve, BRL 233,760.82, after renegotiation of BRL 7,805.00; July, 1st, MR, myocardial revascularization and an aortic valve replacement, BRL 120,941.09, after disallowance of BRL 3,393.84 of medical fees; August, 2nd, MR, a clinical hospitalization, BRL 143,122.84, after disallowance of BRL 2,979.92, due to a mistaken charge of materials; September, 6th, MR, an endovascular neurosurgery, BRL 141,240.36, after disallowance of BRL 2,539.97 of medical

Figure 4. Total value of MHC and high-cost procedures with renegotiations or disallowances from DSau rin 2021 per MR and month (BRL).



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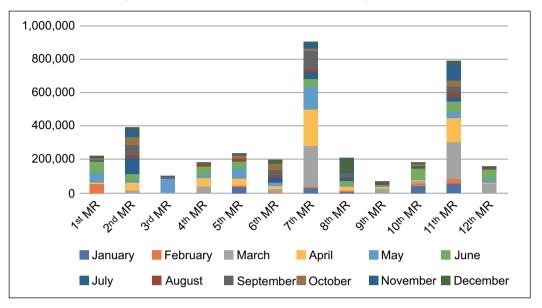
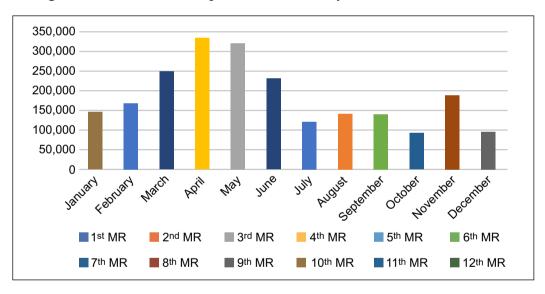


Figure 5. Total value of renegotiation and disallowances by DSau per MR and month in 2021 (BRL).

Figure 6. The highest value of MHC and procedures month by month in 2021.



fees; October, 11th, MR, an implantation of a multisite stimulator by cardiointervention, BRL 92,188.29, after disallowance of BRL 16,446.35 of OPME and medical fees; November, 8th, MR, a clinical hospitalization, BRL 188,450.13, after the disallowance of R\$ 6,000.00 for hemodialysis; and December, 9th, MR, a neurointervention for embolization of a cerebral aneurysm, BRL 97,325.17, after savings of BRL 1,400.00 in renegotiation.

Our results show that the most significant individual expenses in 2021 were cardiology/cardiointervention

and neurosurgery / neurointervention. If we extend the analysis to the total number of MHCs performed in 2021, these medical fields will continue to have high costs. However, other specializations, such as orthopedics, home care, oncology, and urology, deserve attention.

The main reasons for renegotiations or disallowances, both in Figure 6 and in the data set analyzed control spreadsheet of renegotiation and disallowance for MHC and high-cost procedures by DRAS / DSau, there is a clear emphasis on the economy obtained by OPME renegotiations that preceded the authorization to issue the Referral Guide (RG) for the procedures (still in the prior audit), followed by far by disallowances of medical fees (in the prior or subsequent audit), from OPME (in the subsequent) and charge adjustments in other items (in the pre-audit or post-audit).

Despite the 1st MR had the most significant number of SSEx users, it was not among the three highest costs in 2021. It occurs because the 1st MR has the most complex MHO of the SSEx, and HCE, reducing its need for CHO referrals. Regarding the total value of the MHC and highcost procedures of the three MRs with the most expenses in 2021, we observed that, for the 7th MR, the amount saved with disallowances and/ or renegotiations corresponded to 20.72% of the initial value requested for authorization to issue RG, while in the 11th MR, the savings were of 18.43% and in the 2^{nd} MR were of 16.21%. These savings values occurred by DSau's analysis, mainly in the previous audit but, in some cases, in the subsequent audit of the services provided in the CHO and respective MRs. The services had already been audited by the respective MHO involved, but they still reached DSau requiring renegotiations or, in some cases, disallowances.

Santos and Rosa [14] present a study in which they verified disallowances from hospitalized patients during two months of 2012 in a private hospital with 99 beds in São Paulo, Brazil, with about 700 hospitalizations and 150 surgeries per month, it appears that the disallowances made by the supplementary health operator were 11.06% of the total value of the bills analyzed in the first month of the study and 6.21% in the second month.

Comparing our results with those identified by Santos and Rosa [14], there was a lower percentage of disallowances compared to the total amount of invoices. However, while Santos and Rosa [14] analyzed only two months and restricted themselves to the subsequent audit, the current research studied an entire year and the values, both of the previous audit (renegotiations) and later (disallowances and renegotiations). From the analysis of medical specialization that stood out among the expenses of MRs, the predominance was surgical and oncological treatments, followed by home care.

These facts emphasize the importance of checking the DSau's website, in which there are several Protocols and Instruction Booklets (Orthopedics Instruction Booklet, Neurosurgery Protocol, Oncology Protocols, Cardiac Surgery Medical Specialties Instruction Booklet, Oral and Maxillofacial Instruction Booklet, High Complexity Procedures, among others) because these sources are essential to know the SSEx guidelines, on the occasion of the initial analysis of procedures and treatments, within the scope of the MHO and RM.

The results described in this study concern the savings resulting from disallowances and renegotiations. However, such savings could have been directly obtained from the respective MR and MHO involved, avoiding rework and possible economic losses.

Under ideal conditions, the request for authorization for MHC or a high-cost procedure should leave from MHO with the OPME quotations and prior audit, leaving the Dsau with the role of reviewing the process and confirming its compliance, authorizing the RG issue to the procedure. Nevertheless, as we observed in the results of this study, the role of DSau in the renegotiations and disallowances of such procedures is very significant.

Aiming to improve this dynamic, allowing the MHO and the MR with DSau to perform with excellence the work of prior and subsequent audits of accounts, we suggest some measures:

1. SSEx has a peculiar characteristic of turning over its workforce because the staff primarily consists of temporary soldiers. Therefore, even the career ones do not remain in the same MHO for many years. In this way, it is a constant challenge to keep teams trained and updated about the proper execution of processes and tasks. Therefore, MHO managers must establish a training routine for teams, emphasizing attention to newly arrived militaries. In this sense, the role of the audit head sector and other trained members is crucial in establishing standard operating procedures (SOP) and protocols for many processes involving the team's work, doing periodic reviews, and continuing education.

- 2. Another point is the need to keep the audit teams dedicated to their activity, bypassing functional deviations to avoid the accumulation of attributions, and overload, since it can be a decisive factor for the increase in failures and decrease in the quality of work. Strengthening the relationship between MHO, MR, and DSau is very important for conduct adjustments and harmonization, as this allows optimizing mutual knowledge of activities, enabling the understanding of limitations and opportunities for improvement of each other, providing cooperation and improvement of processes, with a reduction in reworking. One way to promote this closer interaction would be to hold periodic face-to-face meetings or videoconferences between the heads of MHO audit teams, MR Health Inspectors, and DRAS / DSau.
- **3.** It is also essential to provide wide dissemination within the teams with the protocols on DSau's website and tools that help to guide the audit. Furthermore, the periodic updating of the protocols is essential for their applicability; therefore, it must be an indispensable initiative of DSau and the BA's technical chambers of medical specialties. DSau should mediate the support of the technical chambers to better guide the decisions of MHO and MR in the prior authorization processes.
- 4. The preparation and updating of databases with indicators, such as OPME prices in the local market, historical series of procedure values, and main reasons for renegotiations and disallowances, among others, are essential measures for the excellent work of several audit teams of SSEx, in its role of advising the management.

Although this study focuses on auditing medical bills, auditing in health is much broader than just accounting. It is also concern to adequacy to standards of quality excellence in assistance. In this sense, a measure that can significantly benefit the quality of the audit work at the SSEx is to bring PASAM closer to the Graduate Course in Auditing in Health Services, as both aims to promote constant improvement in the quality of care for SSEx users.

We cannot forget to point out that the PASAM assessments have served as a subsidy to the evaluated MHO in order to seek and request structural and process improvements by their managers from higher echelons, adjustments in human resources, and new equipment to raise levels of patient safety, quality of care and resolution, which ultimately contributes to the economy and sustainability of the SSEx.

Conclusion

The data collection period corresponds to one year (2021) due to the short-term for the research, which did not allow for drawing a sufficiently reliable profile of values' disallowances historical series, renegotiations, and authorizations for RG in many MRs. Therefore, the theme is far from being exhausted in this work, with space for new studies of similar themes. Although article has focused this on the accounting aspect, it is necessary to expand BA's view of auditing in health. Looking beyond the health accounts by valuing excellence in caring, which also involves cost optimization and sustainability, is a tagline for SSEx. Finally, the SIRE 2.0 system is currently in an advanced stage of preparation by the Center for Development of Systems of BA (CDS, Centro de Desenvolvimento de Sistemas, in Portuguese), which will bring an entire transformation to the Army audit. For example, it will allow an adaptation to the current language of supplementary health operators, indicators' production, integration between the different BA audit teams, a database of principal's recommended tables, and automation of accounting processes, among other benefits.

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Carine Tondo Alves1*, Luciano Sergio Hocevar¹, Jadiel dos Santos Pereira¹,

Maria Cândida Arrais de Miranda Mousinho²

¹FederalUniversity of Bahia Recôncavo; Recôncavo, Bahia; ²Federal Institute of Science and Technology; Salvador, Bahia, Brazil

The Brazilian electricity matrix, with a higher percentage of renewable sources than the world matrix, stands out in hydroelectric generation, an advantage or vulnerability depending on the rainfall regime, the volumes of the reservoirs, and the need to activate the thermoelectric plants. This work analyzes technical, economic, and the management aspects related to decisions about the composition and use of the Brazilian electricity matrix. The method was fundamentally based on the literature review. We seek answers about energy availability to meet Brazilian demand and whether government decisions can be considered the most appropriate. We analyzed the Internal Electricity Supply in Brazil since 1970, crossing it with data on population growth and GDP growth, comparing it with the evolution of the installed capacity of energy generation.

Keywords: Water Resources. Brazilian Electrical Matrix. Thermoelectric Plants. Planning.

Introduction

Energy can be understood as a fundamental means of satisfying human needs. Its use is intrinsic to the access and use of natural resources and with environmental issues, highlighting the challenges and complexity of this intertwined relationship, in contemporary times, in an energy crisis.

Access to energy resources is a crucial challenge because, despite the growing use of energy, millions of homes still need access to essential energy services. Concerning environmental issues, the increase in CO_2 emissions from fossil fuel combustion in the last thirty years (1990-2020) can be highlighted [1]. Also, the global energy demand will increase [2-4], and countries considered emerging as Brazil will play a relevant role in the energy transition process.

The challenges mentioned earlier will make choices for alternatives to traditional sources of energy production emerge, and the Sustainable Development Goals (SDGs) proposed by the United Nations will help to increase renewable energies in the global energy matrix.

The global challenges linked to the energy issue, and considering the role of hydroelectricity, this work has the main objective of presenting an overview of energy planning, analyzing technical, economic, and the management aspects of the composition and use of the Brazilian electricity matrix. We considered two questions in this paper: whether Brazil will have electricity available to meet its demand in the coming years and whether the decisions taken throughout 2021 can be evaluated as adequate considering the technical and economic aspects. This work is divided into two sections in addition to the Introduction. The first one analyzes the Brazilian energy profile and compares it with other countries. The second section analyzes data on the growth of domestic electricity supply, resident population, and gross domestic product.

Brazilian Energy Profile

Brazil was the sixth largest energy consumer in the world in 2020, with 2% of global consumption, and second in the Americas, behind only the United States, with 10%. The country produced 324 Mtoe in 2020 or about 2% of what was produced worldwide [1].

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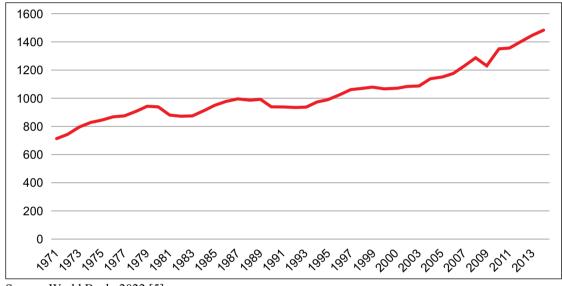
The use of energy per capita in Brazil doubled from 1971 to 2014. However, the country suffered fluctuations in this period, especially after 1979. It increased in 1984, with a new drop in 1990. New growth occurred between 1993 and 2009 when energy use fell again and intensified the following year (Figure 1).

Fossil fuels play a leading role in the Brazilian energy matrix, with about 60% of the

representation. Brazil's total energy consumption converges around oil, natural gas, and coal. In 1973, the Brazilian energy matrix showed a consumption of 82.2; in 2020, this consumption was 286 Mtoe [1].

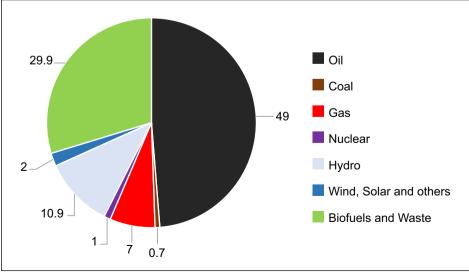
In 41 years, the Brazilian electricity matrix presented an annual growth rate of almost 6%, from consumption of 65 TWh to 624 TWh, with hydraulics being the most used source since the

Figure 1. Evolution of energy use in Brazil (kg of oil equivalent per capita) (1971-2014).



Source: World Bank, 2022 [5].

Figure 2. Brazilian energy matrix, 2020.



Source: IEA, 2021a [6].

1970s, before with 90% and now with 63% of Brazil's electrical matrix (Figure 3).

In the context of the production and consumption of the principal non-renewable energies, we noted that CO₂ emissions had increased consecutively for over thirty years [1] (Figure 4).

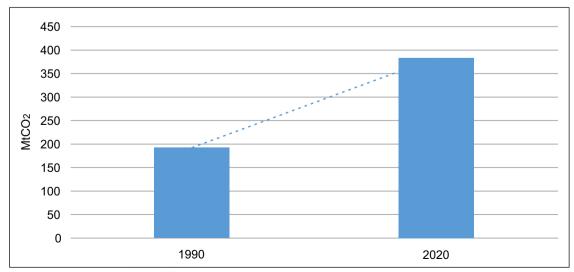
The current global hydropower generation capacity is estimated to be 1,150 GW in total, with China (326 GW), Brazil (109 GW), Canada (81 GW), the United States (80 GW), Russia (48 GW) GW) and India (45 GW) together accounted for around 60% of the world's installed capacity. Global hydropower generation in 2019 was 4,306 TWh, an increase of 2.3% over the previous year. New increases were made or incorporated into the installed capacity in several countries in 2019, among them Brazil, which stands out with the highest percentage of increase (4.9%), having gone from 76 GW in 2007 to 109 GW in 2020 [8-11]. Adding five GW to the Brazilian hydroelectric generation capacity represents almost a third of the global additions, the majority related to the

2.6 Oil Coal 9.6 Gas 3.4 Nuclear 1.6 63.5 Hydro 0.06 Solar PV 0.3 8.9 Biofuels Wind Waste 8.7 Others 1

Figure 3. Brazilian electrical matrix, 2020.

Source: IEA, 2021b.

Figure 4. CO₂ emissions in Brazil (1990-2020).



Source: ENERDATA, 2021 [1].

final six turbines added to the Belo Monte plant, completing 11.2 GW. At the end of 2019, Belo Monte became the fourth largest hydroelectric plant in the world, representing 7% of Brazil's electricity generation capacity. At 418 TWh, Brazil's hydroelectric production has remained unchanged since 2018. Despite Brazil's seemingly robust market in 2019, the country's incremental hydropower development increasingly is constrained by available resources. Furthermore, only 12 GW are in areas with no ecological or social restrictions. This remaining potential is further limited by sociopolitical limitations and the environmental costs associated with development, estimated to be an order of magnitude higher than typical for wind and solar PV in Brazil [10].

According to the National Energy Balance 2021, the Brazilian electricity generation matrix is composed mainly of renewable sources (85%), at a much higher level than the world matrix (23%) [12]. The same document also informs that the hydraulic source occupies a prominent place among renewables, with 65%, followed by biomass and wind, with 9% each, and solar, with 2%.

Considering its dependence on the rainfall regime, hydroelectric power generation can be a vulnerability of our electricity matrix, especially in periods of low rainfall when the volume of reservoirs decreases.

Analysis of Growth Data (OIEE, Population, and GDP)

According to the BEN – Historical Series [13], the installed capacity for power generation increased from 33 GW in 1980 to 74 GW in 2000 and 175 GW in 2020. The population was 122 million in 1980, to 175 million in 2000, and reached 213 million in 2020 [14]. Analyzing the data on the Internal Electricity Supply – OIEE in Brazil, population growth, and GDP, it is possible to establish an OIEE / GDP / inhabitant ratio and compare it with the evolution of the installed capacity for energy generation (Table 1).

From 1980 to 2020, the Domestic Electricity Supply - OIEE grew almost five times, while the Gross Domestic Product - GDP and the Resident Population grew twice. As a result, the OIEE/ Pop ratio grew almost three times over the same period, and the OIE/GDP was approximately twice. In other words, the OIEE always grew more than the indicators related to Demand, such as Population and GDP.

The demand for electric energy without significant mishaps, as demonstrated by the OIEE, can be known by planning and observing the rainfall cycles; regional characteristics; the amount of water that reaches the plants, converted

	Installed Generation Capacity (GW)	Internal Electric Energy Offer - IEEO (GWh)	Gross Domestic Product – GDP (10 ⁹ US\$ppc (2010))	Resident Population (10 ⁶ habs)	IEEO/POP	IEEO/GDP
1980	33.472	139.170	1.298	122	1.142	107
1990	53.050	249.358	1.517	150	1.665	164
2000	73.671	393.259	1.953	175	2.251	201
2010	113.327	550.447	2.804	196	2.812	196
2020	174.737	645.915	2.858	213	3.039	226

 Table 1. Internal Energy Supply/GDP/Population.

Source: Prepared by the authors from EPE data (BEN – Historical Series) [13].

into energy (or Affluent Natural Energy – ENA); and the various generation modalities available in the National Interconnected System – SIN, and managed by the National Electric System Operator – ONS.

However, a fact that draws attention is that, despite the increase in the OIEE, hydroelectric generation has not followed this growth, due to the unfavorable volume of rainfall, with rainfall rarely above the historical average, indicating a tendency for scarce rainfall.

The importance of planning is revealed since the models that define the dispatch of the plants to meet the demanding work with the rain projection scenarios can decide, through the Electric Sector Monitoring Committee (CMSE – *Comitê de Monitoramento do Setor Elétrico*, in Portuguese), when dispatching thermal plants to adjust supply/demand relationships.

In the Minutes at the 242nd Meeting of the CMSE held on July 12, 2020, ONS informs that "there were no significant volumes of rainfall in the main basins of interest to the SIN, from the point of view of electric energy generation" in November 2020. Moreover, continuing: "storages of 17.7%, 18.3%, 52.2%, and 28.9% were verified in the Southeast/Midwest, South, Northeast subsystems and North, respectively, evidencing the impossibility of starting the recovery of the storage of the main reservoirs of the SE/CW and South, contrary to the expected behavior for the beginning of the typically wet period" [15]. However, there was relevant information about the reservoirs' condition and the rainfall regime in the following months, which should have led to decisions that were appropriate to the gravity of the situation.

Available data from the SIN's Equivalent Volume show that the historical series from 2014 to 2021 has resulted in between 29% and 42% for December [16].

ANA – National Water Agency publishes regular and periodic monitoring of the drought situation, whose consolidated results are published through the Drought Monitor Map. In addition, monthly information on the situation of droughts is made available up to the previous month, with indicators that reflect the short-term (3, 4, and 6 months) and long-term (12, 18, and 24 months), indicating the evolution of the drought in the region [17]. The Drought Monitor consolidates the technical and scientific knowledge in a different state and federal institutions in a standard document containing information on drought conditions (severity, temporal and spatial evolution) and impacts on the different sectors involved. The Monitor facilitates the translation of information into tools and products used by decision-making institutions and individuals to strengthen Monitoring, Forecasting, and Early Warning mechanisms, a valuable tool to aid the management of water resources and energy planning.

For 2021, the Drought Monitor showed that in the Northeast Region, January, February, and March had a worsening in the drought condition, a condition intensified with a worsening of the drought in May, June, July, August, September, October, and November. The same Monitor shows a worsening scenario in the Southeast Region, with a drought worsening in January, February, March, April, May, June, July, August, and September.In the South Region, rainfall below average worsened the drought in the three states in April, May, July, August, November, and December. Finally, in the Midwest, there was an advance of severe drought in January, March, April, May, June, July, August, September, and October, in addition to the persistence of the intense drought scenario, as a result of accumulated rainfall deficits in the long term. more than 12 months.

Final Considerations

The analysis of the available data and their correlations showed that the supply of electric energy, characterized by the Internal Electricity Supply – OIEE, has always been more significant than the demand. It is inferred by the increase in

the resident population and purchasing power, thus by the consumption power obtained by the evolution of the Gross Domestic Product - GDP. Even the OIEE/Resident Population and OIEE/ GDP ratios show favorable rates for the growth of the OIEE. Therefore, there is no growing demand for electricity that exceeds the supply. However, the OIEE needs to be managed, as it is composed of several sources, with a predominance of hydropower. The management of water resources alternation between hydroelectric with an and thermoelectric generation can be done preventively, taking into account the indicators published by ONS, SIN, EPE, and ANA. Having ruled out the technical causes for a possible but unlikely electricity supply crisis, it remains to investigate other causes, such as decision-making and administrative ones.

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Technologies Involved in the Material Storage Processes

iterial Storage Processes

Daniel Rodrigues dos Santos^{1*}, Carlos César Ribeiro Santos¹, Vitória Almeida de Araújo¹, Leandro Henrique Araújo Mascarenhas¹ ¹SENAI CIMATEC University Center; Salvador, Bahia, Brasil

Technological advancements in storage logistics have been gaining strength and bringing benefits to companies. We highlight the automation of operations and the optimization of storing materials' process. However, it is still perceived nowadays that several companies need to use these technological benefits, providing a direct reduction in their organizational competitiveness. This work aims to analyze the impacts of technology's absence in companies' processes of storing materials. We used bibliographical research to visualize the reason for the non-investments in technologies in the storage processes. The results revealed that companies that make technological investments in the storage of materials obtain a significant cost reduction and productivity improvement, eliminating work's repetitions, improving the internal processes, and turning the operations into a continuous flow model. Therefore, it is crucial to invest in technologies to obtain these results. Keywords: Storage. Technology. Optimization.

Introduction

Modern logistics demand that all activities within a company be done at the right time and the right moment with the lowest cost. So, logistics can be defined as managing finances, people, materials, and information flow to satisfy the customers' desires.

Within the scope of logistics, the storage area has unique importance because it is responsible for receiving, storing, and dispatching various products, raw materials, and inputs, among others, to meet the needs of internal and external customers. Therefore, more administration in the storage process is needed to avoid a mismatch of information, customer dissatisfaction, excess or lack of products, and a failure to control warehouse inputs and outputs.

There are several technologies and/or technological tools to mitigate problems in the storage area, such as Warehouse Management

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System (Warehouse Management System); Radio Frequency Identification (RFID); Picking by Light; Picking by Voice; among others. Based on the above, the problem of the present work is: how does the lack of investment in technologies affect the processes of storing materials? In this sense, the general objective is to analyze the impacts of the lack of technology in the storage processes of materials. Moreover, the specific objectives are: to define storage logistics and its activities, list the principal technologies involved in the processes of storage of materials, and demonstrate the impacts of the absence of technologies in the storage of materials.

Storage Logistics

Storage is the management of products received, stored, moved, and shipped from a location, whether raw materials or finished or semi-finished products. As it is an important area in logistics processes, it is necessary to have efficient and qualified management in this space, good organization, correct addressing, product labeling, and a place to move the materials and equipment used for storage.

For efficient storage logistics, it is necessary to have good planning and control in performing operations, which products will be stored and managed, who the customer is, and which operation

Received on 10 September 2022; revised 22 November 2022. Address for correspondence: Daniel Rodrigues dos Santos. Rua da Floresta, 28 – Casa – Santa Cruz – BA, Brazil. Zipcode: 41905-770. E-mail: danielcfj@hotmail.com. DOI 10.34178/jbth.v5i4.256.

will be used at the time of shipment of the materials. The main advantage of a storage structure is to generate better use of space. According to Paolheschi [1], it is necessary to have minimum rates of breakdowns, ease of movement of products, and good inventory evaluations, providing cost reduction and improving its efficiency when serving its customers. The disadvantage is the financial value applied in this structure and expenses with administrative processes.

The main advantage of a storage structure is to generate better use of space. According to Silva, the objective of the warehouse is to reduce handling and the time spent on handling because this activity adds cost to operations but does not add value to the customer. The ways to move products in a warehouse vary from someone manually loading an item to computerized equipment that separates the item and places them on automated conveyor belts.

In addition, warehouse operations also use forklifts, pallet trucks, and conveyor belts, among other equipment used to transport products. The choice of handling equipment should be determined according to the following variables: route to be traveled, frequency of movement, the internal environment of the warehouse, and the direction of flow [2].

So, storage is a meeting of receipt of goods to store and ship finished or semi-finished products, organization of space, and administration of this so that there are no losses or customer dissatisfaction. Moreover, an advantage is the better use of space, and a disadvantage is the high investment to acquire these structures.

Thus, storage is also the conditioning of finished and/or unfinished materials, which follow steps such as receiving, checking, storing, and picking, among others, making it meet the demand and satisfy the final customer. In this sense, in the storage area, there are routine activities so that the materials are stored and shipped correctly; these are: receiving goods, in which the operator checks the documentation, the quantity, and the quality for later the goods to be stored using the appropriate handling equipment and the structure as well. As orders are placed for the area, the picking activity is initiated. It consists in checking the list of materials, separating them according to characteristics and destinations, and then packaging, generating the documentation, and placing them in the shipping area. The expedition is responsible for ensuring that the products are sent to their respective destinations at the right time and in the correct quantity.

Thus, storage is a place to store goods and the separation sequence of these items. There are steps such as receiving, checking, storing, retrieving, separating, packing, and shipping to ensure the minimum possible error.

<u>Main Technologies applied in the Process of</u> <u>Storing Logistics</u>

Managing stock is always a challenge. An organization with a large mix of products will need help with receiving, checking, storing, warehousing, retrieving, separating, shipping, and turnover of these items. Using information technology in these processes is a great option to reduce failures. A warehouse management system can guarantee the quality and speed of information, optimizing storage logistics. Warehouse Management Systems (WMS) are the primary tool used in logistics activities. A company with large flows of incoming and outgoing products must use this vital management tool.

The WMS is a warehouse and/or DC management system that optimizes all operational activities (material flow) and administrative (information flow) within the warehousing process, including activities such as receiving, inspection, addressing, storage, separation, packaging, loading, shipping, issuing of documents and inventory control [3]. Some of the main advantages of implementing the WMS tool are:

- Greater control of storage and inventory information;
- Reliability of information;
- Productivity control;

- Control of tasks performed by employees;
- Inspection and quality control;
- Inventory control;
- Resource planning and allocation.

Implementing a system of this complexity also has its disadvantages, among them are:

- Specialized labor;
- High investment in equipment;
- Integration with other systems;
- Long implementation period;
- Resistance from employees.

Besides the WMS, another software widely used in logistics operations is RFID. RFID technology is based on labels that work as chips, carrying product information. This data is captured by antennas that work as a reader. With the deployment of this information technology, the company gains more productivity of its employees, time and money savings, elimination of errors, more accuracy in the control of logistics processes, and security from claims and losses by customers, suppliers, and employees.

The RFID tool was developed to obtain better efficiency in tracking and locating products and physical assets, assisting inventory management, and also helping to increase productivity, thus making companies more competitive. To improve picking and reduce picking time, Picking by Light and Picking by Voice technology avoids paper lists and drastically reduces picking errors. Furthermore, companies need to decide which technologies suit their business and, from there, find the best way to use them to achieve competitive advantage.

Impacts of the Absence of Technology in the Storage of Materials

The constant race for the excellence of services that please the final consumer has impacted companies and organizations in the logistics sectors that seek to automate daily. Modernizing is essential for the company to seek to please its customers.

According to a survey conducted by Totvs disclosed by CIMM [4], it reveals that Brazilian industries still need to invest more in technology to support their logistics management. The industries appear among the shippers. It occurs with 84% of 740 companies heard between national and multinational, with revenues above or equal to R\$5 million. However, the vast majority of industries have departments to take care of transportation management (97%) and storage (94%). However, in the same research, these sectors are not yet equipped with technology to support their activities, i.e., only 25% claim to have a transport management system and 42% a storage management system. Both results are below the average of the other shippers interviewed by the study (agribusiness, retail, and distribution). The use of technology is essential without the use of this tool, the number of errors and human failures in the processes will be high, which generates rework and more time for the execution of activities. For example, using the WMS system is essential in storing products because reading a particular product will determine which address it will be stored, containing the correct address, lot number information, reference, and bar code of the same. Thus, without this information, the number of errors is much higher. The storage of a product would be random, with the correct address where it will be stored, with the need for more information about the product type. It would lead to errors in separation, delayed delivery, stock-outs, and dissatisfaction of the end customer, which would generate financial losses for the company and low competitive power in the market.

So, it is essential for companies that wish to reduce costs, and time of execution of activities, among others, to use technologies.

Materials and Methods

This study utilized bibliographical research to visualize the reason for the noninvestment in technologies in storage processes, analyzing what authors have to say about and, thus, comparing these causes and effects. For Gil and Colleagues [5], the bibliographical research is a process that involves the stages:

a) Choice of topic;

- b) Preliminary bibliographical survey
- c) Problem formulation;
- d) Elaboration of the provisional subject plan
- e) Search for sources
- f) Reading the material;
- g) Summarizing;
- h) Logical organization of the subject; and
- i) Text writing.

The search for articles about "storage logistics" and "technologies involved in the process of storing materials" was carried out from 2000 to 2022. Figure 1 shows the materials used (11 articles, 2 theses, 3 books, and 1 news site related to the title.

Results and Discussion

This study demonstrated that technologies change the aspects of companies, making them competitive in the marketplace because this process information will be constantly updated, leaving the production without mismatches of information, whether in the storage, receipt, storage, separation, or transportation of materials. The search for implementing ways to automate processes with investment in information technology in the logistics area has become key to the growth of companies.

Subsequently, we realized that the Warehouse Management System is the technology that can more efficiently meet an inventory because of its ease in meeting the storage processes, leaving the entire sequence informed as to what is happening in the receipt and dispatch of goods. Using technology in storage brings cost reduction, competitiveness, and satisfaction to the final customer. On the other hand, the lack of technology in storage processes means that the operation needs to control what is happening in the processes, causing failures, and disorganization, among others.

Finally, the results of this research contributed to the understanding that, with the advancement of technology, companies need to keep up with this evolution to satisfy their final consumer, becoming agile in the deliveries and having productivity.

Conclusion

After all the analysis, it was possible to verify that the absence of technology in the storage process brings problems that affect the supplier, the production chain, and the final client. For efficient

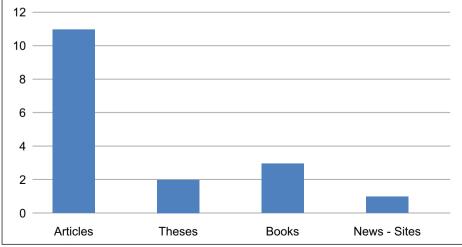


Figure 1. Theoretical reference.

Source: Authors.

storage, several types of structures go according to the company's needs. Storage, as seen, is the management of products (inputs, finished or unfinished) with activities to be followed so that they get to the final consumer.

The research had its objective reached, and it is clear that there is much to be explored on the subject, one of them being the types of structures, their functionality, how much they support, and other technologies to be explored. For example, RFID is a technology that works through chips, thus being able to gain agility, accuracy, deviations, and others, which works processing data and the WMS, which controls the entry and exit of goods or inputs, providing a decrease in delays, low productivity, deviations, among others.

In addition, this research used a bibliography to define storage logistics, describe the activities of the storage area, list the principal technologies involved in storing materials, and demonstrate the impacts of the absence of technologies in storing materials. The question was: how does the lack of investment in technologies affect the processes of warehousing materials? It was based on the analysis of other authors on the subject. As an advantage of using technology, companies can have reliability in processes and inventory, information being updated all the time, and greater access to the quality of the products that arrive.

The results revealed that by reducing costs and improving productivity, they are able to eliminate the repetition of work due to human error during processes and leave operations more fluid. However, other studies can be conducted to identify, for example, the degree of technological maturity of companies in Brazil, and the use of technology in other crucial activities in companies (production and transportation), among others.

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Ethics Applied to Development in Robotics

Tiago B. Sant'Anna^{1*}, Marco A. dos Reis^{1,2}, Roberto L.S. Monteiro²

¹Robotics and Autonomous Systems Competence Center; ²Computational Modeling and Industrial Technology Program; SENAI CIMATEC University Center; Salvador, Bahia, Brazil

Technology is increasingly present in everyday life. With this, there is an increase in the interactions between men and machines. As a result, ethical dilemmas arise. These ethical dilemmas occur both as a consequence for the developer and as part of the machine's problems. However, one can affirm that the moral differences between citizens interfere with how to solve these dilemmas. Furthermore, these ethical differences can be collected and used to model machines based on ethics. Thus, this work aims to study the relationship between ethical values and robotics, both in the development of new technologies and in the decision-making of machines. Thus the importance of ethics in technological development becomes evident.

Keywords: Artificial Agent. Ethical Issues. Robot Ethics. Machine Ethics. Moral Machine.

Introduction

From vacuum cleaners to virtual attendants to autonomous cars. the modern world is one in which humans increasingly use technology in their everyday lives.

According to the International Federation of Robotics [1], the market for robots performing services will grow 12% from 2020 to 2021, which will be a \$6.7 billion mark worldwide.

The interactions between humans and machines will become more and more indispensable. However, increasing these interactions may grow ethical dilemmas for consumers and developers.

Thus, as man-machine relations are inevitable, ethical dilemmas must be thought through and solved as soon as possible to minimize their damage. Thus it is necessary to understand how ethics relates to developing these new technologies in all spheres. Therefore, this paper proposes to study the relevance of ethics in the development of robotics and elaborate on the development of machines that make ethical decisions, such as autonomous

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cars. Moreover, it also seeks to elaborate on the development of technologies that could hurt ethical values or generate new dilemmas.

Materials and Methods

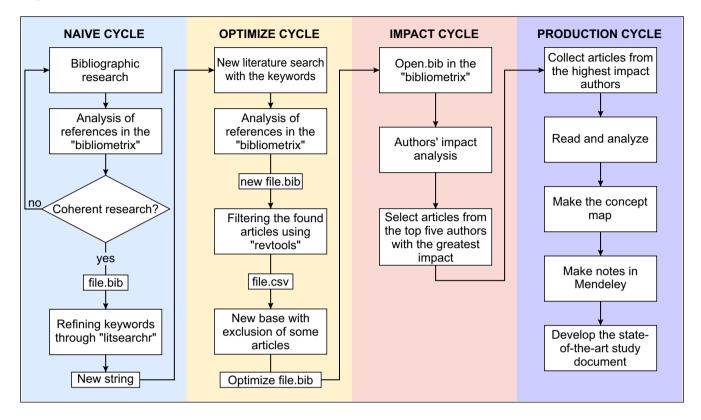
The work developed consists of applied research on the relationship of ethics in development in robotics. Thus, it starts from a qualitative approach to the problem, being analyzed from several points of view.

We did a bibliographic review of articles related to the central theme of the research. The research was carried out using the bili method [2] to start from an objective general for a specific objective and find the articles most relevant to the topic. Figure 1 shows that the research method comprises four cycles: naive, optimized, impact, and production. These phases consist of statistical analysis to define a research focus, analyze its relevance and find the most important articles.

Using the Scopus site, a search was made using keywords related to the subject of ethics in robotics. The articles were collected, and a bibtex file was generated. This file was placed in a tool called Bibliometrix. This tool was used to analyze this file. With Bibliometrix, the annual scientific production was first analyzed, showing the number of articles published yearly and a growth of 16.36%. Next, the co-citation network was analyzed, where it was verified if the articles were related to each

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Figure 1. Bili method.



other. After that, the historiographic and word cloud were analyzed. It was observed that the word cloud contained words that did not make sense with the theme.

This project stage was repeated a few times until consistent results were found. Then, with these results, the lit search was used to refine the results further. Figure 2A shows an annual growth of 30.26% was arrived at, with an even more intertwined co-citation network (Figure 2B), and now with a word cloud without words that had no connection with the theme.

This new file is opened again in the Bibliometrix, where authors with the highest impact are selected. With that, its articles are selected and read in the next step.

At this stage, the articles with the most significant impact are studied, producing concept maps and annotations of each article. Finally, it generates a study document state of the art, and the article begins to be written.

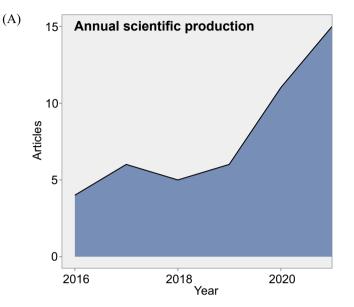
Results and Discussion

How Ethical Issues Impact Technology Development

Our society has depended on hundreds, if not thousands, of automated systems, processes, and robotic systems. For example, we fly in airplanes that fly themselves. Our power grid can reroute itself to avoid power outages. Nevertheless, it leads us to expect these systems to be reliable and safe and to do what they have been programmed to do and nothing more.

The machines that are in focus in this article will need to be able to make decisions based on three essential points:

- Using and processing large amounts of data;
- Understanding and using human relationships and behaviors, and
- Considering in their decision algorithms the social rules of society, such as customs, laws, and values that humans use to relate to the real world.



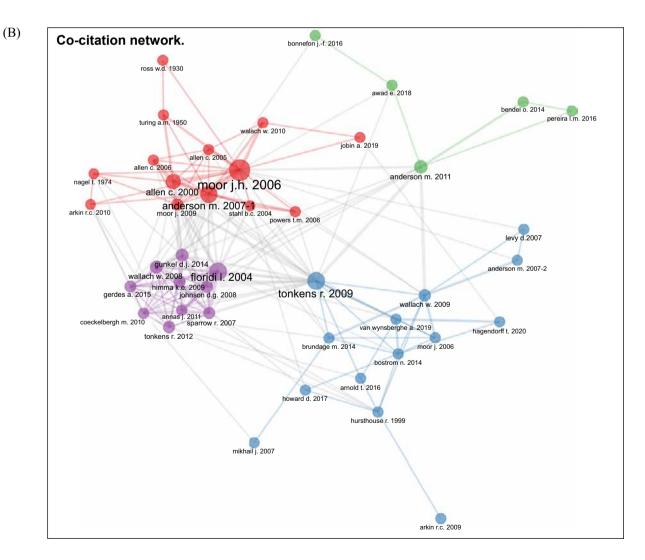


Figure 2. Bili method results.

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These machines should be able to figure out the "right" thing to do in real-time to deflect a moving pedestrian, perform a life-saving surgical maneuver, or distinguish friendly citizens from enemy soldiers in a war zone, all without a helping human hand. The tricky part of designing robots is considering what people say they want a machine to do and what they want it to do.

If we ask people if they want robots to be 100% truthful, everyone is likely to start saying yes. Nevertheless, we know from psychological studies that if a robot is 100%, people start to resent it [1,2]. Designers, therefore, need to consider giving it a range of truthfulness-not unlike our own. Robotic systems will also need to show some more reliable ways. We will be much more likely to trust machines that can explain their intentions and ask our permission before they undertake their work. Also, another vital part of the development of robotic systems will be the integration with the fields of psychology, sociology, linguistics, and anthropology. Otherwise, a wide range of scientists better understand the nuances of what makes us trustworthy and reliable in our different roles.

Technologies Aimed at the Organizational Scope

With technological advances, companies will undoubtedly want to use these technologies to increase productivity and production. With that comes investments in industrial automation [3] and people management. Thus, new technologies aim to increase this productivity.

However, Telkamp and Anderson [4] used artificial intelligence to monitor employees and it raises ethical questions about these practices generating abuse. Amazon has already applied the creation of systems that monitor employees, but there is no lack of reports that these practices are abusive to employees [5,6].

Technologies with Foresight

In the study by the University of Chicago, machine learning is used to predict future crimes through areas of incidence [7]. Although carrying out the prediction of crimes is very positive for society, other problems can be generated. For example, the government may collect personal data to improve the forecasting system, injuring its privacy.

Machines that Make Ethical Decisions

Due to the use of artificial intelligence and the increasing automation of machines, devices are increasingly responsible for more significant decision-making. However, this decision-making can carry a vital moral aspect. As in dilemmas with self-driving cars or in triage hospitals. So machines need to have a moral basis in them to make decisions. The need to analyze the ethical thinking of machines arises when robot decisions with a high level of autonomy can negatively impact human life. One of the ways to solve this type of problem is to train artificial intelligence with the capacity for ethical thinking.

Graham and colleagues [8] showed that just because a robot is in a situation of ethical conflict, it does not need to be a moral machine. This issue can be resolved with algorithms without the need for ethical judgment. With that, then, ethics in robotics can be separated into two main branches: those that need moral machines or those that only need algorithms that work with ethics. The problem with working with moral values is that they vary from person to person. Therefore, communities or groups may perceive measures differently from others. For example, in the case of an AI model that makes choices about what a car will crash if the brakes fail, people may realize that newer ones should be prioritized. In contrast, other people may think this is a form of discrimination and that this choice should be random [4].

According to the Moral Foundations Theory [9], people differ on six main moral foundations: care or prejudice, honesty or dishonesty, loyalty or betrayal, authority or subversion, purity or degeneration, and freedom or oppression. These variations can generate conflicts about decisions on a given moral problem. There are different worldviews conflict with the same moral dilemma (Table 1). Thus, it is essential to consider how the population will receive certain algorithmic decisions. It is interesting to study them to know how most people perceive them. In this way, a study was carried out by asking people about what would be the best decision to make in the case of the autonomous car.

Figure 3 presents the results of a study that asked people from about 130 different countries. From these results, it is possible to observe the majority's preferences concerning the common trade-offs in this situation.

After these conclusions, the data obtained can be used to model artificial intelligence that follows this type of information. A work using this same database managed to develop artificial intelligence that makes decisions based on already established moral values.

Figure 4 shows the result of the data obtained by the artificial device compared to different sizes of databases. Showing how the prediction model has good accuracy.

Conclusion

From the article presented, it is possible to show the power that technological advances generate in ordinary life. However, to minimize the problems that future machines may cause, one must have a look based on ethics. In the first position, it is observed how the development of new technologies can be harmful, and with that, the developers must analyze the impacts of their projects well. In addition, ethics impact the production of algorithms that work together with human life. Thus, the importance of ethics in technological development is evident. The areas that work with research and development must act to solve this type of problem because this area generates projects that significantly impact social life.

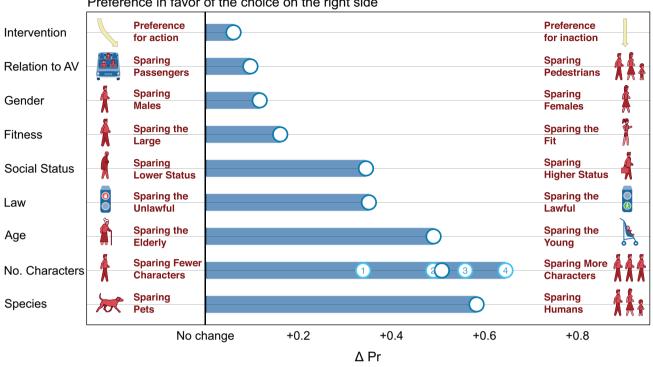
Acknowledgments

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AI issues Conflicting concerns based on moral foundation				
	Authority—Save respected members or leaders of the community over those who are at the bottom of the hierarchy. Prioritize law-abiding citizens over those who are breaking the law (e.g., someone jaywalking)			
An Alexatom's desision of	Care—Prioritize children first and attempt to reduce the overall number of people injured or killed			
An AI system's decision of whom or what to crash into when the brakes fail on a	Fairness—Do not consider characteristics such as age or status and instead, randomly pick the outcome			
self-driving car	Loyalty—Protect the vehicle's passengers at all costs because one family member or friend is more important than several out-group members			
	Purity—A self-driving car in and of itself is morally wrong because human judgment is sacred			

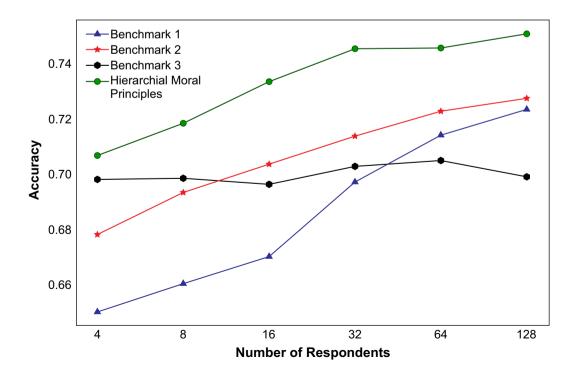
Table 1. AI issues involving moral foundations [4].

Figure 3. Results of the moral machine experiment [10].



Preference in favor of the choice on the right side

Figure 4. Comparison of model results with research [11].



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A Survey on Humanoids Robots: Perception, Mechanism, and Control

Juliana Maria S. de Santana^{1*}, Vagner dos S. da Silva¹, João Gabriel da A. Calmon¹,

Marco A. dos Reis², Roberto L.S. Monteiro²

¹Robotics and Autonomous Systems Competence Center, ²Computational Modeling and Industrial Technology Program, SENAI CIMATEC University Center; Salvador, Bahia, Brazil

Anthropomorphic robots, also known as humanoids, have a structure based on the human body, with limbs and movements designed for better mobility that allows the robot to perform various tasks, mainly to assist people in daily activities, for entertainment, or to perform risky tasks. The development of this document aims to present some of the results obtained in the research conducted on the state-of-the-art study about humanoid robots based on some of the main articles related to their study, highlighting some of their characteristics of perception systems, control, and physical configurations.

Keywords: Anthropomorphic Robots. Humanoids. Biped Locomotion.

Introduction

Anthropomorphic robots, also known as humanoids, possess attributes similar to the human form, such as heads, arms, and legs. They can therefore be bipedal, allowing them to maneuver in uneven terrain. These characteristics are essential since more than 50% of the earth's surface is inaccessible to traditional wheeled vehicles [1]. In addition, they offer other advantages, such as turning around their own body by rotating their feet and having free hands for manipulation, fundamental for interaction with objects designed to be used by humans, such as door handles, switches, levers, valves, and work tools [2].

According to Verified Market Research [3], the global humanoid robots market is expected to grow by about 52.53% by 2028 over 2020, mainly due to their use for security, surveillance applications, detection of intruders and terrorist activities, in hazardous environments, in healthcare, in academic research, and to support daily tasks [3]. Thus, these robots have been applied in varied applications. As reported by the Royal Aeronautical Society [4], SoftBank's Pepper robot, for example, is used as an attendant at the Oakland airport in California, providing information about directions and recommendations on food and beverages. Also, this same robot model has been used in airports in Belgium and Japan and other environments such as schools, hospitals, restaurants, and stores in the United States [4].

Humanoid robots have applications to assist caregivers and patients, especially in risky areas such as contaminated environments, and thus can be used for medical and surgical uses [5]. For example, as stated by Catherine Clifford [6], the startup CloudMinds made robots available to various medical facilities to help care for patients amid the Coronavirus pandemic. Meanwhile, the humanoid robot Ginger assisted admissions to a hospital by providing information and dancing for patient entertainment [6,7].

One of the factors driving the development of hardware innovations and research related to humanoid robots is the challenges promoted by different institutions. For example, the DARPA Robotics Challenge, promoted from 2012 to 2015 by the Defense Advanced Research Projects Agency, aimed to develop robots with the ability to perform several tasks that may be needed in a disaster and rescue scenario [8]. This event generated a breakthrough in the

Received on 16 September 2022; revised 21 November 2022. Address for correspondence: Juliana Maria S. de Santana. Rua Des. Wilde de Lima, house 11 - Salvador - BA, Brazil | Zipcode:41480-335. E-mail: julianamaria.s.santana@gmail. com. DOI 10.34178/jbth.v5i4.258.

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state-of-the-art of anthropomorphic robots. It was also one of the drivers for the investment return of research in these robots in the United States.

Another challenge promoted with humanoid robots is the soccer championships, such as the RoboCup Humanoid League, an international educational and research initiative focused on advances in artificial intelligence and robotics. This program aims to develop robots capable of beating a human team by 2050, thus encouraging the development of technological innovations [9,10].

However, the high initial cost of robots and the need for a high-level infrastructure for their development and manufacturing could have prevented growth in this area. Also, they have complex mechanisms and control modes. Therefore, their performance is related to several factors, including their mechanisms, actuation, perception, and control methods [11].

Given this type of robot's great applicability and relevance, it is of utmost importance to conduct studies and research to improve the performance of humanoid robots so that they can be more widespread in everyday activities. Thus, this document presents some of the results obtained in the research on the state-of-the-art studies about humanoid robots based on main articles related to developers, focusing on the principal characteristics of perception systems, control, and physical configurations.

Materials and Methods

The BILI method (Bibliographic and Literary Review Method) was used to develop this research, which is a literature review methodology for identifying the works of authors with the most significant impact on a given research theme. This process uses data mining techniques implemented by algorithms in R based on the laws of Zipf, Lotka, and Bradford, rules arising from bibliometrics. Therefore, these packages were used: bibliometrix [12], litsearchr [13], and revtools [14]. This method comprises four phases (Figure 1) and uses tools to select, review

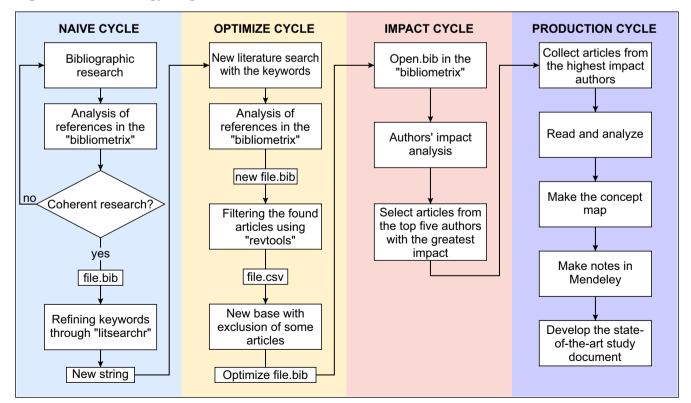


Figure 1. Methodology diagram.

and organize the documentation found, which is described in more detail in reference [15].

The base used to search for articles was Scopus [16], considered one of the largest databases of abstracts and citations in the literature. Then, the references were analyzed to obtain selected articles with relevant information that contributed to the research development. This analysis was carried out using biblioshiny, an interface from the bibliometrix package that allows the evaluation of references through bibliometric indicators. In the first cycle (naive) of the Bili method, 419 articles were obtained, 215 of which refer to the years between 2015 and 2021. After filtering this data in cycle 2 (optimize), 93 articles were obtained, 56 of which were published between 2015-2021, with an average annual growth of 17.08%.

The analysis by the authors used bibliometrix based on the total citations' indexer among the authors. Then, the selection of the articles was made based on their availability. So, the following articles were selected: Gait Controllers on Humanoid Robot Using Kalman Filter and PD Controller [17], Modifying the estimated ground height to mitigate error effects on bipedal robot walking and Mechanism [18], Actuation, Perception, and Control of Highly Dynamic Multilegged Robots: A Review [1] as a priority for reading. In addition, another author who was a reference for the study was Dragomir Nenchev through his contributions presented in the book Humanoid robotics: a reference [24], which was also very relevant to this research.

Results and Discussion

The section Robots Models will discuss the main characteristics of some humanoid robots used by researchers to perform studies on biped locomotion. The main characteristics of anthropomorphic robots' perception, mechanical structure, and control systems are presented in the second, third, and fourth subsections. These are significant issues in developing these robots because they influence the efficiency of their system.

Robots Models

NAO was developed by SoftBank Robotics and used for research and education. Among its applications is its use as an assistant in companies and health institutes. NAO is 58 cm tall, has two 2D cameras to recognize objects and people, and can communicate in several languages through its four microphones and speakers. The robot has seven touch sensors on its head, hands, feet, sonar, and an IMU to find itself in space. It has 25 degrees of freedom (DOF), allowing it to move and adapt to the environment [19].

The Darwin-OP (Dynamic Anthropomorphic Robot with an Intelligence-Open Platform) is a small humanoid (45.5 cm) developed by Robotis. It has 20 DOF and weighs 2.9 kg; it has an HD camera, gyroscope, accelerometer, and stereo microphone. Darwin can walk, talk, and dance, and it is widely used by researchers and programmers [20].

Lola is a humanoid robot developed at the Technical University of Munich (TUM) and used in research on biped locomotion dynamics and control aspects. The robot has 24 DOF, a height of 180 cm, and weighs 60 kg. Its design was developed to have low weight, high rigidity, legs with low inertia, and a high center of gravity. Regarding the sensors used by the robot, Lola has encoders on the axes of its motors and custom force/torque sensors (FTS) on its feet; it has an IMU on its torso and an Intel RealSense camera on its head [21].

HUBO 2 was developed in the HUBO lab at KAIST (Korean Advanced Institute of Science and Technology) in South Korea. It is 125 cm long, weighs 45 kg, and has 40 DOF. Its design was intended to be very light, which allowed the HUBO 2 to run at a speed of 3.6 km/h. Its perception system comprises cameras, inertia, inclination, and force/torque sensors. Its major differentiator from other bipedal robots is the ability to use a gait with outstretched legs [22].

Mechanisms

Humanoid robots have many DOFs to perform a human-like bipedal movement. It is recommended

to consider a redundant configuration with additional DOFs to make this movement more natural and flexible [23].

To improve the dynamics of the robot legs, one should ensure sufficient mechanical stiffness, a high center of mass, and low moments of inertia of the leg links. The primary goal of a humanoid robot is to balance the structural stiffness and actuator performance with the lightness of the mechanical components. Lola's mechanical structure, for example, is characterized by a consistent lightweight design with high effective stiffness. Lightweight servo actuators are used, and the resulting inertia of the legs is minimized by a sophisticated structure and drive mechanism design, resulting in superior acceleration behavior.

One of the NAO robot's DOF, located at the waist, is shared by its two legs. This modeling differs from the format used by most humanoid robots, in which there is a joint in the horizontal axis at the waist and rotating joints in the vertical axis for each of the legs. The model applied in NAO provides advantages to the robot, such as reduced walking problems and costs, because only one motor needs to be used to control the pelvis [24].

Therefore, to ensure that the robot achieves stable and fast locomotion, it is necessary to pay attention to the design of the robot's kinematic structure and to some design goals to improve the dynamics of its limbs.

Perception

Two groups currently classify the humanoid robot sensors: proprioceptive, which measures the state of each joint and the robot's body; and exteroceptive, which obtains information from the environment [1]. Internal sensors measure the robot's state, such as the joints' angles, velocities, and torques. IMU (Inertial Measurement Unit) sensors, including accelerometers and gyroscopes, detect information from the robot's posture. At the same time, the interaction between the robot and the environment can be detected through tactile and force/torque sensors. Furthermore, the cameras and range sensors measure and estimate the information around the robot [24].

In the design developed by Kien, Shanmugavel, and Ragavan, four ultrasonic sensors, two on each leg, are used for position feedback for walking and turning. The accelerometer measures the tilt angle and detects the robot's instantaneous fall. Resistive Force Sensors (RSF) are used to determine the center of pressure (COP), which in turn is used to calculate the robot's ZMP (Zero Moment Point) [25].

Thus, perception sensors are vital to allow robots to interact with the environment and people, and it is through the data obtained by sensors that the control systems are implemented.

<u>Control</u>

The first step for humanoid robot walking control is planning the footsteps and setting some parameters through a robot model. Four models are often used as an approximate representation of the biped robot. First, the Linear Inverted Pendulum Model (LIPM) considers that all the mass of the robot is concentrated at one point, moving at a constant height, and assumes that the legs are weightless. This model has been widely applied in various research, such as by Kashyap and Parhi [26], who used the particle swarm optimization (PSO) technique to refine the conventional PID controller and widely studied and applied by Kajita and colleagues [27].

Another model is the Inverted Pendulum with Flywheel (IPF), which does not consider the height constant and adds a flywheel to account for internal angular momentum. The Springloaded Inverted Pendulum (SLIP) adds a spring to model the legs of the robot as a mass-less jumper. Moreover, the Compass Gait Biped (CG) treats the robot as a double pendulum with masses concentrated at the center of mass (COM) and the swinging legs. Wahrmann and colleagues conduct the strategy in real-time control using a reduced robot model, making the robot more robust against

perception errors and uneven surfaces [18-28]. Afterward, a trajectory generator must be implemented, which generates some movement considering the displacement of the mass center and the Zero Moment Point (ZMP) and the description of the inverse kinematics. Thus, the robot's joint angles are obtained, but a controller must stabilize them to ensure that the robot remains upright and performs all tasks without falling [26]. Kasaei et al.present a framework of a controller with a closed loop based on the Central Pattern Generator (CPG) method that proposes a control model inspired by biological features. In this way, this method tries to produce a stable gait through rhythmic patterns concerning the movement of its limbs. This test was performed on a simulated NAO robot with the proposal of generating a stable and fast movement [29]. Thus, there are several strategies under study that researchers and developers share to create more effective systems, which has allowed an advance in the performance of these robots.

Conclusion

There is growing research and implementation of anthropomorphic robots due to their numerous applications, as in the case at the Oakland airport and CloudMinds' works. Due to their human body shape, these robots can remarkably adapt to our environments. Furthermore, due to their endurance and strength, they can perform tasks difficult for humans. The humanoid robots whose main characteristics were presented, especially NAO and Lola, are reference models for the development of humanoid robots due to their application in research with innovative results, being addressed in several of the selected articles through the methodology applied. This research aids decision-making and serves as a starting point for further investigation into the techniques and procedures addressed.

In the future, more information can be added to the implemented documentation to aggregate and contribute to the development of other projects. This study was necessary for analyzing and learning about anthropomorphic robots, and the information provided is very relevant for developing new projects.

Acknowledgments

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Virtual Reality Applied to Product Development in the Oil and Gas Industry: A Brief Review

Luiz Gutemberg Santiago Dias Junior^{1*}, Cristiano Vasconcellos Ferreira², Ingrid Winkler¹

¹SENAI CIMATEC University Center; Salvador, Bahia; ²Federal University of Santa Catarina, Engineering Center; Florianópolis, Santa Catarina, Brazil

The oil and gas industry has become more competitive and unpredictable, and technology is a route to thrive. Developing solutions for the oil and gas sector entails the incorporation of cutting-edge technology, such as virtual reality. This study examines the role and potential of virtual reality in the oil and gas industry's product and solution development. The method consisted of a systematic literature review of works published over the past decade and adhered to the PRISMA guidelines. We observed that the use of virtual reality technology presents opportunities for the oil and gas industry since it lowers the costs, mitigates risks, increases production and efficiency, and provides long-term economic viability.

Keywords: Virtual Reality. Product Development. Oil and Gas Industry. Digital Twin.

Introduction

Companies in this sector are more actively pursuing innovative applications that make them more efficient by streamlining production, lowering costs, and improving the safety of operations, among other things [1]. In addition, the oil and gas industry is becoming more competitive and unpredictable due to the impending scarcity of fossil fuels. Therefore, these companies senior management sees digitization as a way to protect themselves against market shocks while maintaining profitability at lower costs and creating a competitive advantage throughout the production recovery phase [1]. Using artificial intelligence (AI) and machine learning-based technologies, together with the deployment of technologies that are quickly evolving and being embraced across the value chain, is how some industry leaders [1] see the future unfolding. Although the numerous benefits cloud technology provides and its tools' usage, it has yet to fully permeate the oil and gas sector due to various limitations. The oil and gas business

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relies heavily on data capture, aggregation, and storage, and data security and compliance are essential concerns when contemplating using cloud computing and related capabilities [2]. One example is the enormous amount of seismic data that must be shared and the significant investment in information technology infrastructure that is already a legacy of the oil and gas exploration and production business. However, increased data collection and storage investment is required to adopt more sophisticated technology.

Along with the challenges of data collection and storage during the oil and gas exploration and production stages, there is also the need to maintain the development and transportation structures. It necessitates reliable, accurate, robust, and efficient control systems for detecting leaks, cracks, or gusts on the pipeline and piping systems widely used by this industry [3]. In this context, research is being conducted on the sorts of equipment that can fulfill the different working conditions and technical specifications in a sturdy and technologically sound manner.

There are existing technologies used for remote control of processes, such as remote monitoring and control of a pipeline system pressure is known as Supervisory Control and Data Acquisition (SCADA) [3] system to monitor the pressure, for example. In this environment, cutting-edge technologies like Virtual Reality (VR) have become vital for developing solutions for the oil

Received on 6 September 2022; revised 20 November 2022. Address for correspondence: Luiz Gutemberg Santiago Dias Junior. Rua Juracy Magalhães, 788 - Ap 103 - Lauro de Freitas - BA, Brazil | Zipcode: 42701-890. E-mail: luiz,j@ aln.senaicimatec.edu.br. DOI 10.34178/jbth.v5i4.259.

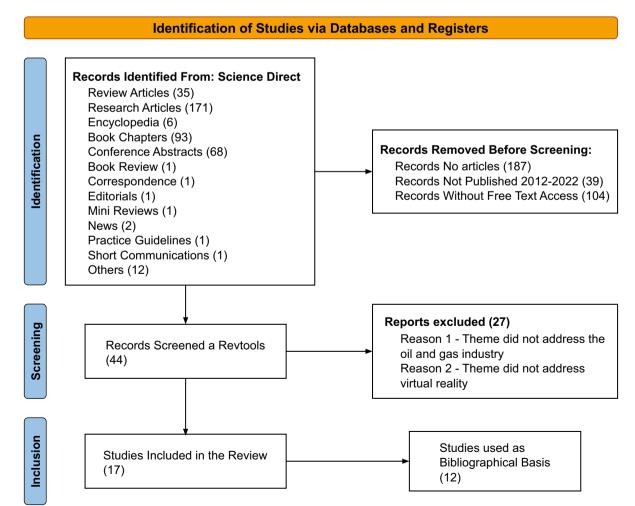
and gas sector. The focus of this paper is the uses of VR in the context of product development for the oil and gas sector, which is addressed in a brief overview of the literature produced over the last ten years.

Materials and Methods

The research searched literature linked to the subject inside the Science Direct platform database, where 393 publications were located under the search string "VIRTUAL REALITY," "PRODUCT DEVELOPMENT," and "OIL AND GAS INDUSTRY." The search was then refined based on publishing review papers and research articles in the recent ten years (2012 to 2022) publicly accessible to the full text. This refinement resulted in 44 papers chosen based on a study of the titles and abstracts to find those with more substantial relevance and conformity to the subject. Following the debugging of the study using the Revtools [4] program to choose articles with adherence to the subject, 17 publications were chosen and formed part of the bibliographic apparatus of this research. We chose 12 articles from 17 as references for this work. The bibliographical survey entailed examining existing works and evaluating each one's contribution to the suggested subject using the PRISMA [5] guideline (Figure 1).

Table 1 shows the articles used from 2015 to 2022. Many articles were published in periodicals with a tenuous connection to the petroleum and gas industry.

Figure 1. Systematic review flow diagram, adapted from PRISMA 2020 [6].



Author	Publication	Periodical	Year
Bolodeoku PB and colleagues	Perceived usefulness of technology and multiple salient outcomes: the unlikely case of oil and gas workers.	ultiple salient outcomes: the unlikely	
Sircar A and colleagues	Digital twin in hydrocarbon industry	Petroleum Research	2022
Sircar A and colleagues	Application of machine learning and artificial intelligence in oil and gas industry.	Petroleum Research	2021
Priyanka EB, Thangavel S, Gao X-Z	Review analysis on cloud computing based intelligent grid technology in the oil pipeline sensor network system	Petroleum Research	2021
Roberts R colleagues	Psychological factors influencing and technology adoption: A case study from the oil and gas industry.	Technovation	2021
Aramco	Digitalization technology development	Aramco.com	2021
Shahkarami A, Mohaghegh S	Applications of intelligent proxies for subsurface modeling.	Petroleum Exploration and Development	2020
Lawan MM, Oduoza CF, Buckley K	Proposing a conceptual model for cloud computing adoption in upstream oil & gas sector	Procedia Manufacturing	2020
Raboy K and colleagues	A proof-of-concept field experiment on cooperative lane change maneuvers using a prototype connected automated vehicle testing platform.	Journal of Intelligent Transportation Systems	2020
GEP	The increasing popularity of digital twins in oil and gas.	Oil and Gas Blogs	2020
Andoni M and colleagues	Applications of smart proxies for subsurface modeling.	Renewable and Sustainable Energy Reviews	2019
Medvedev D	A new reality: Russia and global challenges.	Russian Journal of Economics	2015

Table 1. Authors, publications, publication, and year.

The short period, less than a decade, results from the rapid development of virtual reality devices starting in 2016. According to the literature, 2016 was a turning point in technological advancement with the public release of the first technologically advanced VR glasses[7]; in addition, 2016 had the most significant increase in global research into virtual reality [8]. Academics and professionals agree that the 2016 equipment launched was a "great advance" for virtual reality applications [9,10].

Results and Discussion

Research published this year in the scientific journal Heliyon [11] gave data illustrating the influence of the perceived utility of technology by workers of an oil and gas company in analyzing the implications of technology adoption in the oil and gas scenario. According to the study, the perceived utility of technology has a direct and considerable impact on employee performance. The findings indicate that employees are more likely to commit to their employment and the organization when they value the firm's technology. Furthermore, the higher the awareness of the value of the technology chosen by the business, the more happy workers will be with the organization's progress.

On the other hand, one of the hurdles to advancing and accepting cutting-edge technologies such as VR is the need for fundamental changes in industrial culture and removing barriers beyond financial investments. Barriers such as corporate culture are real hurdles that must be overcome for new technology to be introduced. It is made clear by research published in Technovation [12], which performed a case study in the Oil & Gas (O&G) business to evaluate the effect of psychological variables on technology adoption in the sector. According to the research, the fear of failure was one of the reasons for not implementing the technology.

The role of human capital engagement in adopting new technologies has proven to be a vital and preponderant aspect. It is no surprise that global economies have prioritized the human component as a foundation for significant transformation. Despite this, nations that have accomplished high levels of innovative development in recent decades have made significant investments in human capital [13].

With frontier technologies, particularly the usage of VR in the O&G business, as barrier issues connected to changes in human capital perception, such relevance becomes even more essential. New technology and breakthroughs fundamentally alter marketplaces and whole sectors [13]. It needs new market behaviors, such as new techniques for accomplishing massive, long-term projects involving significant crowd participation. There are several opportunities for implementing cutting-edge technology in the oil and gas business, notably using virtual reality (VR) to assess reservoir conditions. Reservoir simulation models may be implemented because of the cheap computational simulation cost associated with multiscale and multiphase reservoir-type simulation [14]. The success of models developed and validated in a virtual environment capable of reproducing results in fractions of time and with meager computational costs benefits other streams of reservoir management work operations such as sensitivity analysis, production optimization, and uncertainty assessment [14].

Another use of cutting-edge technology in the oil and gas business is the use of Artificial Neural Networks (ANN) [1], a collection of algorithms used in machine learning of data models and, in this case, are precursors to the use of VR and AR. Deep learning algorithms used in the oil and gas business help process large amounts of data, which is extremely necessary for VR adoption. Seismic pattern recognition, drilling diagnostics, improving gas well productivity, identifying sandstone lithofacies, predicting and optimizing performance, and providing pipeline condition prediction. The model can calculate the percentage of sand in the reservoir, bringing all this data together in Virtual Reality as a tool for field staff and creating design solutions [1]. One solution for the oil and gas industry to mitigate the uncertainties and risks of using technology in operations is to use more

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technology. In this case, enabling technologies, such as Blockchains [15], can potentially be used for thoughtful device communication, transmission, or storage of data such as that required for VR use. In addition to providing secure data transfer, intelligent grids can further benefit from data standardization enabled by blockchain technology. This would enable the accuracy and validity of information to be used in proofs of concept in the case of virtual prototypes enabled by VR adoption in product development[15,16].

Another example of cutting-edge technology in the oil and gas industry is the use of Digital Twins (TD) in a variety of domains, such as numerical analysis to represent different scales and scenarios, data validation and maintenance in process industries such as refineries, as well as drilling and transportation [17]. Shale reservoirs, for example, are highly challenging to simulate because of the complexity of unconventional systems. However, modeling complicated scenarios, such as studies of gas absorption, flow, and transport of gas in shale reservoirs, understanding the features of adsorption and diffusion of this gas in water carriers, and other possibilities are achievable with the aid of digitalization [17]. In addition, developing products for the petroleum industry sector that go through the exploration, assessment, production, performance, and replacement stages must consider the underlying HSE (health, safety, and environment) dangers [13].

The industry is turning to Digital Twins technology to optimize its exploration processes to improve productivity by increasing efficiency, lowering HSE risks, lowering operating and capital costs, increasing revenues, and improving regulatory compliance [17].

Although the word DT is new to the drilling business, the oil sector has employed the concept for over two decades. DT in real-time drilling operations is increased further by installing diagnostic modules that automatically detect occurrences or issues in operations, allowing potential dangers to be avoided or handled as soon as feasible [17]. Using a DT in a drilling operation combines digital and physical data with predictive analytics and diagnostic signals, boosting the capability of drilling operations planning and decision-making accuracy [17].

In the oil and gas industry, for example, the DT is more than just a three-dimensional model (physical entity, virtual entity, and their connection). It mixes modern technology while considering various relationships and companies within a specific situation [17]. For decades, upstream professionals have worked tirelessly to acquire data from offshore sites to analyze and develop better-informed business plans. An internal audit of an industrial organization discovered that upstream staff spent approximately 80% of their time searching for and then changing data, mainly because the data was previously housed outside a platform [17]. Employees have always had to acquire massive volumes of data from many sources, such as database spreadsheets, data streams, and implicit knowledge. Currently, sensors attached to on-site or in-field equipment may send 1,000 data points per minute to engineers, conveying a massive quantity of data for them to review critically [17].

A practical example is that of the oil giant Saudi Aramco that are implementing certain new technologies such as Big Data Analytics, Industrial Internet of Things (IIoT), Robotics and Drones, Artificial Intelligence (AI), Cloud Computing, 3D Printing, Augmented Reality. /Virtual Reality (AR). /VR). Through advanced modeling and simulations, Aramco uses AR/VR technology to improve emergency preparedness, repair procedures, and facilities [17,18].

Another example is BP, which has created APEX [17,19], a very complex simulation and surveillance system that builds virtual models of all of the company's production systems. BP may design modifications and interventions in the digital twin before delivering them in the actual world using APEX. It identifies issues as a surveillance tool before they significantly impact output. The traditional simulation approach takes many hours and produces significant inaccuracies [17]. On the other hand, APEX may run the same simulation

in minutes and analyze the impact of potentially harmful activities in the safe virtual world setting with a smaller rate of errors [17,19].

Conclusion

This brief analysis concludes that using Virtual Reality and other cutting-edge technologies offers several application possibilities in the oil and gas business, despite the obstacles that overcome capital investments. The use of VR in product development for the oil industry has already demonstrated its potential for cost reduction, risk mitigation, increased productivity in efficiency, and long-term economic viability. The use of virtual reality (VR) in the petroleum industry is already a reality that will increase significantly in the coming decades, enabling new research as well as the generation of essential information for the issue.

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Hydrogen Production via SMR with Carbon Capture: A Bibliometric Analysis

Jade Spínola Ávila^{1*}, Julio Augusto Mendes da Silva¹, Fernando Luiz Pellegrini Pessoa¹, Petrucio Leal Pereira² ¹Federal University of Bahia; ²SENAI CIMATEC University Center; Salvador, Bahia, Brazil

The global energy demand should double by 2030, reaching a peak of 80 to 120 million barrels of oil per day. Therefore, to mitigate climate change and reduce the high demand for oil imports, future energies must be clean (carbon-free), renewable and recyclable. A promising solution to reduce dependence on fossil fuels and meet future demands for sustainable energy is to use H₂ as an energy vector. In the literature, some works involve H₂ production via SMR and CO₂ capture. Therefore, a bibliometric analysis of this topic is developed to assess its level of maturity and map the publications most adhering to this research line. From the results obtained, it was observed that the focus of the research already has a particular maturity, but there are still many gaps to be addressed and developed.

Keywords: H2 Production. Steam Methane Reforming. Carbon Capture. Bibliometrics.

Introduction

Fossil fuel's historic consumption has caused climate change and several environmental and health problems that threaten the global community because, in its combustion, there is significant greenhouse gas emission. In addition, the global energy demand is expected to double by 2030, reaching a peak of 80 to 120 million barrels of oil per day [1]. Therefore, to mitigate climate change and reduce the high demand for oil imports, future energies must be clean (carbon-free), renewable and recyclable [2].

Climate change mitigation is directly related to the circular economy concept, which is characterized as an economic model that proposes the efficient use of resources through the waste, costs, and raw materials reduction and the closed cycles development of products and materials to promote the sustainability and economic growth of activities without causing resource depletion and environmental degradation [3].

The circular economy concept is associated with green chemistry, which focuses on using

(bio)renewable resources and the processes and product development that promote human health and environmental protection [4]. From a technological point of view, green chemistry is viable through integrating renewable and greener processes that aim to achieve high production efficiency and yield, using resources efficiently, and generating reduced waste streams [4]. However, the supply of CO₂-free or nearly CO₂free energy is a big technological challenge that requires significant developments, government initiatives, and industrial innovations. A promising solution to reduce dependence on fossil fuels and meet future demands for sustainable energy is to use H₂ as an energy vector. Then its molecule is carbon-free and has a high energy content, being an essential pillar in the energy transformation that can contribute to global warming mitigation [1].

The hydrogen production route is a determining factor for its environmental feasibility. It can be produced by water electrolysis using renewable energy sources, known as green H₂, by steam methane reforming (SMR) from fossil fuels, gray H₂, by SMR associated with carbon capture and storage, blue H₂ [5], and alternatively can be produced by pyrolysis generating solid carbon as a by-product, turquoise H₂ [6]. With the blue H₂ production characterized by CO₂ capture, a potential for decarbonization of the energy scenario and compliance with climate goals is highlighted. It is expected that, in the long term,

Received on 10 September 2022; revised 18 November 2022. Address for correspondence: Jade Spinola Ávila. Rua Amazonas, 1155, apto 204, Pituba. Salvador –BA. Zipcode: 41830-380. E-mail: jade.engavila@gmail.com. DOI 10.34178/ jbth.v5i4.260.

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the investment and production costs of green hydrogen obtained by electrolysis will reduce due to large-scale applications, better production processes, and possibly new technologies [7].

However, in the short and medium term, blue H_2 (low carbon) can be supplied on a large scale from the optimization and improvement of existing technologies, being considered a transition route to the green H_2 exclusive consumption of the future.

In the literature, some works involve H₂ production via SMR and CO₂ capture. Therefore, a bibliometric analysis of this topic is developed to assess the maturity level and map the publications that most adhere to this research line.

Bibliometrics

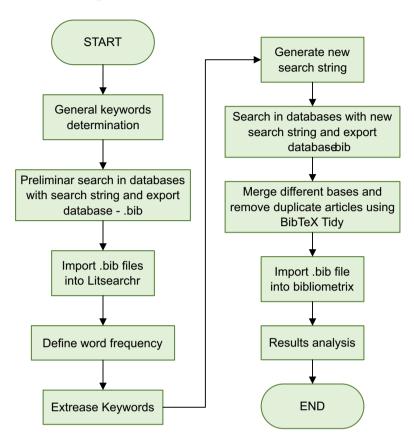
In the research bases, there is a constant increase in publications in the most several areas, so we observed the difficulty for authors to map publications adhering to their research, selecting them according to specific criteria, processing the data obtained, and then using the primary references obtained in the project development [8]. This way, bibliometric analysis tools can guide authors in their search for adherent works. Bibliometrics is a complex scientific mapping that is difficult to execute because it comprises multiple steps and uses different tools. Nevertheless, bibliometric analysis can assess the relevance of publications through indicators and guide the author in selecting references that are more adherent to the exciting topic in a quantitative way. Therefore, this methodology aims to develop a systematic, transparent and reproducible review process based on the statistical measurement of science, scientists, or scientific activity [9].

In the literature, there are several methodologies for bibliometrics development. According to Zupic and Cater [10], a systematic review is based on five steps: (1) Study design – the bibliometric analysis is performed at a specific time to represent a static image of a given research area. In this step, the time interval is defined as what the researcher wants to work on; (2) Data collection - step in which the

databases selection of interest occurs, filtering the set of principal documents and exporting the data; (3) Data analysis – use of bibliometric or statistical software tools; (4) Data visualization: stage of choosing the visualization of the results obtained by the software; (5) Interpretation: evaluation and description of the data obtained at the bibliometric research end.Based on Qyyum and colleagues [1], Reis and do Vale [12] proposed the use of the Litsearchr tool to develop a more assertive search string from the development using text-mining and keyword co-occurrence networks to identify important terms to include in a search strategy, associated with the Bibliometrix methodology [13], with the objective of setting up a data matrices for co-citation, coupling, scientific collaboration analysis, and co-word analysis, a methodology known as the Bili Method. This way, Reis and do Vale [12] propose an open-source tool called bibliometrix. With this tool, it is possible to carry out comprehensive bibliometric scientific mapping analyses developed in the R language. Moreover, this tool is flexible and can be quickly updated and integrated with other statistical R packages and is therefore constantly changing, like bibliometrics. In this context, this work presents a bibliometric analysis methodology, based on Reis and do Vale [12], about the H₂ production via methane steam reforming with carbon capture. From the bibliometric analysis, it is possible to consolidate the results of previous research in order to effectively utilize the existing knowledge base and move toward a particular line of research [13].

Materials and Methods

Figure 1 represents the methodology flowchart used. First, a keyword set (string) is created using Boolean operators for the general research context. Then, from the words set, a preliminary search is carried out in the leading research bases, SCOPUS [14] and WEB OF SCIENCE [15], both available on the CAPES PERIODIC Portal. The results obtained in the two databases are exported in bibtex format and used in the Litsearchr platform. Figure 1. Flowchart of the developed method.



Source: Authors based on Reis & Vale (2022) [12].

In this platform, it is possible to check the word frequency of the publications mapped in the search and generate a new, more specific boolean. At this stage, the user can enter other keywords that they consider relevant in that search, thereby making the set of terms even more specific to the topic at issue. Finally, a new search is performed in the databases from the new word set, and the obtained results are exported and submitted to an analysis for the existence of duplicates by RStudio (BibTeX Tidy) [16]. This way, a more specific database is generated without repeated documents on the exciting topic, so the bibliometric analysis can be performed using Bibliometrix, a tool available in RStudio.

Results and Discussion

From the proposed theme for the development of the bibliometric analysis, H₂ production via

steam methane reforming with carbon capture, a general keyword set was elaborated: "hydrogen production" AND ("steam methane reforming" OR "blue hydrogen") AND (simulation OR modeling). The results obtained using these word sets were exported from the SCOPUS and WEB OF SCIENCE databases. It was found that both databases presented very adherent results, but is still necessary to refine the search to map more specific publications. With the ListSearch support and contributions from the authors, new keywords generated: ("methane reforming" set was OR "steam methane reforming process" OR "steam methane reforming" OR "methane conversion" OR "hydrogen Production") AND ("carbon capture" OR "CO2 removal" OR "CO2 capture" OR "CO2 separation") AND (hydrogen OR "blue hydrogen") AND (simulation OR modeling) AND ("natural gas" OR methane).

Making a preliminary results evaluation was found that some publications were outside the interesting niche since the research objective is restricted to the H₂ production via steam methane reforming from natural gas. Therefore, we generate a new search string by inserting a boolean exclude term. The new keywords set is: ("methane reforming" OR "steam methane reforming" OR "methane conversion" OR "hydrogen Production") AND ("carbon capture" OR "CO2 removal" OR "CO2 capture" OR "CO2 separation") AND (hydrogen OR "blue hydrogen") AND (simulation OR modeling) AND ("natural gas") AND NOT (biogas OR pyrolysis OR coal OR gasification OR renewable OR ammonia). After defining the new search strings, new results were obtained and analyzed. Table 1 presents the general results of the research, and it was verified that the results more adherent to the proposed theme appeared from 2005, highlighting that it is a relatively new theme and the annual growth rate and the production graph are in increasing development annually (Figure 2).

Figure 2 shows that this topic increased the number of publications in 2016, with peaks in 2018 and 2020. It was found that, even though the COVID-19 pandemic intensified in 2020, this year, there was a high number of publications in the area, but in 2021 there was a decline that can be justified by the economic crisis resulting from the pandemic.

The most relevant sources in the group of publications related to research were the International Journal of Hydrogen Energy, with 11 publications; Applied Energy, with 5 papers and Energy, with 5 publications. Among these three sources, the International Journal of Hydrogen stands out as the one with the most significant impact, according to the Bibliometrix. Thus, this is the most adherent and renowned journal to publish research on the topic addressed. When evaluating the region with the highest frequency, it was verified that Italy has 20 publications, followed by Norway (16), Spain (15), the United States (15), China (10), and the United Kingdom (9), indicating that Europe is leading the way in this Table 1. General results.

Results
05:2022
32
68
11.12
14.75
2,927
217
206
9; 3; 6

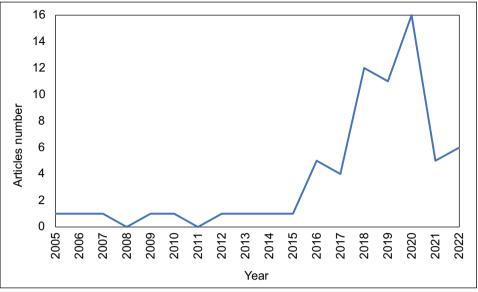
Source: BibTeX Tidy.

research niche. Figure 3 shows the occurrence of keywords in the results. The carbon dioxide term is cited more often than hydrogen production, highlighting a global concern regarding CO₂ emissions when works in this niche are published since the steam reforming method emits a high amount of CO₂.

Conclusion

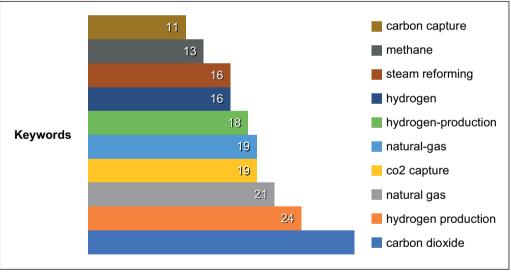
H₂ production is of significant relevance in the global energy challenge today. From the results obtained, it was observed that the research focus already has a particular maturity. However, there are still many gaps to be addressed and developed concerning the research expansion in offshore production, seawater desalinization for generating steam (raw material), and CO2 compression and injection in mature wells. The SCOPUS and WEB OF SCIENCE databases provide an expressive amount of results (68 publications). However, new search strings must be used, and a manual analysis of the results (title, abstract, and keywords) should be executed to define and map the works even more adherent to the research focus. Was verified that Brazil does not have any representation on the discussed topic, reinforcing the importance of developing this investigation.

Figure 2. Annual Scientific Production.



Source: Bibliometrix.

Figure 3. Occurrence of keywords.



Source: Bibliometrix.

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Techniques Used for Determining the Hydrotreated Vegetable Oil Presence in Diesel

Fabio de Sousa Santos^{1,2*}, Marcelo A. Moret^{1,2}, Lilian Lefol Nani Guarieiro¹

¹SENAI CIMATEC University Center; ²Computer Modeling and Industrial Technology Program; Salvador, Bahia, Brazil

Determining HVO content in diesel is essential for fuel quality control and other important aspects, so studying the techniques used for this purpose is necessary. In this article, the authors did a systematic review to determine the techniques used to define HVO in diesel and the efficiency of each technique. The results of the study showed that the use of techniques that are based on measuring the amount of C14 radiocarbon in the sample have good efficiency, but concerning the cost and time used to perform the exams, FTIR spectroscopy together with the use of Chemometric techniques is an excellent alternative for the study.

Keywords: HVO. Determination Techniques. Liquid Cinstillation. Mass Spectrometry with Accelerators. FTIR Spectroscopy.

Introduction

Renewable energy is an essential energy source that humans can use to carry out their activities sustainably. In its life cycle, renewable energies are of great importance because both in the area of transport and in other areas in which this energy has influence, scholars believe that, with a lower presence of agents harmful to the environment, more incredible benefits, both for government agents, entrepreneurs, and for society as a whole. The traditional production of biofuels, regulated by the ANP, uses essential plants in the structuring line, also highlighting the use of animal fat, in addition to the addition of vegetable oils, soybean, one of the best known, in addition to others, such as "the palm, sunflower, babassu, peanut, bean, and jatropha, through alkaline transesterification, but it can be obtained by cracking and esterification as well [1].

Hydrotreated vegetable Oil (HVO), also called green diesel or renewable diesel, has a chemical composition similar to fossil-based diesel oil; however, it comes from renewable raw materials. This biofuel can be produced from the hydrotreatment of vegetable oils or animal fats, from the synthesis of molecules from synthesis gas obtained by the gasification of organic waste, and by the fermentation of sugar cane, among other processes. Its composition is similar to petroleumderived diesel, so it can be mixed with mineral diesel in any proportion, even as a complete replacement [2].

The chemical process of producing HVO is carried out through hydrotreatment (HDT). Through it, the raw material reacts with hydrogen gas under controlled conditions of pressure and temperature to produce a fuel similar to fossil diesel. A range of technologies for its preparation, that is, different raw materials, can be used, both of animal and vegetable origin [3]. In addition to these factors, Kalnes and colleagues [4] list the classification of HVO as a "second generation of biofuels" since it comes from the green chemistry process, according to the authors as mentioned earlier. Furthermore, the HVO already has production in other countries, facilitating learning and placement in the national territory without significant obstacles in its production. The differential issue between biofuel and green diesel is the number of hydrogen molecules [1].

The use of biofuels is highly likely due to their contribution to preserving the environment, reducing environmental pollution, and being a renewable energy option to replace or mitigate the market of petroleum products in the future.

Received on 25 September 2022; revised 16 November 2022. Address for correspondence: Fabio de Sousa Santos. Rua Professor Viegas,186 - Condomínio Mirabeau Sampaio, Block B.apto 012 - Salvador - BA, Brazil. Zipcode: 40301-075. E-mail: fabiosousasantos4@gmail.com or fabio11@ ba.estudante.senai.br. DOI 10.34178/jbth.v5i4.261.

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Among the renewable sources, the most favorable is certainly HVO, as it has immense advantages compared to biodiesel, such as a more significant amount of energy density, lower NOx emission, superior storage properties, and production without the presence of glycerol., in addition to being a fuel that can fully replace diesel without any engine modification [5].

This article aimed to identify and evaluate the techniques used to determine the percentage of HVO-type renewable content in diesel fuel of fossil origin. This study will present the fuel mixtures and techniques that can be used to determine HVO inserted in diesel oil. In addition, the efficiency of the techniques used to determine the HVO present in diesel will be evaluated. From this perspective, this work was supported by theoretical references in the scope of determination of the HVO content present in diesel to identify these techniques and evaluate their efficiency in this process.

Materials and Methods

The research was carried out through a systematic review of the period between 2007 and 2022 of national and international publications that study the techniques used to determine the HVO content in diesel oil.

We made a methodological choice of investigation for the survey of the studies carried out. All searches took place on reference sites with consolidated studies. With few studies in Brazil, international journals and repositories dominate the research on the techniques to determine the HVO content present in diesel oil.

The systematic review represents an investigation focused on the recovery and careful analysis of literary productions already carried out on the proposed theme. These studies test hypotheses to raise, analyze, evaluate, and understand a given phenomenon studied, systematizing and synthesizing the research already carried out in the studied field [13]. In this systematic review process, the software dimension and read cube were used to survey the articles to be studied. Then their selection took place through the impact factor of the periodical. They were also organized into groups considering the year of publication from 2007 to 2022. After data collection and material selection, twenty-eight articles were kept, all of which were searched using the descriptors "prediction of HVO (Hydrotreated vegetable Oil) in diesel", "HVO (Hydrotreated vegetable Oil) in diesel", "techniques for prediction of HVO (Hydrotreated vegetable Oil)". In this research, some techniques were found that are used to determine the HVO content present in diesel.

Results and Discussion

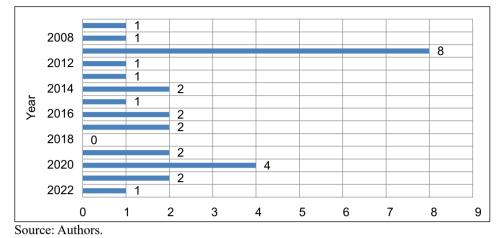
Research and studies carried out with the techniques to determine the HVO content in diesel oil have shown significant relevance due to their applications for the evolution of renewable contents about fossil fuels. The articles selected for this study expressly present in their abstracts the discussion about these techniques used to determine the HVO content in diesel.

Thus, in this writing, data collected from a survey carried out in a virtual environment from banks and repositories that host these studies are presented in the light of a bibliographic study. One of the most important revelations that we can point out is the low academic production in Brazil, which highlights the importance of this writing. Figure 1 presents the evolution of the research in the selected period.

The scientific literature presents reports on using infrared (IR) spectroscopy to monitor the transesterification of vegetable oils with methanol and ethanol, determining the conversion rate of this reaction. As diesel and biodiesel have different chemical functions, the infrared spectra of these fuels contain specific bands. Therefore, this technique can also quantify the percentage of biodiesel in biodiesel: diesel mixtures [6].

Determining the HVO content in the HVO/ diesel mixture is a challenging task, as the two fuels are a mixture of the same or very similar hydrocarbons.

Figure 1. Number of publications on the determination of the HVO content in the HVO/diesel mixture x year.



Moreover, standard analytical methods differentiate hydrocarbons belonging to HVO from hydrocarbons belonging to fossil fuels [7].

To determine the HVO present in diesel, we have that can be based on the measurement of the number of radiocarbon C14 in the sample. The methods based on the measurement of C14 (carbon 14) can be divided into two main groups, which are: accelerator mass spectrometry (AMS) and the other is liquid scintillation counting (LSC); however, both methods have relatively good accuracy but are very time-consuming and expensive[7]. Liquid Scintillation Counting is a radiocarbon dating technique that was popular in the 1960s. In this method, the sample is in liquid form, and a scintillator is added. This scintillator produces a flash of light when it interacts with a beta particle. A vial with a sample is passed between two photomultipliers, and only when both devices register the flash of light is a count made. Accelerator mass spectrometry (EMA) is a modern method of radiocarbon dating that is considered the most efficient way of measuring the radiocarbon content of a sample. In this method, the carbon 14 content is directly measured to the carbon 12 and 13 present. The method does not count beta particles but the number of carbon atoms in the sample and the proportion of isotopes [8,9]. Another technique currently used is FTIR spectroscopy, combined with chemometric techniques that are partial least squares regression (PLS) and principal components regression (PCR), which are used to determine the HVO content in HVO/ diesel. This technique, developed by Dan Vrtiška and Pavel Šimác ek from the University of Chemistry and Technology, Department of Petroleum Technology and Alternative Fuels, is a methodology for determining the content of hydrotreated vegetable oil (HVO) present in Diesel using Fourier transform infrared spectroscopy (FTIR) and chemometric analysis for some fuel mixtures existing in Europe [7]. The results in Table 1 refer to the techniques currently used to identify the HVO content present in diesel, in addition to informing the efficiency of these techniques used.

The results in Table 1 show that the techniques used to determine the HVO content present in diesel have excellent efficiency. However, liquid scintillation counting and accelerator mass spectrometry (AMS) has disadvantages concerning the high time used. Furthermore, to perform the exams and the high cost of analyzing a sample. Therefore, FTIR spectroscopy, combined with chemometric techniques, is a process that has great potential to become the most used in the determination of contents. Mainly the HVO is present in diesel because, in this process, we have a lower cost per sample. In addition, the time for carrying out the tests is

Fuel Blend	Technique Used	Limit of Detection	Efficiency of Technique	Ref.
HVO /DIESEL	Measurement of the amount of C14 radiocarbon in the sample using accelerator mass spectrometry (AMS)	47000	Relatively good accuracy but they are very time-consuming and expensive	[7,10]
HVO / DIESEL	Measurement of the amount of C14 radiocarbon in the sample using scintillation countingRelatively good but they are very time- consuming and expensive		[7,10]	
HVO / DIESEL	FTIR spectroscopy, together with the use of chemometrics techniques	-	Best predictive ability of all. The maximum error of the prediction of the HVO content did not exceed 0.25% by weight	[7]

Table 1. Comparison between the techniques used to determine the HVO content present in diesel.

DL = Detection Limit (AP = 1950 DC).

shorter, and the amount of sample used is reduced. Determining the fraction biogenic based on the measurement of the carbon 14 content is possible in different ways. The measurement directly from the carbon 14 activity of fuels liquids by scintillation counter net (LSC) is fast but overloaded by some disadvantages. For example, the color of fuels causes different quenching properties in the scintillation cocktail and affects _ The measurement efficiency [11]. The disadvantages of the AMS measurement technique are sample preparation, combustion, and graphitization, while the time of a regular AMS measurement is fixed. Nevertheless, the AMS 14C measurement technique is excellent for determining the biological base content in fuel mixtures, even below 1.0 m/m % [12].

Conclusion

The systematic review carried out to determine the techniques used to determine the HVO content

present in diesel was very important because, through this investigation, we found the articles that dealt with this being possible, thus, bringing the procedural definition of each technique and power. Evaluate the efficiency of each of these. It was noted in the study that the technique involving mass spectrometry with accelerators (EMA) is the most effectively used because it has a shorter time in sample preparation and requires a smaller number of samples. However, it was found that as the cost and the time required to perform the exams were high, it became evident that the FTIR spectroscopy technique and the use of chemometric techniques began to gain great visibility because the efficiency in the results was excellent. The cost concerning other techniques is much lower. In addition to these factors, there is no short-term reduction in the costs of exams performed by the techniques of mass spectrometry with accelerators (EMA) and liquid scintillation counting, which, in addition to this fact, take longer to perform. What makes this work, in addition to others, a differential?

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Number of Words – Text	5,000 including spaces	5,500 including spaces	2,500 including spaces	1,000 including spaces	1,000 including spaces	550 including spaces	5,000 including spaces	5,500 including spaces
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