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# Journal Renewable Energy



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# **Journal Renewable Energy**

## **Definition of the Journal**

#### **Scientific Objectives**

To support the International Scientific Community in its written production of Science, Technology and Innovation in the Area of Engineering and Technology, in the Subdisciplines Solar Energy and its Applications, Renewable Energies and Climate Change, Environmental Impact, Hydroelectric Plants, Polluting Renewable Energies, Wind Energy, Geothermal Energy in the World.

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#### **Presentation of the Content**

As a first article we present, Thermodynamic study for the recovery of lithium and cobalt from waste batteries, by Farias-Gonzalez, Miguel Angel, Farias-Gonzalez, Francisco Javier and Perez-Castro, Laura Luz, with assignment in the Universidad Tecnológica de la Región Carbonífera; as the following article we present Using latent heat from a water purification system to improve the performance of an absorption heat transformer, by Morales, L.I., Siqueiros J., Juárez-Romero D. and Hernández-Soria, A. H., with assignment in the Universidad Autónoma del Estado de Morelos; as the following article we present Ships decarbonization is an urgent technology and responsibility challenge that impacts global warming, by Flores-Cruz, Luis Antonio, Cruz-Gómez, Marco Antonio, Correa-Nieto, Marco Antonio and Mejía-Pérez, José Alfredo, with assignment in the Benemérita Universidad Autónoma de Puebla; as the following article we present Design of a High Performance Hybrid Tricycle (THAR) to assist people with motor disabilities, by Mendoza-Derramadero, José De La Cruz, Mandujano-Nava, Arturo, Chihuaque-Alcantar, Jesús and Paz-Cabrera, Mauro, with assignment in the Universidad Politécnica de Guanajuato: as the following article we present Comparison of Canna indica, Pontederia sagittata and Heliconia rostrata as phytoremediator species in the treatment of gray water in Úrsula Galván, Ver., by Acosta-Cadenas, Montserrat, Jimenez-Flores, Juana Fabiola, Utrera-López, Daniel and Arellano-Montero, Edgar Javier, with assignment in the Tecnológico Nacional de México, Campus Úrsulo Galván; as the final article we present Integration of green technologies for the generation of electric energy using microgenerators and atmospheric batteries in the irrigation district #043 Alejandro Gascón Mercado, Canal Centenario, State of Nayarit, by Jaime-Navarro, Agustín, Bonilla-Alejo, Sergio Raúl and Rodríguez-Rodríguez, Joel, with assignment in the Universidad Tecnológica de Nayarit.

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# Thermodynamic study for the recovery of lithium and cobalt from waste batteries

# Estudio termodinámico para la recuperación de litio y cobalto a partir baterías de desecho

Farias-Gonzalez, Miguel Angel\*a, Farias-Gonzalez, Francisco Javierb and Perez-Castro, Laura Luz<sup>c</sup>

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#### Abstract

Lithium and cobalt are a fundamental raw material for the manufacture of portable batteries widely used in mobile phones, laptops, electric cars, etc., due to their properties in the accumulation of electrical energy. While it takes approximately 250,000 kg of lithium ore or 750,000 kg of brine to extract 1,000 kg of lithium, it takes only 28,000 kg of discarded lithiumion batteries to obtain the same amount of metal. For this reason, this project seeks to improve and optimize the recycling process through the selective precipitation of lithium (Li) and cobalt (Co) from ammonium oxalate (NH<sub>4</sub>):C<sub>2</sub>O<sub>4</sub> and sodium carbonate Na<sub>2</sub>CO<sub>5</sub>, through a detailed study of variables such as reagent concentration, pH and temperature. This will be achieved through thermodynamic simulations, with the aim of maximizing the recovery of lithium and cobalt from discarded batteries.

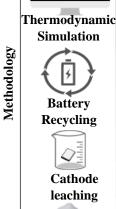
Objectives

Literature review Evaluate hydrometallurgical treatments Sustainability

## **Contributions:**

Improve hydrometallurgical processes for lithium and cobalt recovery through thermodynamic simulation.







#### Resumen

El litio y cobalto son una materia prima fundamental para la fabricación de baterías portátiles, ampliamente utilizada en los teléfonos móviles, laptops, autos eléctricos, etc., debido a sus propiedades en la acumulación de energía eléctrica. Mientras que se necesitan aproximadamente 250,000 kg de mineral de litio o 750,000 kg de salmuera para extraer 1,000 kg de litio, se requieren solamente 28,000 kg de baterías de ion litio desechadas para obtener la misma cantidad de metal. Por esta razón, este proyecto busca mejorar y optimizar el proceso de reciclaje mediante la precipitación selectiva de litio (Li) y cobalto (Co) a partir de oxalato de amonio (NH<sub>4</sub>):C<sub>2</sub>C<sub>0</sub>4 y carbonato de sodio Na:CO<sub>3</sub>, mediante un estudio detallado de variables como la concentración de reactivos el pH y la temperatura. Esto se lograría a trayés de simulaciones termodinánicas. de reactivos, el pH y la temperatura. Esto se logrará a través de simulaciones termodiamicas, con el objetivo de maximizar la recuperación de litio y cobalto de las baterías desechadas.

Revisión bibliográfica Evaluar tratamientos hidrometalúrgicos Sostenibilidad Aplicación de modelos

#### Contribuciones:

Mejorar procesos hidrometalúrgicos para la recuperación litio cobalto mediante simulación termodinámica.

Metodología



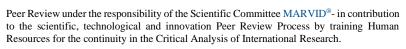
# Thermodynamic simulation, Batteries, Lithium

# Simulación termodinámica, baterías, litio

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#### Introduction

Lithium and cobalt are fundamental raw materials for the manufacture of portable batteries, widely used in mobile phones, laptops, digital cameras, electric cars, and more. due to the advantages of light weight, large capacity and long life. As a result, the production and consumption of lithium batteries skyrocketed (Kaya, 2022).

The main use of lithium and cobalt in Mexico and globally is in battery manufacturing, accounting for 39% of total usage. Other uses include ceramics and glass (30%), lubricating greases (8%), flux powders for continuous casting and polymer production (5%), air treatment (3%), and miscellaneous applications (10%). In 2016, Mexican lithium exports were only valued at \$658, while imports amounted to 219 tons, representing a value of \$1.6 million. These figures show that, in 2016, Mexico's trade balance for lithium had a deficit of \$1.6 million. Finally, it is noted that 90% of Mexico's lithium imports came from Chile, 9% from Slovenia, and the remaining 1% from other countries (Secretaría de Economía, 2018).

In Mexico there are currently 36 foreignowned mining projects focused on lithium extraction, controlled by 10 companies. These projects represent 97 thousand hectares of concessions, with an addition to 537 thousand hectares still in process. As a result, there is not yet a lithium or cobalt mine with significant productions, due to the low grades in the deposits, lack of adequate extraction technologies, in addition to the high costs of extraction (Geocomunes, 2021).

Advances in the commercial development of lithium-ion batteries have led to significant growth in demand for lithium (Li), cobalt (Co), manganese (Mn), and nickel (Ni). In 2019, lithium-ion batteries for electric vehicle production were estimated to consume around 19,000 mt (Million tonne) of cobalt, 17,000 mt of lithium, 22,000 mt of manganese, and 65,000 mt of nickel. With the projection of 245 million electric vehicles by 2030, the required demand for cobalt expands to around 180,000 mt/year, lithium to around 185,000 mt/year, manganese to 177,000 mt/year, and nickel to 925,000 mt/year (Kaya, 2022).

After hundreds of charge and discharge cycles, the expansion of the batteries and the capacity decreases until they are discarded, the lifespan of the batteries is around 3 to 15 years depending on the device. Consequently, the huge battery consumption also generates a surprising number of scrap batteries. (Kaya, 2022).

The largest source of lithium available for recycling is lithium-ion batteries. Once their capacity falls below 80% of their rated capacity, these batteries are considered unsuitable for electronic devices and are consequently discarded. The concentration of lithium in these discarded batteries ranges from 3% to 7%, which is significantly higher than the concentration found in natural sources. While around 250,000 kg of lithium ore, or 750,000 kg of brine are required to extract 1,000 kg of lithium, it takes only 28,000 kg of discarded lithium-ion batteries to obtain the same amount of the metal (Qiao et al., 2021).

There are methods for recycling lithium and other metals present in batteries, one of them is acid leaching from hydrometallurgy (H. Bae et al., 2021), however, this is not yet fully understood, as there is limited information on thermodynamic simulations. This lack of data prevents the identification of optimal conditions for maximizing the recovery of lithium and other metals

As can be seen, a possible solution to meet the demand for lithium and avoid the accumulation of waste batteries is to improve recycling processes. Therefore, in this project he proposes from the collection of electronic scrap, to carry out a study to recover the lithium and cadmium present in these wastes, based on thermodynamic models, considering different concentrations of reagents, pH and temperature to maximize the release and recovery of metal species, in turn to make the extraction processes via hydrometallurgy more efficient.

# **Background**

The process of hydrometallurgical extraction, or chemical leaching, that is practiced commercially in China, for example, offers an alternative that consumes less energy and lower capital costs.

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These processes employ reagents such as hydrochloric acid (HCl), nitric acid (HNO<sub>3</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) to extract and separate metals from the cathode, generally operate below 100  $^{\circ}$ C, and can recover lithium in addition to the other transition metals (Jung et al., 2021).

Various hydrometallurgical methods have been developed over the past ten years to recycle lithium-ion battery cathode materials from various different battery chemistries, including lithium cobalt dioxide, LiCoO<sub>2</sub> (LCO), lithium manganese dioxide, LiMn<sub>2</sub>O<sub>4</sub> (LMO), lithium nickel manganese cobalt oxide, LiNiMnCoO<sub>2</sub> (NMC), and lithium oxide, nickel, cobalt, and aluminum, LiNiCoAlO<sub>2</sub> (NCA), and lithium-iron phosphate LiFePO<sub>4</sub> (LFP), to recover cobalt, nickel, magnesium, and lithium (Jung et al., 2021).

The process can be classified into four main sections, which are leaching, impurity removal, metal recovery such as Ni, Co, Mn and lithium recovery, the spent cathode material is first suspended with weak acid and then transferred to the leach tanks. Acid and reducing agent are then added to the tank leaching to leach  $Li^{+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ , and  $Al^{3+}$ . In the impurity removal section, unwanted impurities will be removed by adjusting the pH. After impurity removal, the solution is transferred to the metal recovery section, where the metal can recovered through crystallization precipitation using sodium carbonate.

For the hydrometallurgical treatment for the acid pathway in lithium and cobalt recovery, the leaching process of LiCoO<sub>2</sub> in a sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) solution could be represented as follows (H. Bae et al., 2021):

$$2\text{LiCoO}_2(s) + 3\text{H}_2\text{SO}_4(aq) + \text{H}_2\text{O}_2(aq) \rightarrow$$

$$2\text{CoSO}_4(aq) + \text{Li}_2\text{SO}_4(aq) + 4\text{H}_2\text{O}(g) + \text{O}_2(g) \quad [1]$$

Subsequently, to selectively precipitate cobalt from the leachate liquor, ammonium oxalate is added to precipitate cobalt oxalate  $CoC_2O_4 \cdot 2H_2O$ . The precipitation process can be expressed by (H. Bae et al., 2021):

$$\begin{array}{l} CoSO_{4(aq)+}(NH_{4)2}C_2\mathbf{O}_{4(aq)\rightarrow} \\ CoC_2O_{4(s)\downarrow} \quad \ \ _+(NH_{4)2}SO_{4(aq)} \end{array} \eqno [2]$$

After recovering  $CoC_2O_4$ , a high amount of sodium carbonate is added, to precipitate lithium carbonate ( $Li_2CO_3$ ). The reaction in this system is shown below (H. Bae et al., 2021):

$$2Li^{+}+Na_{2}CO_{3}\rightarrow Li_{2}CO_{3}\downarrow +2Na^{+}$$
 [3]

# Methodology

# Thermodynamic simulation of lithium and cobalt leaching

To thermodynamically model the leaching in different pH scenarios, Pourbaix and species distribution diagrams of the Li-H<sub>2</sub>O, Co-H<sub>2</sub>O systems will be constructed using the MEDUSA © software (Puigdomenech, 2010), considering the presence of sulfuric acid in different concentrations. This to find the most favorable conditions to maximize the release of lithium and cobalt from battery cathodes.

# Thermodynamic simulation of lithium and cobalt precipitation

To thermodynamically model the leaching process under different pH scenarios, Pourbaix and species distribution diagrams for the Li-H<sub>2</sub>O and Co-H<sub>2</sub>O systems will be constructed using MEDUSA© software (Puigdomenech, 2010). This modeling will consider the presence of sulfuric acid at varying concentrations to identify the most favorable conditions for maximizing the release of lithium and cobalt from battery cathodes.

# **Leaching of battery cathodes**

Based on conditions obtained from the thermodynamic simulation, the leaching of the cathodes of the waste batteries will be carried out; in order to release the lithium and cobalt they contain in solution. A simplified diagram of the process that will be carried out in the leaching of the battery cathodes is presented (Figure 1).

(2)

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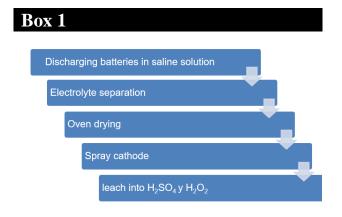


Figure 1

Process used for leaching cathodes from mobile phone batteries

Source: Own elaboration

# Precipitation of Li<sub>2</sub>CO<sub>3</sub> and CoC<sub>2</sub>O<sub>4</sub>

Once the leaching of the battery cathodes has been carried out and based on the conditions obtained in terms of reagent concentration, pH and temperature in the thermodynamic simulation, the recovery from the precipitation of lithium and cobalt will be carried out as follows:

Addition of sodium hydroxide to the leachate solution to adjust pH to maximize cobalt recovery.

Addition of ammonium oxalate in the solution to selectively recover cobalt, precipitating as cobalt oxalate (CoC<sub>2</sub>O<sub>4</sub>).

Filter the (CoC<sub>2</sub>O<sub>4</sub>) precipitates from the solution and dry them in the oven.

Add sodium carbonate to the cobalt-free solution to precipitate lithium in the form of lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>).

Filter the Li<sub>2</sub>CO<sub>3</sub> lithium carbonate precipitates from the solution and dry in an oven and discard the solution.

# **Results**

One of the easiest ways to determine if it is possible to form a chemical compound is by employing the Nernst equation (Eq. 4) from the dissolution reaction, where  $aO + ne^- \rightarrow bR$  the pH range for its formation can be calculated.

$$E_{Rxn} = E_{Rxn}^{\circ} + \frac{RT}{nF} \ln \frac{a_o^a}{a_R^b}$$
 [4]

In this way, in the present work, thermodynamics was used through the construction of Pourbaix diagrams to identify the possible species that can be formed, in addition to the use of species distribution diagrams to identify the conversion fraction associated with a certain pH.

It should be noted that these thermodynamic simulations are carried out at room temperature (25 °C) which would lead to a more cost-effective process.

The Pourbaix diagram was constructed for the Co-Li system by adding the oxalate ion, in order to elucidate the formation of cobalt oxalate, Figure 2 presents this diagram with an oxalate concentration of 1 M, highlighting the different phases that predominate in the system. Notably, cobalt oxalate stands out, which is formed only in the acidic window of pH 0.1-5.

# Box 2

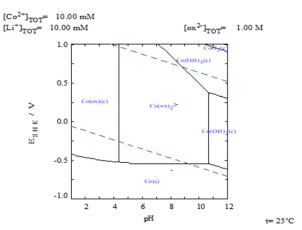


Figure 2

Pourbaix diagram of the Co-Li system with the oxalate ion.

Source: Own elaboration

According to the molar fraction diagram at different pH values of this same system (Figure 3), it can be elucidated that the most appropriate pH to maximize the formation of this cobalt oxalate compound is 2.85, since it is there where the maximum conversion peak is 0.96.

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## Box 3

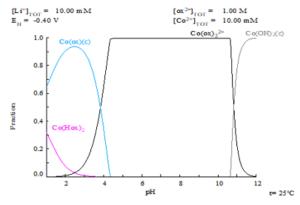


Figure 3

Distribution diagram of species of the Co-Li system with the oxalate ion.

Source: Own elaboration

Additionally, the Pourbaix diagram was elaborated by decreasing the oxalate concentration to 0.5 M (Figure 4), in which it is observed that the cobalt oxalate formation window was greatly expanded, in a pH range of 1-10, with respect to that found in Figure 2.

# Box 4

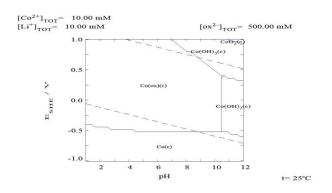


Figure 4

Pourbaix diagram of the Co-Li system with oxalate ion Source: Own elaboration

Regarding the distribution diagram of species with the concentration of 0.5M oxalate (Figure 5), the maximum fractional conversion of cobalt oxalate crystals is achieved at a pH of 2.85, obtaining a conversion of 0.98 greater than that of 1 molar (Figure 3).

# Box 5

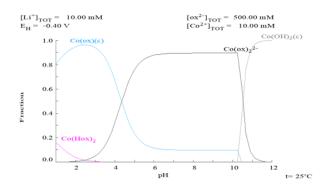


Figure 5

Distribution diagram of species of the Co-Li system with the oxalate ion.

Source: Own elaboration

Similarly, the Pourbaix diagram was constructed by increasing the concentration of oxalate to 10 M (Figure 6), in which it is observed that the window of cobalt oxalate formation was greatly decreased, in a pH range of 2-3, in this sense the more the oxalate concentration is increased, the cobalt oxalate formation window will decrease.

# Box 6

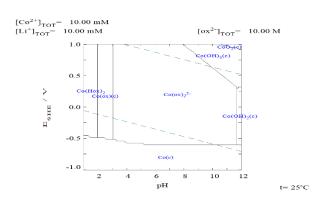


Figure 6

Pourbaix diagram of the Co-Li system with the oxalate ion.

Source: Own elaboration

As for the distribution diagram of species with the concentration of 10 M, it is observed that the maximum peak of fractional conversion to cobalt oxalate is observed to be 0.4, which is reached at a pH of 2.8 (Figure 7).

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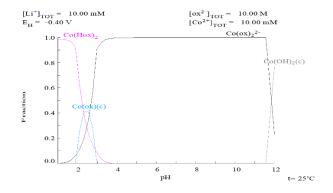


Figure 7

Distribution diagram of species of the Co-Li system with the oxalate ion.

Source: Own elaboration

It is interesting to mention that (Chen et al., 2015; Li et al., 2023; Zhu et al., 2012) carried out research where they recovered cobalt in lithium-ion batteries, precipitating it in the form of cobalt oxalate, obtaining good results with a recovery close to 90% with an oxalate concentration of 0.5 M at a pH of 2, however, according to the results of the thermodynamic simulation, an increase of 8% can be achieved if a pH of 2.85 is used (Figure 8). Additionally, the simulation indicated that regardless of the concentration, the pH that maximizes the conversion or recovery of cobalt oxalate is around 2.8-2.85.

# Thermodynamic Modeling for Lithium and Cobalt Recovery

On the other hand, the Pourbaix diagram was constructed for the Li-Co system by adding the carbonate ion, in order to find the formation of lithium carbonate. Figure 8 presents this diagram with an oxalate concentration of 1 M, where the different phases that predominate in the system can be appreciated. In this the presence of lithium carbonate is highlighted, which is formed in a wide window of pH 1-14, it should be noted that the Pourbaix diagrams remain unchanged regardless of variations in the carbonate ion concertation.

# Box 8

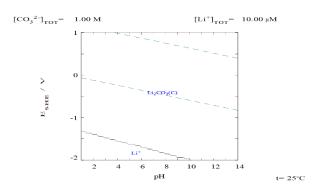


Figure 8

Pourbaix diagram of the Li system with the carbonate ion.

Source: Own elaboration

According to the molar fraction diagram at different pH values with a carbonate ion concentration of 0.001M (Figure 9), it can be elucidated that at low carbonate concentrations the formation of lithium carbonate is low, only 0.2 (20%) in a pH range of 10-14.

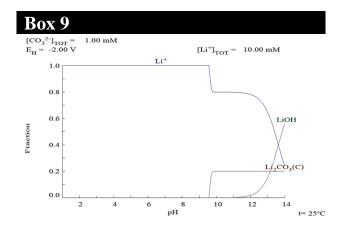


Figure 9

Distribution diagram of species of the Li system with the carbonate ion.

Source: Own elaboration

Regarding the distribution diagram of species with the concentration 0.5M of the carbonate ion (Figure 9), the maximum fractional conversion of sodium carbonate crystals is reached at a pH greater than 10, obtaining a conversion of 0.98, higher than that of 0.001 molar (Figure 8).

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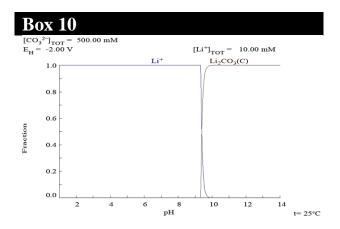


Figure 10

Li System Species Distribution Diagram with Carbonate ion.

Source: Own elaboration

Finally, the simulation was carried out by increasing the concentration of the carbonate ion up to 10 M (Figure 11), obtaining results very similar to those obtained with a lower concentration 0.5 M (Figure 10), based on this it can be observed that it is not convenient to use a high concentration of carbonate ion, since it does not reflect an improvement in the recovery of lithium carbonate.

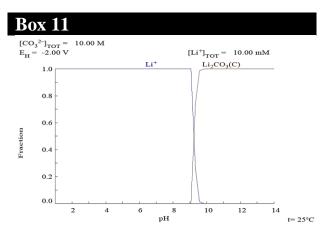


Figure 11

Distribution diagram of species of the Li system with the carbonate ion.

Source: Own elaboration

Additionally, studies carried out by different authors, where they recovered lithium in lithium-ion batteries, precipitating it in the form of lithium carbonate, obtaining recoveries around 70%, the concentration of carbonate, nor the pH used for such recovery is not mentioned, according to the results obtained in the present study 25% more can be recovered, if a concentration of 0.5 M and a pH close to 10 are used. (Chen et al., 2015; Li et al., 2023; Zhu et al., 2012).

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# Acid leaching of battery cathodes

Initially, the dismantling, electric discharge in saline solution, separation and pulverization of the cathodes present in the batteries, obtained in the recycling campaign, was carried out, then the leaching was carried out to release the cobalt and lithium with a solution a concentration of 3M, agitation of 300 rpm, time of 2 hours and a temperature of 25 °C. these conditions were used because, according to the authors (Chen et al., 2015; Zhu et al., 2012; Kaya, 2022), it is possible to obtain a 100% release of the cobalt and lithium present in the cathodes of the battery  $H_2SO_4$  (Figure 12).

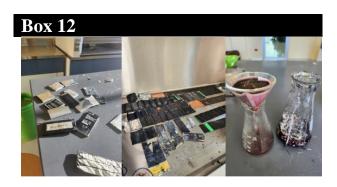


Figure 12

Disassembly, leaching, and filtering of battery cathodes.

Source: Own elaboration

# **Recovery of cobalt from leachate solution**

After leaching the cathodes, the solution rich in cobalt and lithium was filtered to add ammonium oxalate (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) at different concentrations and pH (Figure 13), to evaluate the results obtained in the thermodynamic simulation (Table 1).

#### **Box 13**



Figure 13

Addition of ammonium oxalate and precipitation of cobalt oxalate.

Source: Own elaboration

Farias-Gonzalez, Miguel Angel, Farias-Gonzalez, Francisco Javier and Perez-Castro, Laura Luz. [2024]. Thermodynamic study for the recovery of lithium and cobalt from waste batteries. Journal Renewable Energy. 8[20]-1-10: e10820110.

## **Box 14**

Table 1

Cobalt recovery results at different concentrations and pH.

Temperature (°C)	pН	Concentration (M)	Recovery (g)
25	2.85	0.5	3.4172
25	2	0.5	3.1774
25	2.85	10	2.1178
25	2	10	1.8733

Source: Own elaboration

By comparing the recovery of cobalt oxalate with the following conditions: pH 2.85 and a concentration of 0.5 M oxalate, with that used by with a pH of 2 and an oxalate concentration of 0.5 M, it was possible to increase recovery by 7.017% (Chen et al., 2015; Li et al., 2023; Zhu et al., 2012).

This same phenomenon occurs when the oxalate concentration is increased to 10 M. Comparing pH 2 and pH 2.85 under these conditions, recovery increases by 11.54% at pH 2.85. The thermodynamic simulation results are conclusive for the recovery and precipitation of cobalt as cobalt oxalate. It was identified that the pH maximizing cobalt recovery is 2.85 at any concentration. Moreover, with an oxalate concentration of 0.5 M, it is possible to recover up to 98% of cobalt.

# Recovery of lithium from leachate solution

Finally, after recovering the cobalt, sodium carbonate was added to the solution without cobalt to precipitate the lithium in the form of lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>) using different concentrations of sodium carbonate (Figure 14), it should be noted that fixed at a pH of 10, this because according to the thermodynamic simulation at this pH the highest lithium recovery is obtein.

# **Box 15**



Figure 14

Lithium carbonate recovery

Source: Own elaboration

When comparing lithium carbonate recovery with different concentrations of sodium carbonate (Table 2), it was found that low concentrations greatly reduce lithium recovery.

# **Box 16**

Table 2

Lithium recovery results at different concentrations

Temperature	pН	Concentration	Recovery
(°C)		(M)	(g)
25	10	0.01	1.5784
25	10	0.5	3.8557
25	10	10	3.8487

Source: Own elaboration

In addition, it was obtained that it is not necessary to use large concentrations of sodium carbonate to increase recover, since by using 10 M or 0.5 M, very similar recoveries were obtained, furthermore, it was also found that it is not necessary to use high temperatures to obtain good recovery results.

The thermodynamic simulation results are conclusive for the recovery and precipitation of lithium, in the form of lithium carbonate, since it was possible to identify that the pH that maximizes lithium recovery is 10 in any concentration, however, it was found that it is not necessary to use high concentrations of sodium carbonate to have a good lithium recovery, a low concentration 0.5 M is enough, these results contrast with those obtained by various authors (Chen et al., 2015; Li et al., 2023; Zhu et al., 2012), where they suggest using saturated lithium carbonate solutions to obtain satisfactory lithium carbonate recoveries.

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#### **Conclusions**

Based on the objectives set, it was possible to carry out the thermodynamic study for the recovery of lithium and cobalt, from lithium-ion batteries, collected through an electronic scrap recycling campaign.

The optimal conditions that maximize cobalt recovery were shown to be pH 2.85 and 0.5 M oxalate. For lithium recovery it was found that low concentrations of sodium carbonate of 0.5 M and pH 10 are required to efficiently recover lithium.

It was possible to make the lithium and cobalt extraction process more efficient from the precipitation of lithium carbonate and cobalt oxalate, based on the data obtained by the thermodynamic simulation and the experiments carried out.

Finally, the present study collaborates with an innovative contribution in the area of lithium and cobalt extraction processes in lithium-ion batteries, since there is no reported history to make these processes more efficient.

#### **Conflict of interest**

The authors declare no interest conflict. They have no known competing financial interests or personal relationships that could have appeared to influence the article reported in this article.

# **Author contribution**

Farias-Gonzalez, Miguel Angel: Contributed with the main idea of the project and carry out thermodynamic simulations to find the operating conditions for the experiments.

Farias-Gonzalez, Francisco Javier: Contributed by interpreting the data obtained through thermodynamic simulation, as well as carrying out experiments for the recovery of lithium and cobalt.

Perez-Castro, Laura Luz: Helped in the review of the systematization of the background for the state of the art, the research design, the type of research, the approach, the method and the writing of the article.

#### Availability of data and materials

The lithium-ion batteries were collected from a recycling campaign, and the experimentation was carried out within the institution's laboratories.

#### **Funding**

The research did not receive any funding.

#### **Abbreviations**

Co Cobalt

CoC<sub>2</sub>O<sub>4</sub> Cobalt oxalate

Li Lithium

Li<sub>2</sub>CO<sub>3</sub> Lithium carbonate

M Molarity

pH Hydrogen Potential mt Million tonne

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# Using latent heat from a water purification system to improve the performance of an absorption heat transformer

# Uso del calor latente de un sistema de purificación de agua para mejorar el desempeño de un transformador térmico por absorción

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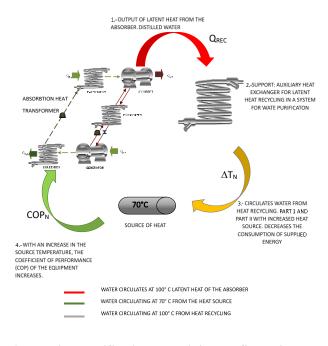
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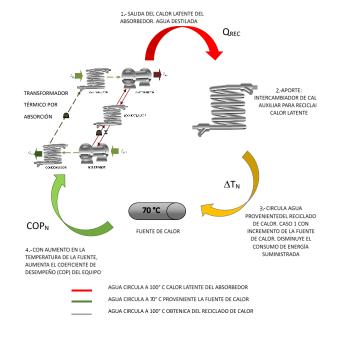
#### **Abstract**

Absorption heat transformer for water purification (AHTWPs) are an option for utilizing energy from industrial or natural sources. Previous studies have demonstrated the feasibility of recycling the heat produced by the distillation of impure water, increasing the coefficient of performance (COP) values and reducing the energy requirements in the AHTWP. The present work presents a heat recovery proposal consisting in combining two cases: with source temperature increase (Case II). The new configuration allows the fractionation of the available amount of heat ( $\Box \eta QAB$ ) between the two heat recovery cases. A simulation was carried out for different absorber operating conditions, using H2O-LiBr as the working mixture at different concentrations. The results show that it is possible to increase the initial COP values up to 74%.



#### Resumen

Los sistemas de transformador térmico por absorción para purificación de agua (TTAPA) son una opción para la recuperación de energía proveniente de fuentes industriales. Estudios anteriores han demostrado la viabilidad de reciclar el calor latente producto de la destilación simple del agua impura, incrementar los valores del coeficiente de operación (COP) y disminuir los requerimientos de energía primaria en el sistema de absorción. El presente trabajo presenta una propuesta para el reciclado de calor, que consiste en combinar las dos formas reportadas en la tieratura: con incremento en la temperatura de la fuente (Caso I) y sin incremento de la temperatura de la fuente (Caso II). Se realizó una simulación para diferentes condiciones de operación del absorbedor, utilizando H2O-LiBr como mezcla de trabajo a diferentes concentraciones. Los resultados muestran que es posible incrementar los valores iniciales del COP hasta un 74%.



# Absorption, purification, combining configuration

#### Absorción, purificación, configuración combinada

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#### Introduction

Heat pump systems represent an alternative in energy savings because they can be coupled to industrial processes for heat recovery. The absorption heat transformer (AHT) is a type of heat pump that operates with waste heat that can come from an industrial source or a solar collector and raise its thermal level to be used in a secondary process [1]. AHT are used to boost energy from low thermal level heat sources [2]. AHT could supply the world's demand [3]. AHT is considered environmentally friendly and an excellent alternative to traditional systems. One of the most widely used working pairs is LiBr/H<sub>2</sub>O [4]. The absorption system using LiBr/H<sub>2</sub>O as the working fluid plays an increasingly important role in heating [5].

LiBr must operate near the ideal temperature and mass fraction to achieve its highest efficiency [6]. The main objective of the heat exchanger is to have the minimum heat transfer surface area for better performance, lower cost. The surface area is determined by the overall heat transfer coefficient. The correlation of heat transfer coefficient plays an important role in the optimization of the heat exchanger [7]. Several configurations of heat transformers have been proposed and studied. these configurations were designed to improve the coefficient of performance (COP) [8]. A AHT of 5000 kW capacity with a steam stream at 98°C coming from a plastics plant was used to heat water in a range of 95-110°C, the COP obtained was 0.47, with a GTL of 25°C and using H<sub>2</sub>O-LiBr as working mixture [9]. At pilot scale a AHT was tested using a partially miscible mixture of n-heptane/N,N-dimethylformamido, the values of thermal efficiency obtained were between 30 and 40% and a maximum temperature difference of 8°C [10]. feasibility of coupling a AHT to a textile plant for heat recovery at 92°C and heating process water up to 120°C with 50% heat recovery using H<sub>2</sub>O-LiBr as the working mixture has been demonstrated [11]. In some countries absorption heat exchangers play an important role in district heating. [12]. Absorption heat transformer systems have also been studied as an alternative to conventional water desalination techniques. Experimentally, the results of a 1 kW water purification AHT are reported, the COP obtained was 0.228 with a distilled water flow rate of 448 mL/h, the working mixture H<sub>2</sub>O-LiBr [13].

A water purification system by AHT with a capacity of 4.1 kg/h was operated and analyzed, the COP values were from 0.3 to 0.38 and the water obtained is considered within the limits to be drinking water [14]. Thermodynamic models of AHT for water purification have been reported in the literature. [15] designed a model of a water purification system integrated to a AHT using H<sub>2</sub>O-(LiBr+LiI+LiNO<sub>3</sub>+LiC1) as working mixture and showed that this mixture provides higher COP values than those obtained with the H<sub>2</sub>O-LiBr mixture. Studies, simulations and experiments have been carried out on absorption technology, but more development and research on it is needed, because they are cost-effective, very energy efficient, compact in size and environmentally friendly [16].

Absorption systems have generated interest in industry and research in recent years. They consume less electricity, which is the main advantage over conventional systems [17]. [18,19] and [20] developed models using neural networks. AHT integrated water purification systems have also been analyzed from the point of view of the second law of thermodynamics [21,22]. It has been found that the main resistances for mass and heat transfer are those between the vapor and the interface [23]. In addition to the fact that the absorber is the most critical component in absorption systems, complex heat and mass transfer phenomena occur simultaneously in the absorber [24].

The absorber affects the efficiency of the absorption equipment. The mass transfer flux increases with increasing solution concentration at the inlet [25]. Understanding the heat and mass transfer between the solution and LiBr vapor is a crucial issue in absorption to intensify the transfer [26]. Investigations on mass and heat transfer behavior should be carried out under realistic operating conditions of adsorption cycling [27]. Heat recycling in water purification systems integrated to AHT is also reported in the literature [28,29,30]. Recent studies have evaluated heat recovery [31]. They propose models for the "maximum temperature rise" of a typical absorption heat transformer cycle [32]. The thermal energy by latent heat of casing and tubing not only improves the melting process of the phase change material, it also improves the overall performance of these systems [33].

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Innovative strategies have been presented to simplify the latent heat migration steps in the heat recovery process, results indicate that the new heat recovery strategy exhibits higher growth rates in both flow and throughput ratio [34], these studies show that it is possible to reintroduce the latent heat from water distillation into the AHT and increase the COP values and the performance of the equipment.

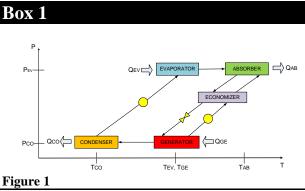
Based on the literature review, no theoretical works were found that propose the combination of two forms of heat recycling in a water purification system integrated to an AHT. This work presents the results obtained by simulation using H<sub>2</sub>O-LiBr as working mixture and different operating conditions. The results show that it is possible to increase the COP values by adding an auxiliary condenser to the conventional AHTWP scheme and obtained increased from 74% from original value.

This article shows the mathematical model and the analysis of results from the simulation, finally the conclusions of the present work.

## **Basic concepts**

Figure 1 shows a schematic diagram of an absorption heat transformer (AHT). Absorption systems use working pairs, formed by a working fluid, circulating through the primary circuit, and an absorber located in a secondary circuit. The primary circuit begins in the condenser, where the working fluid condenses, releasing a quantity of useful heat (QCO), then passes to the evaporator, where it evaporates, exchanging energy with the heat source, at a PEV pressure higher than the P<sub>CO</sub> pressure and a T<sub>EV</sub> temperature higher than the T<sub>CO</sub> temperature. The vapour phase working fluid passes to the absorber, where it mixes with the absorber-rich solution (secondary circuit) and releases a quantity of useful heat (QAB) as a result of the exothermic reaction. The secondary circuit starts when the working mixture rich in working fluid leaves the absorber at a temperature TAB and enters the economizer, where it gives up heat to the working mixture coming from the generator at a temperature T<sub>GE</sub>.

As it enters the generator, part of the working fluid is separated as a result of the heat exchange between the working mixture and the heat source, while the working solution rich in absorbent passes to the economiser to re-enter the absorber.



Schematic diagram of an absorption heat transforme Source: [Own elaboration]

Figure 2 shows a schematic diagram of the water purification process by AHT, which consists of using the useful heat of the absorber (Q<sub>AB</sub>) to bring the impure water to its saturation point and partially evaporate it, the saturated mixture passes to a phase separator where the saturated vapour is sent to an auxiliary condenser by the energy exchange provides a quantity of heat  $(\eta Q_{AB})$  to condense and obtain purified water. The quantity  $\eta Q_{AB}$  [28] represents the heat that can be recycled to the AHT. The recycling of this heat can reduce the energy requirements of the system and enhance the COP values. Two configurations for recovering this useful heat are described in the literature.

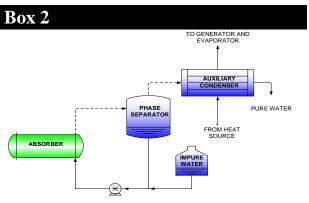


Figure 2

Water purification process using an absorption heat transformer

Source: [Own elaboration]

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Figure 3 illustrates the initial form of heat recycling for an AHTWP system, as reported by Siqueiros and Romero [28]. In this configuration, the stream from the heat source is sent directly to an auxiliary condenser where it exchanges heat with the evaporated water from the phase separator. Upon leaving the condenser, the water's initial temperature increases by an amount  $\Delta T$ , entering the generator and evaporator. The evaporated water then condenses, yielding an amount of heat  $(\eta Q_{AB})$ , to produce purified water. This recycling method will be referred to as 'Case I' in the following discussion.

# Box 3

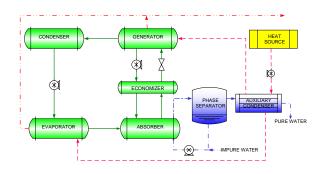


Figure 3

Heat recycling configuration increasing heat source temperature (Case I)

Source: [Own elaboration]

Figure 4 illustrates the second form of heat recycling for an AHT integrated with a water purification system, as reported by Romero et al. [29]. In this configuration, the useful heat ( $\eta Q_{AB}$ ) product of simple distillation is recycled to the system by heat exchange in the auxiliary condenser of the heat source streams leaving the evaporator and generator, as well as the vaporized water leaving the phase separator. The vaporized water releases heat as it condenses and purifies, while the heat source stream increases its initial temperature to reenter the system. For the sake of clarity, we will refer to this form of recycling as 'Case II'.

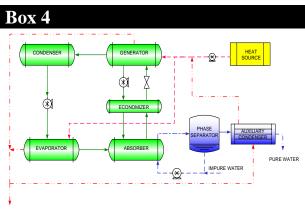
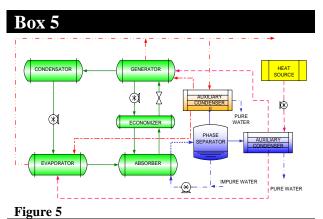


Figure 4

Heat recycling configuration without increasing heat source temperature (Case II)

Source: [Own elaboration]

Figure 5 shows the proposed heat recovery combination for an AHTWP. The useful heat obtained in the absorber (QAB) is used to raise the impure water to its saturation point and partially evaporate it. The saturated mixture then passes to a phase separator, where the liquid phase is reintroduced into the purification circuit, while the vapour phase is split and sent to auxiliary condensers I and II. In the auxiliary condenser I, the vapour is condensed by exchanging energy with the heat source stream, producing purified water. The heat source stream gains an amount of energy, which subsequently enters the evaporator and generator with an increase in its original temperature,  $\Delta T$  (Case I) [28]. In the auxiliary condenser II, the purified water is vaporised and exchanges heat with the stream coming from the evaporator and generator. This stream is heated to a higher temperature and re-enters the system (Case II) [29]. By distributing the latent heat product of distillation ( $\eta QAB$ ) between the two forms of recycling, the energy requirements of the AHT are reduced and the COP values are increased.



[Proposal heat recovery combination

Source: [Own elaboration]

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# Methodology

The mathematical equations used for simulating this system are based on thermodynamic models previously published by other authors [1][9]. This modelling approach has been tested and proven effective. The model was developed based on the following considerations:

- The entire system is in thermodynamic equilibrium.
- The analysis is carry out under steady-state conditions.
- A rectifier is not required since the absorbent does not evaporate under the operating temperature rang of the system.
- The solution that lives the generator and absorber is saturated; similarly, the working fluid leaving the condenser and the evaporator is also saturated.
- Heat losses and pressure drops in the tubing and the components are considered negligible.
- The flow through the valves is isenthalpic.
- The pumps are isentropic.
- Temperatures at the exit of the main components and the heat load in the evaporator  $(Q_{EV})$  are known.
- The efficiency of economizer is well known.
- 1. Calculation of the COP for the proposal for combined heat recycling

The water purification system provides a finite amount of energy recycling to the AHT, which can be calculated by:

$$Q_{REC} = \eta Q_{AB}$$
 [1]

Where  $\eta$  is defined as:

$$\eta = \frac{\Delta H_{V}}{\Delta H_{V} + \Delta H_{S}}$$
 [2]

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For water purification is considered an initial temperature of 25 °C for impure water and a boiling point of 100 °C at atmospheric pressure, so that the value of  $\eta$  is a constant with a value of 0.877 [14]. The Q<sub>REC</sub> can be divided into two fractional components, which correspond to the two possibilities of energy recycling (case I and case II). The energy balance in the heat source can be estimated by:

$$Q_{HS} = m_{HS}Cp\Delta T_{HS}$$
 [3]

In the case I of energy recycling,  $T_{EV}$  and  $T_{GE}$  temperatures can be increased in a quantity  $\Delta T_N$  which is calculated by:

$$\Delta T_{N} = \eta COP_{ET} \Delta T_{HS}$$
 [4]

However, should only a portion of this increase be allocated to case I, the new temperatures in the evaporator and generator can be calculated using the following equation.:

$$T_{EV,N} = T_{EV} + \alpha \Delta T_{N}$$
 [4]

$$T_{GE,N} = T_{GE} + \alpha \Delta T_{N}$$
 [5]

The value of  $\alpha$ , which takes a range of 0 to 1, represents the fraction of heat that is sent to the Case I. To evaluate the effect of the Case I enthalpy-based COP definition for a heat transformer, we used the following methodology:

$$COP_H = \frac{Q_{AB}}{Q_{FV} + Q_{GF}} \tag{6}$$

Depending on the temperatures,  $T_{\text{EV},N}$  and  $T_{\text{GE, }N}.$ 

The temperatures will affect the  $T_{EV, N}$  and  $T_{GE, N}$ . For Case II, we will use the definition of the COP<sub>WP</sub> proposed by Romero *et al.* [14].

$$COP_{WP} = \frac{COP_{ET}}{1 - \eta COP_{ET}}$$
 [7]

In this instance, the proportion of heat transferred to this category of energy recycling is represented by  $\beta$ . Consequently, the ultimate values of the COP, accounting for the impact of both Case I and Case II of energy recycling, can be determined using the following equation:

$$COP_N = \frac{COP_{ET}}{1 - \beta \eta COP_{ET}}$$
 [8]

Morales, L.I., Siqueiros J., Juárez-Romero D. and Hernández-Soria, A. H.. [2024]. Using latent heat from a water purification system to improve the performance of an absorption heat transformer. Journal Renewable Energy. 8[20]-1-10: e10820110.

#### **Results**

The results of simulation are shown below. Three conditions of  $\Delta T$  conditions are presented for the same absorber and condenser temperature T<sub>AB</sub>=115°C, T<sub>CO</sub>=30 °C. In this first condition of  $\Delta T=5^{\circ}$  C and  $T_{GE}=T_{EV}=70^{\circ}$  C in Figure 6, it is observed that if the combination is not made, the COP<sub>H</sub> value will be 0.29, but if the combination is made, the COP<sub>N</sub> increases to a value of 0.42, which is closer to the theoretical value of 0.50. This is a consequence of increasing the concentration of the solution in the generator, which improves a better reaction in the absorber at constant pressure. With respect to the initial COP value, the COP<sub>H</sub> value can be increased by up to 46%. This makes it possible to save more primary energy in the circuit of the absorption heat exchanger and to increase the outlet temperature in the absorber.

# Box 6

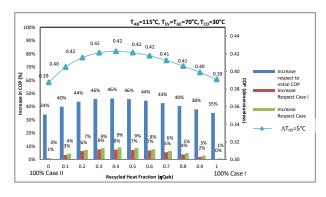


Figure 6

Increases of COPH in function of  $\eta Q_{AB}$  with  $\Delta T_{HS}\!\!=\!\!5^{\circ}C$  Source: [Own elaboration]

Figure 7 presents the COP behaviour when a recycle heat increment of  $\Delta T=10^{\circ}$  C is available. It is possible to increase the COP<sub>H</sub> value up to a maximum value of 0.47 which represents an increase of the initial COP of 62%. So if the combination is carried out, it is possible to increase the original COP<sub>H</sub> value from 0.29 to 0.47, which represents an amount of heat that can be recovered very close to the theoretical And if you compare the percentage increase of the COP<sub>N</sub> of the combination with Case I and Case II, it is convenient to make the combination because the increase is higher, the values goes to 0.34 to 0.47. These increases are the result of the increase the latent heat in auxiliary condenser II and in conclusion increase the vapor in evaporator promoting a better reaction in absorber.

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# Box 7

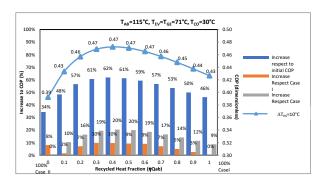


Figure 7

Increases of COP<sub>H</sub> in function of  $\eta Q_{AB}$  with  $\Delta T_{HS}$ =10°C Source: [Own elaboration]

In Figure 8 shows the behavior of the COP when increasing  $\Delta T=15^{\circ}$  C. Increasing the latent heat  $\Delta T$  also increases the steam production at the outlet of the evaporator and facilitates a higher useful heat in the absorber, increasing its power, because a strong exothermic reaction takes place, reducing the concentration of the working solution going to the generator, also increasing the pressure, which increases the power of the generator to satisfy the energy balance. Under these conditions, it is possible to increase the COP<sub>H</sub> values up to 0.51, which represents an increase of 74%, using the combination, in other cases, using Case I or Case II alone, an increase 53% and 39% respectively is possible.

# Box 8

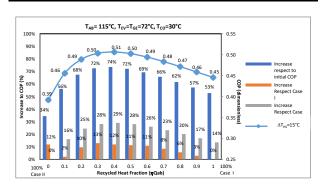


Figure 8
Increases of COP<sub>H</sub> in function of  $\eta Q_{AB}$  with  $\Delta T_{HS}$ =15°C

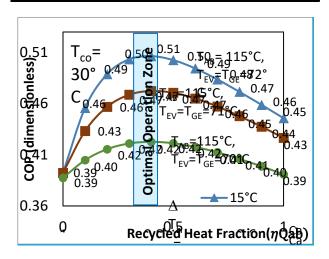
Source: [Own elaboration]

Figure 9 shows the three conditions previously discussed, demonstrating an optimal operational range for the combined utilization of the two forms of heat recycling. The most effective method for achieving an increase in COP is to combine Case I with a 40% increase and Case II with a 60% increase.

Morales, L.I., Siqueiros J., Juárez-Romero D. and Hernández-Soria, A. H.. [2024]. Using latent heat from a water purification system to improve the performance of an absorption heat transformer. Journal Renewable Energy. 8[20]-1-10: e10820110.

This results in an overall COP<sub>H</sub> increase of up to 74% through the utilization of the latent heat of the purified water.

## Box 9



#### Graphic 4

Comparison of COP increase for three different  $\Delta T_{\text{HS}}$  conditions

Source: [Own elaboration]

#### **Conclusions**

In conclusion, adding an auxiliary condenser II to the water purification circuit integrated to a thermal transformer increases the  $COP_H$  values. The  $COP_{WP}$  increases with the latent heat of the purified water, which depends on the quality of the impure water and the atmospheric pressure. When heat is recycled, COP increases from 46% to 74%. This work shows that combining 40% to Case I and 60% to Case II is the best option.

## **Declarations**

# **Conflict of interest**

The authors declare no interest conflict. They have no known competing financial interests or personal relationships that could have appeared to influence the article reported in this article.

## **Author contribution**

*L.I Morales*: was responsible for developing the initial concept, creating the model and analyzing the resulting data.

J. Siqueiros provided valuable input to the project, offering insights on the concept, data analysis and conclusions.

D. Juárez-Romero: Provided input to the analysis of results and conclusions.

A.H. Hernández: contributed to the literature review, data analysis and conclusions.

# Availability of data and materials

Communication with the principal autor laura.morales@uaem.mx

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Absorption host transformer

## **Abbreviations**

АПІ	Absorption near transformer
COP	Coefficient of Performance (Dimensionless)
H	Enthalpy (kJ/kg)
Q	Heat flux (kW)
Cp	Heat Capacity (kJ/kg°C)
m	Mass flow rate (kg/s)
T	Temperature (°C)

## Sub-index

AB

CO	Condenser
EV	Evaporator
GE	Generator
HS	Heat Source
Н	Enthalpy
N	New
REC	Recycled
S	Sensitive
V	Vaporization
WP	Water purification

Absorber

# Greek-symbols

η	Fraction	of	available	heat
β	Fraction of	heat sent t	to Case II	
α	Fraction of	heat sent t	to Case I	
ε	Efficiency.			

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References Classification

Antecedents:

[1], [2], [3], [16]

Basics:

[4], [5], [6], [7], [17], [24], [25], [26], [27]

Support:

[8], [9], [13], [14], [21], [22], [23], [28], [29], [30], [31], [32], [33], [34]

Differences:

[10], [11], [12], [15]

Discussion:

[18], [19], [20]

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# Ships decarbonization is an urgent technology and responsibility challenge that impacts global warming

# Descarbonización de barcos es un reto de urgencia tecnológica y responsabilidad que impactan en el calentamiento global

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#### Abstract

Maritime transport generates 3% of global  $CO_2$  emissions according to the GHG (Greenhouse Gases) report. The aim of this research was to analyze the decarbonization of ships through the technological migration from conventional fuels to alternative types for zero-emission purposes. On the other hand, shipping companies that modernize their fleets to zero emissions will have priority in the provision of services. However, those that do not have these assets will be penalized. A mixed analysis was carried out on the migration of technologies in zero-emission ships based on the quantification and estimation of statistical control variables, decision-making, modernization stages and technologies. The characterization of data obtained from each ship will determine the feasibility of applicable technologies to achieve zero emissions. The optimization of technology applied to each ship according to its use will be the subject of future work.

Objectives	Methodology	Contribution	
Analyze the	This research had	The	
decarbonization	a mixed approach,	characterization	
of ships through	applying both	of data obtained	
the technological	quantitative and	from each ship	
migration from	qualitative	will determine the	
conventional fuels	technologies,	feasibility of	
to alternative	using systematic	applicable	
types for zero-	processes, as well	technologies to	
emission	as records and	achieve zero	
purposes.	estimated data.	emissions.	

# shipping industry carbon footprint, ships decarbonization, zero emissions ships

#### Resumen

El transporte marítimo genera 3% de las emisiones de CO<sub>2</sub> globales de acuerdo con el reporte GEI (Gases de Efecto Invernadero). El objetivo de esta investigación fue analizar la descarbonización de buques a través de la migración tecnológica de combustibles convencionales a tipo alternativos con fines de cero emisiones. Por otro lado, Las navieras que realicen la modernización de sus flotas a cero emisiones tendrán prioridad en el préstamo de servicios. Sin embargo, las que no cuenten con estos activos tendrán penalizaciones. Un análisis mixto fue realizado en la migración de tecnologías en barcos cero emisiones basado en la cuantificación y estimación de variables de control estadísticas, toma de decisiones, etapas de modernización y tecnologías. La caracterización de datos obtenidos de cada barco determinaran la factibilidad de tecnologías aplicables para lograr las cero emisiones. La optimización de tecnología aplicada a cada barco según su uso será motivo de trabajos futuros.

Objetivos	Metodología	Contribución
Analizar la	Esta investigación	La caracterización
descarbonización	tubo un enfoque	de datos
de buques a través	mixto, aplicando	obtenidos de cada
de la migración	tecnologías tanto	barco determinara
tecnológica de	cuantitativas	la factibilidad de
combustibles	como cualitativas,	tecnologías
convencionales a	utilizando	aplicables para
tipo alternativos	procesos	lograr las cero
con fines de cero	sistemáticos, así	emisiones.
emisiones.	como registros y	
	datos estimados.	

huella de carbono industria naviera, descarbonización de barcos, emisiones cero barcos

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#### Introduction

3% of global CO<sub>2</sub> emissions are produced by maritime transport according to the GHG (Greenhouse Gas) report. The IMO (International Maritime Organization) warns that failure to take decisions and measures to reduce this will result in an increase with major consequences for global warming. Decisions on the course to follow are governed by rules and regulations negotiated and agreed upon by the (IMO) and shipping companies with large assets in the maritime fleet industry and port companies. The initial proposal was to bet on the decarbonization of maritime transport and what this implies in deep waters and on land with objectives to be met in the short term 2025, medium term 2030 and long term 2050 to achieve zero emissions in the shipping fleet in transport, loading and unloading (Akgül, 2024 and Baştuğ et al., 2024).

The aim of this research was to analyze the decarbonization of ships through technological migration from conventional fuels to alternative types for zero-emission purposes; in addition, this transition is essential for achieving sustainability in maritime transport. The characterization of data obtained from each ship will determine the feasibility of applicable technologies to achieve zero emissions.

migration Nevertheless, the from conventional petroleum-derived fuels to zeroemission alternative fuels was the proposal with the greatest emphasis. The agreements of the organizations and companies involved decided to adopt alternative fuels with low or zero greenhouse gas emissions. Proposals on new technologies, logistics, change of travel rates, investments, execution times, economic support for modernization, among others, were the basis for focusing mainly on the source of pollution with the greatest impact: ships (Black et al., 2024 and Koilo, 2024)

How to achieve the decarbonization of port assets in line with the objectives of the IMO (International Maritime Organization)? in a sustainable manner and with a circular economy.

The renewal of engines, modernization and renewal of ship fleets must be accompanied by expert personnel in the design of ship engines, who can generate feasible and sustainable proposals for the sector to meet the 2025 aims. IMO representatives are negotiating support and financial aid to help developing countries have equal participation in the evolution and adaptation of maritime transport. However, they also warn that there will be no turning back and that delaying decarbonization would not be more costly due to its impact on climate change (Black et al., 2024 and Karvounis, et al., 2024).

With greater emissions to reduce in a shorter period with higher costs of dealing with pollution emergencies that generate uncertainty and increase implementation costs during transition times. The optimization of technology applied to each ship according to its use will be the subject of future work.

## Research methodology

This research had a mixed approach, applying both quantitative and qualitative technologies, using systematic processes, as well as records and estimated data. The aim of this research was to analyze the decarbonization of ships through technological migration from conventional fuels to alternative types for zero-emission purposes. For this, the application of the quantitative method was relevant in the identification of control variables involved in previous studies such as; statistics, decision making, modernization stages and technologies.

The characterization of data obtained from each ship will determine the feasibility of applicable technologies to achieve zero emissions. Pollution rates from ships in the global port supply chain identified that it is responsible for 3% of greenhouse gases, experiences of shipping and port personnel who identify the carbon footprint of ships and ports reported scientifically, were considered as the application of the qualitative method that allowed the possibility of obtaining results from the estimation of variables, which played an important role in decision making to understand the technological proposals to be implemented in ships, based on the modernization or renewal of zero-emission technologies.

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The operational data resulting from this investigation determined that the renewal of engines, modernization and renewal of ship fleets must be accompanied by personnel expert in the design of ship engines, who can generate feasible and sustainable proposals for the sector to meet the 2025 objectives. Finally, by the mixed method, an analysis of Control variables allows you to get involved in ¿How to achieve the decarbonisation of port assets in line with the objectives of the IMO (International Maritime Organisation)? in a sustainable manner and with a circular economy (Akgül, 2024 and Karvounis, et al., 2024)

# **Dual engines low emissions**

Methanol is a sustainable alternative fuel that helps the marine industry to progressively reduce emissions, which is a key goal in decarbonization. If produced from renewable sources, it can reduce CO<sub>2</sub> emissions by up to 95% compared to conventional fuels. Green methanol would not add CO2 to the atmosphere, which means that engines burning this fuel, when installed as a retrofit project on ships, will have carbon neutral emissions, helping shipping companies adapt to the changing energy landscape and environmental regulations. Ships currently have a flexible design adaptable to any engine and use methanol technologies on board as a source, either as pure fuel or blends in dual LNG-Methanol or Methanol-biofuel engines. (Akgül, 2024, Ammar & Seddiek, 2023, Bayraktar et al., 2023 and Dere, et al., 2024).

Sustainable marine boilers operate with MultiFlame burners and use a plate and box heat exchanger for fuel gasification providing thermal energy transmitted by hot engine water to efficiently utilize energy from LNG (Liquefied Natural Gas), LPG (Liquefied Petroleum Gas), Methanol and biofuels. (Xia et al., 2024).

# Migration from conventional fuels to zero emissions

The keys to decarbonizing maritime transport are a challenge for the migration from conventional fuels to zero-emission fuels, such as hydrogen, ammonia and methanol.

Notwithstanding, when the production processes of these fuels are from a completely renewable source, they are called green and when in any of their processes they are derived from fossil fuels, they are assigned blue, gray and black colors, because, although they are zero-emissions when burned, a source derived from oil was involved in their production (Abeynaike & Barbenel, 2024).

The shipping industry uses internal combustion engines of the Otto, Diesel and Brayton cycles, with pure fuels and mixtures. However, by 2022 the ammonia engine has represented a technological challenge for adaptation in two- and four-stroke engines, with a net zero emissions scope. By 2023 the ammonia engine represents a functional technology that by 2024 will be installed in container ships in prototypes and in 2025 vessels with this technology will sail the seas in a commitment to the environment (Schwarzkopf, et al., 2023).

Hydrogen, Methanol and Ammonia, whether blue or green, will be the transport fuels of the future in the decarbonization of ships. An additional zero-emission alternative electrification, provided that the electrical energy in its generation process comes from alternative energy sources or green sources. However, a transitional fuel is LNG (Liquefied Natural Gas), LPG (Liquefied Petroleum Gas) used in the dual cycle either with Hydrogen, Methanol and Ammonia (blue or green) or in a mixture with conventional fuels such as gasoline diesel. One of the technological complications that currently limit the Otto, Diesel, Brayton thermodynamic cycles and their combinations is precisely the start-up at startup, which must be done with fossil fuels, because they are designed for this type of fuel. That is to say that engines, whether four-stroke, two-stroke or axial, once they have reached their nominal speed require a fuel migration system from conventional sources to zero-emission fuels once they are started, achieving their autonomy in the combustion of zero-emission fuels (Abeynaike & Barbenel, 2024).

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The IMO (International Maritime Organization) reported that tank-to-wake CO<sub>2</sub> emissions measurements have been the basis for mapping the carbon footprint behavior of ships, which has allowed it to identify, in conjunction with other organizations and other studies, that the impact of global maritime trade currently contributes around 3% of the international carbon footprint according to the World Economic Forum, with emissions amounting to 1,076 Mt (million tons) of CO<sub>2</sub>. To ensure that by 2030 global warming does not exceed the 1.5 °C trajectory and that shipping activities continue to grow at the rate projected in recent years in the carbon footprint, it is certain that they will undermine the objectives according to the "Paris Agreement". To reduce greenhouse (GHG) emissions from international shipping, global measures must be adopted covering emissions of CO<sub>2</sub> (carbon dioxide), CH<sub>4</sub> (methane) and N<sub>2</sub>O (nitrous oxide), but the latter two only from 2026 with the gradual implementation of measures on ships using green fuels until reaching the goal in 2050, according to the IMO objectives of zeroemission fleets.

The path of using Hydrogen, Methanol and Ammonia (blue or green) is a production technology known to the industry, mainly with applications for fertilizers, but not for supply as fuel. In Europe and Asia, by 2024, the requirements of some shipping companies that already use these zero-emission alternative fuels in a limited way in prototype ships are already at the stage of supplying maritime fleets. However, in the transition process, the costs of these zeroemission fuels are significantly more expensive than fossil fuels, which makes projects to produce green fuels difficult in a global supply chain. Investment decisions need to be made in companies that take risks in the fuel migration process when, at an early stage towards zero emissions in the shipping industry, demand is limited or non-existent in some developing countries (Baştuğ et al., 2024, and Kamran & Turzyński, 2024)

# Zero-emission fuels: a challenge to current technologies in the shipping industry

Large-scale pure hydrogen in Denmark depends on a hydrogen pipeline connection to Germany to supply industrial Europe, but this infrastructure does not include the shipping industry.

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Entrepreneurs say we have not seen a buyer willing to pay the price to produce methanol or ammonia, some projects may make sense, but we are talking about scale to transition the shipping industry to scale with low-emission fuels, we need the market to be open and evolve.

IMO (International The Maritime Organization) has set the objectives of decarbonization migration from 2023 to 2030 and zero-emission decarbonization for the entire shipping industry by 2050. The shipping industries are willing to carry out the migration aligned with the IMO objectives in a gradual and cooperative manner, but they warn that the introduction of a tax on carbon-intensive marine fuels in 2025 is not in agreement and that the application of this will increase import prices globally and generate shortages in the transition stage. The shipping companies are leaning towards gradual moderate modernization for at least the next decade and propose that once there is a significant penalty in the carbon price for fossil fuels, that will be when the demand for green fuels will really begin to activate with full life cycle fuel standards.

The IMO warns that, without regulation, realistically cannot expect decarbonization of maritime transport nevertheless, this must comply with specific objectives in terms of time, form, execution, and penalties. But there is one thing we must not forget: today we do not pay when we pollute. Is that fair or not? Low-carbon fuels, such as LNG and LPG, are currently used as bridging fuels at 1.2% in marine fleets in different configurations, so setting a carbon price to drive decarbonization in a tax on fossil fuels in the shipping industry will help investment in promoting green technologies in the shipping sector and will be an incentive for maritime transport owners to engage in modernization. The panorama must be seen under the expectation ("It is an opportunity rather than a threat") that there are currently many processes in which shipowners and operators are optimizing as much as they can; that is something very positive and should not be underestimated. These improvements will be even greater when we have carbon penalties incentivizing fleet owners to modernize and commit to sustainability.

The IMO continues to stand by its stated goals and decision on a short-term carbon tax for the shipping sector by 2025, stating that we will all be the owners of the problems unless we manage to find alternative solutions. Shipping companies, based on their scale and profits, are equally committed to complying with the regulations and standards established in the mutual agreements, fulfilling their rights and obligations (Akgül, 2024 and Xia et al., 2024).

The short-term decarbonization objectives establish that 5% of the world fleet must operate with low or zero-emission fuels by 2030. The world fleet must use 28 to 30 Mt (million tons) of Hydrogen, Methanol. Ammonia in its mobility and the demand for green or blue fuels by the energy sector must be covered with port or on-board supply centers depending on the technology implemented on the ship. In a previous evaluation of the shortterm 2025 objectives, significant investments in ship modernization and green fuel loading centers were reported with logarithmic ascent, which implies that the objectives can be met.

The medium-term objectives in the decarbonization of the shipping industry committed to reducing the carbon footprint of its transport operations by 25% by 2030, if this proves technically feasible in the modernized pilot fleet in the first stage assessed in 2025. The feasibility assessment by the shipping companies will be under constant evaluation against the parameters pre-established with the fleet before modernization.

The ammonia engine started in 2019 with the preparation of infrastructure, supply and safety systems both on the engine and on site., the engine was modified, with a cylinder prepared to burn ammonia. The engineers benefited from experience in dual-fuel engines: technical changes to the injection equipment and engine control software. On 03 July 2023, the full-scale two-stroke marine engine with ammonia was finally developed: the first successful test of the ammonia engine. The focus in 2024 is on engine performance, pilot oil energy fraction, ignition and various emission categories. International marine engine and system companies are developing technologies for two-stroke engines using pure ammonia as fuel and dual-stroke engines using fuel mixtures to reduce emissions to zero.

These were adapted during 2023 and tested in 2024, as they leverage previous technologies, generating a technological adaptation that can be quickly implemented by engine technologists, considering that the ammonia-burning engine system did not exist as such. The first ammonia engine is expected to be installed on a ship in 2025. Onboard safety technologies and measures to ensure that the crew of an ammonia-fuelled ship can work safely include ammonia sensors, ventilation, double-walled pipes and special measures such as water screens to completely contain ammonia in the event of a leak. A challenge to be met in line with the short-term objectives of decarbonizing the shipping industry (Ammar & Seddiek, 2023, Chin Law, et al., 2024, Dere, et al., 2024 and Schwarzkopf, et al., 2023).

The potential for the ammonia-fueled two-stroke engine with a tipping point in net zero CO<sub>2</sub> maritime transport during combustion is huge, with the engine aiming to reduce the greenhouse gas footprint by more than 95% compared to a standard diesel engine. The expectation for ammonia is very high and it will become the preferred fuel for maritime transport by 2050 with the lowest production cost of all green fuels. Ammonia is a slow-burning fuel, so the slow-cycle two-stroke diesel engine is ideal for burning it. The ammonia-fueled engine is very flexible and will be applied in a first stage to Ro-Ro (roll on-roll off) vessels, container ships, and tankers. The next stage will be to characterize the operating curves and verify the engine emissions for patenting and commercial use. On the other hand, technologies for the generation of blue and green ammonia on board are being developed in parallel, involving the combination of systems in the supply of ammonia, which will reduce the size of the storage tanks, being used as cargo space, optimizing zero-emission, sustainable and sustainable development ships that at the end of their useful life will be reused through the 9 Rs of the circular economy. Dual-fuel ammonia engines are currently at (Technology Readiness Levels) TRL4, with the technology validated in a test engine configuration, but are expected to reach TRL 9 around 2025 (Ammar & Seddiek, 2023, Dere, et al., 2024, Melideo & Desideri, 2024 and Schwarzkopf, et al., 2023).

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Ammonia is a commodity frequently traded primarily for use as a fertilizer, and the infrastructure for its storage and transportation is available in many places. Green ammonia is produced by combining nitrogen extracted from the air and hydrogen separated from the water molecule using renewable electricity. Safety is paramount, due to the toxicity and pungent smell of ammonia. Burning ammonia carries the risk of emitting N<sub>2</sub>O (Nitrous Oxide), "laughing gas" which is a very potent greenhouse gas. To avoid this, engine combustion mixture regulation parameters must be set to very low levels of laughing gas emissions (Kamran & Turzyński, 2024).

Green fuels will be more expensive than conventional ones, at least initially. Therefore, the industry needs global regulation, a CO<sub>2</sub> tax or some other kind of offset method to cover the additional costs. The IMO will not publish concrete measures to reach that goal until 2027 – too late in an industry where the average lifespan of a ship is 25 to 30 years.

For ships, ammonia has a slightly higher emissions reduction potential and at a lower cost than methanol.

Dual-fuel methanol engines have already reached a Technology Readiness Level (TRL 9), meaning that the system has been tested in an operational environment. The FCM Methanol is a low-flashpoint fuel supply system (LFSS) capable of supplying methanol within the flow, pressure, temperature and filtration parameters specified by the engine manufacturer (Ammar & Seddiek, 2023, Bayraktar et al., 2023 and Karatuğ, et al., 2023).

Since green fuels are not yet available in quantities, **ESD** sufficient (Electrostatic Discharge) is considered promising as it offers emission reduction, high-efficiency propellers, wind-assisted propulsion, air lubrication systems, exhaust gas recirculation and speed optimization. CO<sub>2</sub> emissions can be reduced by using ESD by 30% for container ships, 45% for bulk carriers, 50% for tankers and 60% for LNG carriers.

Around 1,900 ships with two-stroke engines and up to 900 ships with four-stroke engines are currently eligible for conversion and could save more than 97 Mt (million tons) of carbon dioxide (CO<sub>2</sub>) emissions annually if they run on green fuels. To meet the demand for ship engine modernization, shipyards, ships and specialist personnel who will carry out the conversions are already preparing in close collaboration. Conversions to be considered viable should cost less than 25% of the value of a new vessel to be considered commercially viable for the sector. Prices for single-fuel engines will range from 12 to 60 million dollars per vessel, depending on whether it is a retrofit or a new engine change, according to the average established by European and Asian shipyards. This has generated pressure on shipping companies who seek financial support to carry out the modernization. The segments of modernization of 2-stroke engines Hydrogen, Methanol and Ammonia (blue or green), LPG (Liquefied Petroleum Gas) with dual arrangements will satisfy the market of bulk carriers, container ships, Ro-Ro, tankers and LNG. However, four-stroke dual-fuel engines with diesel/methanol, diesel/LNG (Liquefied Natural Gas), diesel/LPG (Liquefied Petroleum Gas) etc. It is more oriented towards cruise ships and cargo ships, such as ferries. (Karatuğ, et al., 2023 and Lu, et al., 2023).

Other options such as electrification or switching to mono-fuel engines such as Hydrogen, Methanol, Ammonia (blue or green) and synthetic natural gas (SNG) are options to consider for zero-emission vessels from the economic perspective that modernizing or changing the engine is cheaper than building a new ship.

# **Emissions certification rates for maritime** transport

The Environmental Ship Index (ESI) identifies ocean-going vessels that perform better in reducing emissions to air than required by current International Maritime Organization (IMO) emissions standards. It assesses the amount of nitrogen oxide (NOX) and Sulphur oxide (SOX) a ship releases and includes a reporting scheme on the ship's greenhouse gas emissions. The ESI is a good indicator of the environmental performance of ocean-going vessels and will help identify cleaner ships overall and achieve their sustainability goals.

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Under the Maritime Regulation (MRV), shipping companies must buy and surrender (use) allowances from the (European Union Emissions Trading Scheme) EU ETS for every tonne of CO<sub>2</sub> (or CO<sub>2</sub> equivalent) emissions reported under the EU ETS system. It is up to shipping company authorities to surrender allowances by 2025: for 40% of their emissions reported in 2024; 2026: for 70% of their emissions reported in 2025; 2027 onwards: for 100% of their emissions reported. These rules were adopted on 16 May 2023 and entered into force on 5 June 2023 (Christodoulou & Cullinane, 2024, Melideo & Desideri, 2024 and Xia et al., 2024).

From 1 January 2018, large ships over 5 000 gross tonnes loading or unloading cargo or passengers in ports in the European Economic Area (EEA) must monitor and report related greenhouse gas (GHG) emissions (currently only CO<sub>2</sub> emissions, but also nitrous oxide and methane emissions from 1 January 2024). Monitoring, reporting and verification (MRV) of the information must be carried out in accordance with the 'Maritime MRV Regulation'.

Carbon dioxide (CO<sub>2</sub>) emissions are projected to increase by 130% by 2050, this threshold is likely to be reached by 2040, or sooner, if emissions are not reduced leading to increasing risks of extreme heatwaves, droughts and floods. Implementing the policies outlined in the IMO targets will reduce this temperature increase by between 2.4 and 2.6°C by 2100.

The Energy Efficiency Design Index for Existing Ships (EEXI) and Carbon Intensity Index scheme implemented from 2023 measures their structural efficiency in terms of energy efficiency level per capacity mile and would reduce fleet CO<sub>2</sub> by 2030 by 0.7 – 1.3%. Meeting this EEXI, which follows the IMO's zero-emissions targets for 2050, will not be a problem for relatively new green ships. However, for older ships, this may not be cost-effective and could lead to increased scrapping (Pivetta, et al., 2024 and Sahraie, et al., 2024)

# Reducing the carbon footprint: a commitment between ports and shipping companies

From 2030, the IMO has established within its objectives that island-type, wet and dry ports must provide ships that set sail in their port facilities with a connection to a land-based electricity supply for stays of more than two hours, which will promote the decarbonization maritime transport with responsible environmental behavior. In addition to providing climate alignment, loan portfolios to the shipping industry, charterers and operators, chartering activities, global ship climate alignment, chartering, clean energy accordance with the agreements made by the International Chamber Shipping, International Association of Ports, Ministerial of Clean Energy, public-private platform for the energy sector, maritime value chains to promote the consumption of green fuels in port (bunkering) in support of the global energy transition 2050 (Zhang, et al., 2024).

Fuel costs represent a significant portion of ship operating costs and will determine freight rates. Transitioning to cleaner fuels may be more expensive and increase these costs. In December 2022, ultra-low sulfur fuel oil was \$635 per metric ton, heavy fuel oil was around \$515. Green hydrogen was \$2,500 per metric ton, ammonia cost \$1,239 per metric ton (fuel oil) and methanol was around \$1,400 per ton. The final costs of chartering low- or zero-carbon vessels will be more expensive during transition periods, however the IMO will generate decarbonization certifications that compensate for the prioritization of the use of vessels that have this certification, making compliant vessels have more work to do and although non-certified vessels will be able to offer lower charter prices, their income to ports will be limited and they will be fined for non-compliance, placing them in the position of responsibility and compliance sooner or later (Pivetta, et al., 2024 and Zhang, et al., 2024).

The maritime fleet currently uses different fuels with a share of alternative fuels of 1.2% with the following distribution: diesel, 98.8%, batteries and hybrid system (dieselelectric cycle) 29.4%, LNG 68.4%, Methanol 0.8% and LPG 1.4%.

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However, it is intended that the pending portfolio for 2025 will be covered with a greater share of alternative fuels with 21.1% with the following arrangement: diesel, 78.9%, batteries and hybrid system (diesel-electric cycle) 39.9%, LNG 52.1%, Methanol 3.4%, LPG 5.5% and hydrogen 0.3%.

The design of new ships and engines must be done now to allow the deployment of zero carbon emissions. Modernization, engine change or ship change should be evaluated, remembering that the average useful life of ships is 25 to 30 years and considering that by 2050 they will be in working condition (IRENA, 2021). Shipowners must decide or pose challenges to shipowners, which complicates their investment decisions. Capacity and fleet renewal regulations will not come into force until 2027. The demand for a new fleet of ships during the last three decades grew by around 4.8%. However, for the period 2023-2027 a decline is projected with a growth rate of 2.5 during the period (McKenney, T. A., 2024).

# Fuels in the shipping industry; with supply in port or on board

Fuels based on their origin or production process can be considered grey, black and brown, those generated from fossil fuels. "Blue", direct carbon capture and storage from air is considered "Green"; electrolysis renewable energy. Green fuels include those produced by biomass, alternative fuels, biofuels and advanced fuels.

E-fuels (synthetic fuels), Methanol and Ammonia; electrolysis Water and electricity Hydrogen (electrolytic); natural gas extraction gaseous energy Methane (natural gas); Biogas production agricultural waste Biogas; biogas upgrading Biogas Methane (bio), CO<sub>2</sub>; Steam methane reforming Methane Synthesis gas; Synagas Syngas Pressure Swing Absorption Hydrogen (blue or bio) and CO<sub>2</sub>; Nitrogen separation (PSA or cryo) Air Nitrogen and oxygen (and other traces); Haber Bosch process Nitrogen, hydrogen and thermal energy Ammonia; Carbon capture (industrial) Fuel gas CO<sub>2</sub>; Carbon capture (air) Air and electricity CO<sub>2</sub>; Sabatier process CO<sub>2</sub> and hydrogen Methane (synthetic) and oxygen; Methane liquefaction Methane (natural gas, bio) and electricity LCH<sub>4</sub> (liquid methane).

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Hydrogen liquefaction Hydrogen and electricity LH<sub>2</sub> (liquid hydrogen); Ammonia liquefaction Ammonia and electricity LNH<sub>3</sub> (ammonia); Liquid biofuels Residues, oils and crops Hydrotreated vegetable oil, fatty acids; Methanol synthesis CO<sub>2</sub> and hydrogen Methanol (synthetic); Fischer-Tropsch Hydrogen and CO<sub>2</sub> Blue crude, e-diesel; Hydrogen ICE (internal hydrogen; combustion engine) Hydrogen Water oxides); (+nitrogen Hydrogen fuel Hydrogen Water; Methane ICE Methane (+diesel) CO<sub>2</sub>+ NOx + CH<sub>4</sub> (methane); Methanol ICE Methanol (+diesel) CO<sub>2</sub>+ NOx; Ammonia ICE Ammonia + diesel CO<sub>2</sub>+ NOx +  $NH_4$  (ammonium) +  $N_2O$ ; (Nitrous oxide); Diesel ICE Diesel CO<sub>2</sub>+ Nox

Without new emission control measures, emissions could reach up to 1,500 Mt in 2050, an increase of 50%, the IMO approved a program to reduce greenhouse gases (GHG) by at least 50% by 2050, committing to establish at least six green maritime corridors between two or more ports worldwide by 2025, and more green maritime corridors will be included by 2030 to decarbonize the shipping industry by 2050.

The fuels of ships maneuvering for 2040 are expected to be 420.6 Mt, 79.1% more than consumed during 2020. Container ships use "heavy fuel oil" (HFO) during cruising and "marine gas oil" (MDO) during maneuvers and berthing. HFO = 40200 kJ kg - 1, MDO = 42700kJ kg-1, short term (now to 2030), medium term (2031-2040) and future long term (2041-2050). The focus of the industry should be on promoting clean hydrogen-based ZEFs and incentivizing their widespread adoption, to align with the Global Maritime Forum (GMF) Currently, transition strategy. ammonia, methanol and hydrogen are derived from natural feedstocks. Clean hydrogen-based production for maritime applications is currently limited to demonstration projects. In addition to clean hydrogen, methanol production will require CO<sub>2</sub>, which can be obtained from industrial point sources or through DAC (direct air capture) technologies. Clean hydrogen production facilities and carbon capture technologies must be of sufficient industrial scale to advance ZEF production. The largest Danish clean methanol plant in Europe in northern Sweden is due to start operations in 2025. It is expected to supply 50,000 tonnes of clean methanol annually.

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Around 30 ships were identified as running on methanol during 2023 and the world's first clean methanol-powered container ship will start operating by the end of the year. Liquid hydrogen and ammonia engines are still in development and are expected to be deployed on ships after 2025 (Lu, et al., 2023 and Zhang, et al., 2024).

Fueling and onboard storage technologies for methanol, ammonia and liquid hydrogen must advance beyond the prototype stage. ZEF (Zero Emission Ferry) accounts for less than 1% globally. Investments of USD 0.8 to 2.1 trillion will be needed by 2050. Production of 160 MTPA (million tonnes per annum) of green liquid hydrogen and around 130 MTPA of CO<sub>2</sub> feedstock will require investment of USD 0.6 to 1.9 trillion. If industrial CO<sub>2</sub> is not located at point sources adjacent to ZEF production facilities, an infrastructure will have to be established with investments of USD 10 to 23 billion. ZEF (Zero Emission Ferry) stations must be supported by a fueling infrastructure with an investment of USD 132 to 176 billion and accelerate the implementation of FAME (Fatty Acid Methyl Ester Biofuels). Fleet operators have committed that 5% of deep-sea shipping and 10% of ship-based freight volume will be powered by ZEF (ISO 14083 standard, EEXI), with an estimated investment of USD 450 billion by 2030. The International Chamber of Shipping (ICS) submitted a Fund and Reward proposal to the IMO for shipowners to make mandatory contributions per tonne of CO<sub>2</sub> emitted to create a new IMO fund to be operational in 2024. Scalable Zero Emission Fuels (SZEF) account for 5% of fuels for international shipping by 2030.

At least 20 G20 countries and 10 developing countries have public services, financing mechanisms and the direct use of green hydrogen (H<sub>2</sub>) through fuel cells (FC) and internal systems. Internal combustion engines (ICE) are an option, for short voyages. Green H<sub>2</sub> costs range from 66-154 USD/MWh and from 2030, the price is expected to be regulated at 32-100 USD/MWh. For renewable Methanol, biomethanol, renewable e-methanol: e-methanol 107-145 USD/MWh, Renewable Ammonia: e-Ammonia 67-114 USD/MWh (Tu, et al., 2024).

In 2050, the production of around 46 million tonnes of green H<sub>2</sub> is forecast, of which 73% will be needed for e-ammonia production, 17% for e-methanol and 10% will be used directly as liquid hydrogen via FC or flared via ICE. Renewable ammonia will be the basis of decarbonization with 43% blended, around 183 Mt transient blue ammonia; IRENA Ammonia is achieved through four key indirect electrification advanced biofuels; The most advanced commercial and bunkering ports are; Singapore (~22%), Fujairah (UAE) (~8%) and Rotterdam (Netherlands) (~6%). Most critical are Panama Canal, Strait of Malacca and Suez Canal (Dere, et al., 2024 and Hui, et al., 2024).

The implementation of energy efficiency mechanisms in ships that reduce the carbon footprint are; voyage performance management Information and Communication Technologies (ICT), just-in-time arrival (JIT), speed optimization, route planning, autopilot software, smart devices for energy consumption savings, trim, draft and ballast optimization, reduction of energy demand on board of all machinery and equipment, continuous analysis of operating curves through software, total scheduled maintenance TPM (hull roughness, propeller, corrosion, contamination, mechanisms, engine, auxiliary systems), load, structural weight, bulb design, hydrodynamics aerodynamics, design optimization (waterline, bow and settina shoulder, stern body, wave mitigation devices, propeller), propulsion improvement, balance tank flows, boundary layer systems as a means of levitation and lubrication reducing hull friction, hybrid auxiliary power generation systems fuel cells (FC) (Chin Law, et al., 2024 and McKenney, T. A., 2024).

There are 200 LNG bunkering ports in Europe and Asia. LNG must be stored under cryogenic conditions, is considered highly dangerous and requires safety and handling precautions. LNG has 26% more CO<sub>2</sub> than fuel oil. These loading ports will be displaced in less than 20 years by methane, ammonia and hydrogen bunkering ports. (Pivetta, et al., 2024).

Renewable energy fuels have current market costs; HFO \$41/MWh, LNG \$19/MWh, advanced biofuels \$72/MWh, fatty acid methyl ester (FAME) biodiesel \$238/MWh. hydrotreated vegetable oils (HVO) such as methanol from lignocellulosic biomass \$25/MWh to \$176/MWh, green H<sub>2</sub> via fuel cells (FC), internal combustion engines (ICE) and efuels \$66 to \$154/MWh, and are expected to reach costs from 2030 of \$32 to \$100/MWh (Tu, et al., 2024).

#### **Results Discussion**

Renewable methanol, i.e. bio methanol and renewable e-methanol, requires few modifications to the ICE engine and can provide significant carbon emission reductions compared to conventional fuels. The renewable e-fuels, methanol and ammonia, are the most promising fuels.

However, ammonia is more attractive, due to its zero carbon emissions. On the other hand, green  $H_2$  produced from renewable energy through the electrolysis process, is the only viable alternative shipping fuel, as it produces net zero life cycle emissions. Each alternative fuel has advantages and disadvantages in terms of physical characteristics such as calorific value, density, temperature, pressure that contrast with respect to their feasibility characteristics for use as fuel.

Liquid green H<sub>2</sub> stands out, then MGO similar to Methanol and Ammonia, followed by LNG similar to liquid H<sub>2</sub>. Internal combustion engines (ICE) for cargo ships with high torque and power requirements require high calorific value from the fuels supplied; to conserve it they require fuels with similar or higher calorific value.

If it is replaced by fuels with lower calorific value, the power can be compromised, causing the ship's structures to be lightened or the load to be reduced. However, for cargo ships this can be a weapon against them, because reducing the weight of their structure with light, high-strength materials can make them more expensive and the amount of cargo in global trends does not turn in the direction of reduction, on the contrary, to increase, making them more profitable in their services.

Therefore, although Ammonia and Hydrogen are emerging as the two winning fuels in their green state, Ammonia is feasible for ferries and ships with less weight. On the other hand, the fuel that has all the possibilities and the winner in terms of power is the green liquid H<sub>2</sub> (1 bar at -283°C and 120 MJ/Kg) and compressed (700 bar at 20°C and 120 MJ/Kg) due to its technical characteristics and adaptability to internal combustion engines of the Diesel cycle.

The application of hydrogen as a fuel in Diesel cycle engines is feasible if the quantity of liquid or compressed H<sub>2</sub> supplied to the engine is regulated, which, depending on the injection temperature, determines the supply pressure before the explosion. For this, the injection system must be regulated through intelligent closed-loop systems with feedback signals, with solenoid valves and high-frequency injector systems that regulate the supply based on the pressure. An overpressure in the engine heads can generate a destructive explosion of the same, because within the internal combustion chamber certain pressures can be supported that can vary depending on the design of the engine that the manufacturer applied in its manufacture varying by model, year, materials among others, so it is necessary to know the maximum pressure that the engine supports in the combustion zone in order to supply hydrogen intelligently without exceeding those pressures so that the operation can be carried out without the heads exploding due to overpressure until the fracture (Agarwala, 2024, McKenney, T. A., 2024 and Wang et al., 2024).

The process of adapting liquid or compressed H<sub>2</sub> to diesel engines and not to Otto cycle engines is precisely that diesel engines have a more robust construction that allows them to withstand pressure in better conditions, but not for what Hydrogen produces at burning pressure. Hydrogen auto ignites between 536 to 585 °C. However, the temperatures in the combustion chambers in an ICE engine are 1960 to 2200 °C, for this reason Diesel engines are a functional option if they are regulated in the injection systems considering that this is directly proportional to the temperature of the ignition zone (Agarwala, 2024).

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Diesel engines, although they are a limited option and can work, do NOT represent a viable option for use with hydrogen, because as a technology they require specialized systems for regulating pressures in the ignition zone, which represents danger and a large amount of investment. So why is there an interest in wanting to apply fuels such as ammonia or liquid or compressed hydrogen in both cases green? This is because 95% of the international fleet of ships use diesel engines as a means of propulsion and to modernize them to zero emissions, the adaptation of the existing systems in the fleet is proposed to improve these emission conditions. But incorporating fuels such as LNG, LPG, Methane and green ammonia due to their pressures in the combustion chamber do not represent a problem and provide advantages in reducing emissions, the only problem is to regulate the fuel input intelligently to keep the engine stable according to its operating curves. For compressed H<sub>2</sub>, the problem is twofold, apart from regulating the fuel inlet to provide stability to the engine, now the combustion chamber pressures must be regulated so as not to reach its breaking point due to overpressure. Engine tests require testing times based on their performance and safety, which must be followed before implementing modifications that have not been fully evaluated. It is true that we are in a race for zero emissions and that it is urgent to modify the shipping fleet, but a hasty administrative decision can cause engineering decisions to achieve these objectives to claim lives and great losses of ships that explode on the high seas, even worse in port areas where they intend to generate fuel loads from green H<sub>2</sub> plants inside the port, causing highly dangerous chain explosions (Wang et al., 2024).

The migration of engines with zeroemission fuels is the reason for identifying existing technologies in this article and based on experiences and work in the research group in the area of different types of engines, it is stated that the Brayton cycle or gas turbine for highpressure fuels is already well studied simply because it is an axial machine with higher compression ratios than those of the Otto and Diesel cycles (ICE), therefore the approach mainly for container ships, bulk carriers and Ro-Ro is to replace the engines of their ships that can still fulfill part of the service life with gas turbines with speed reduction systems that use hydrogen as a zero-emission fuel.

This proposal is within the proven technologies and even offers something better "the use of the Brayton cycle that uses nuclear as an energy source", which is also within the alternative energy sources mainly tested in the military industry. All this means that fleet modernizations can be done with LNG, Methane and Ammonia, with Diesel cycle engines so that from 2024 when this article is being written to 2030 the decarbonization objectives in ships can be met. But the large shipbuilders must redirect their designs in these 26 years towards replacing the Diesel engine with gas turbines with gearbox systems that use green H2 as an energy source or nuclear to achieve a sustainable and sustainable shipping industry that complies decarbonization by 2050 (Agarwala, 2024, Karvounis, et al., 2024, Melideo & Desideri, 2024 and Xia et al., 2024).

# Ammonia and green hydrogen

To obtain green ammonia, products such as water (H<sub>2</sub>O) and air (21% oxygen, 78% nitrogen, 0.89% noble gases, 0.1% water, water vapor; 1% at sea level and 0.4% in the entire atmosphere and small amounts of other gases) are used. Both water and air are a renewable source of power. When water is exposed to an electrolysis process, the bonds in O2 and H are separated, while on the other hand, air is exposed to nitrogen production, separating O<sub>2</sub> and N<sub>2</sub> mainly. The H<sub>2</sub> and N<sub>2</sub> obtained through the Haber Bosch process, obtain ammonia (NH<sub>3</sub>), considered green due to its renewable sources (Abeynaike & Barbenel, 2024, Agarwala, 2024 and Inal, et al., 2024).

Japan and South Korea have devoted significant R&D to developing engines that use ammonia as a power source by the method of electro-reduction of nitrogen to ammonia and are with considered green scalability infrastructure. The global ammonia industry produces approximately 180 Mt of ammonia per year, 80% of which is used by the agricultural fertilizers. Current for production takes place in eastern China, Europe, southwest Asia and North America. China produces 32% of ammonia from coal, while natural gas is used in the rest of the world.

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South Korea and Japan are developing technologies to use ammonia as a fuel and forecast a large use of H<sub>2</sub>. By 2030, renewable ammonia is projected to account for about 183 Mt of ammonia per year compared to 17 Mt of ammonia per year currently produced. Some countries have the infrastructure to produce renewable H<sub>2</sub> and ammonia, such as Morocco, Australia, Chile, Denmark, the Netherlands, New Zealand, which use solar, wind or a combination of renewable energy sources (Abeynaike & Barbenel, 2024, Hui, et al., 2024 and Nerheim, et al., 2024).

The world's first ammonia-powered container ship November 30, 2023, the vessel, named Yara Eyde, will be the first to sail the emission-free shipping route between Norway and Germany and will operate between Oslo, Porsgrunn, Hamburg and Bremerhaven from 2026 in anticipation of critical 2030 climate targets. internal combustion engine (ICE) that uses ammonia (NH<sub>3</sub>) and hydrogen H<sub>2</sub> as fuel in gas turbines, towards a cleaner and more sustainable energy future (Nerheim, et al., 2024). Hydrogen-fueled gas turbines will need to be regulated in their operating parameters and be able to provide combustion stability, flame dynamics and controlled combustion process. Onboard hydrogen production has been shown to be a cost-effective alternative and eliminates the need for a large hydrogen storage tank. However, it requires the installation of intensive waste heat recovery networks and additional unit operations, such as high-temperature steam generators, steam turbines, reformers and blue and green hydrogen systems, and onboard blue hydrogen production could be a cost-effective alternative (Chin Law, et al., 2024, Kamran & Turzyński, 2024, Karvounis, et al., 2024 and Lu, et al., 2023).

#### **Conclusions**

The objectives set out in common agreement between the international shipping sector and the IMO (International Maritime Organization) in the decarbonization of ships to zero emissions by 2050 will be carried out in stages. To reduce the carbon footprint of both ships and ports, the primary objective has been set to migrate from conventional fuels to environmentally friendly alternative fuels.

Some of these fuels are considered transitional fuels with reduced CO<sub>2</sub> emissions, such as LPG, GNS, LNG and Methanol in a dual cycle with diesel. However, to achieve zero the 2050 emissions towards objectives, Hydrogen and Ammonia (green) are in descending order of importance. These fuels, as they do not come from regulated sources of alternative origin, can be classified as blue and although their degree of production is minimal, they cannot be considered zero emissions, but in large mass production they represent great potential for the shipping industry and even on board.

In the analysis in accordance with the objectives of this research, it is identified that to achieve the decarbonization of ships by 2050 with zero emissions, a future based on green hydrogen is required as a promising technology applied to gas turbines driving ships, towards a cleaner and more sustainable energy future. On the other hand, it has been shown that the production of (blue) hydrogen on board is a cost-effective alternative, eliminating the need for a large hydrogen storage tank on the ship and reducing explosiveness in supply ports, also being a sustainable alternative. And, finally, is the gas turbine as a driving source for ships with nuclear energy.

If the useful life of ships is 25 years by 2050, the eradication of dual engines by manufacturers and shipping companies must be present. According to this, investing in a modernization of a dual ICE will be a very short-term decision, which is why it is considered a transition investment. Therefore, to be competitive and meet the IMO's zero-emissions targets, ship production from 2030 onwards must use hydrogen or green ammonia gas turbines as a power source.

#### **Declarations**

#### **Conflict of interest**

The authors declare no interest conflict. They have no known competing financial interests or personal relationships that could have appeared to influence the article reported in this article.

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#### **Authors' Contribution**

The contribution of each researcher in each of the points developed in this research, was defined based on:

Flores-Cruz, Luis Antonio: Contributed to the project idea, research method and technique, about to develop all the project.

*Cruz-Gómez, Marco Antonio*: He supported the design of the field instrument. He also contributed to the writing of the article.

Correa-Nieto, Marco Antonio: Contributed to the research design, the type of research, the approach, the method and the writing of the article.

*Mejía-Pérez, José Alfredo*: Resarched multiple papers and information about the topic.

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# **Abbreviations**

$\mathrm{CH}_4$	Methane
$CO_2$	Carbon dioxide
EEA	European Economia

EEA European Economic Area
ESI Environmental Ship Index

EU ETS European Union Emissions Trading

Scheme

FC Fuel Cells

FAME Fatty Acid Methyl Ester

GHG Greenhouse Gas

GMF Global Maritime Forum

H<sub>2</sub> HydrogenHFO Heavy Fuel Oil

HVO Hydrotreated Vegetable OilsICE Internal Combustion EngineICS International Chamber of Shipping

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IMO	International Maritime Organization
ISO	International Organization for
	Standardization
$LH_2$	Liquid hydrogen
LNG	Liquefied Natural Gas
LPG	Liquefied Petroleum Gas
Mt	Million tons
MTPA	Million Tonnes Per Annum
MWh	Megawatt-hour
$N_2O$	Nitrous oxide
$NH_3$	Ammonia
NOx	Nitrogen Oxides
SNG	Synthetic Natural Gas
SZEF	Scalable Zero Emission Fuels
TPM	Total Scheduled Maintenance
USD	United States Dollar
ZEF	Zero Emission Ferry

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# Design of a High Performance Hybrid Tricycle (THAR) to assist people with motor disabilities

# Diseño de un Triciclo Híbrido de Alto Rendimiento (THAR) de asistencia para personas con discapacidad motora

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#### **Abstract**

In Mexico, there is a delay in the mobility process of people with motor disabilities. At the same time, in our country there are nearly 3 million people with motor disabilities according to what INEGI reports in its 2020 census. Therefore, a virtual prototype is being proposed as a result of the first stage of its own methodology for the design of a hybrid tricycle to transport people with motor disabilities, which offers versatility in terms of transport configurations in the facilities of the Polytechnic University of Guanajuato (UPG). In a second stage, it is proposed to build a scale prototype using additive manufacturing to identify areas of opportunity before building the final prototype and carrying out its real physical tests in order to obtain sufficient data to implement a commercial model that can be reproduced. reliable way.

#### Goals

- \* Conceptual design of a hybrid tricycle. \* Comply with the required technical conditions.
- \* Meet economic requirements.

#### Method

- \* Needs detection.

  \* Development and selection of the conceptual solution proposal.
- \* Virtual
- prototypes in CAD.

#### Contribution

\* Development of a hybrid assistance vehicle for people with motor disabilities. Existe en México un rezago en el proceso de movilidad de las personas con discapacidad motriz. Al mismo tiempo en nuestro país se presenta cerca de 3 millones de personas con discapacidad motriz de acuerdo a lo que informa INEGI en su censo 2020. Por lo anterior se está proponiendo un prototipo virtual como resultado de la primera etapa de una metodología propia para el diseño de un triciclo híbrido para transportar a personas con discapacidad motriz, que ofrezca una versatilidad en cuanto a las configuraciones de transporte en las instalaciones de la Universidad Politécnica de Guanajuato (UPG). En una segunda etapa se propone construir un prototipo a escala empleando la manufactura aditiva para lograr identificar áreas de oportunidad antes de construir el prototipo final y realizar sus pruebas físicas reales para poder obtener la data suficiente para implantar un modelo comercial y que pueda ser reproducido de manera confiable.

#### Objetivos

- \* Diseño conceptual de un triciclo híbrido. \* Cumplir con las
- Cumplir con las condiciones técnicas requeridas.
- \* Satisfacer los requerimientos económicos.

#### Metodología

- \* Detección de necesidades.
- \* Desarrollo y selección de la propuesta conceptual de solución.
- \* Prototipos virtuales en CAD.

# Contribución

\* Desarrollo de vehículo híbrido de asistencia para personas con discapacidad motriz.

# People with motor disabilities, hybrid tricycle, design methodology

# Personas con discapacidad motriz, triciclo híbrido, metodología de diseño

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#### Introduction

Currently the world's population depends excessively on the energy produced from hydrocarbons, in Mexico in 2019 there was a shortage of gasoline in the central states of the Mexican Republic.

One of the motives behind this project is the search for environmentally friendly and economical mobility alternatives, so that an ecological and economical means of transport is available, which can be acquired and used by the sector of the population that suffers from motor disabilities, to transport themselves in a safe, fast and economical way. Another important aspect is that in Mexico the national market is dominated by distribution companies and only one manufacturer, Vetelia, located in Guanajuato [5].

According to the 2020 Population and Housing Census, there are 6,179,890 people with some kind of disability in Mexico, which represents 4.9% of the country's total population. Of these, 53 % are women and 47 % are men [7].

Box 1



Figure 1

Percentage of the population with disabilities according to difficulty in activity 2020

Source: INEGI. Population and Housing Census 2020

Specifically within the Polytechnic University of Guanajuato (UPG) we are pursuing the development and manufacture of a hybrid tricycle of our own design as a means of transport within the campus, whose purpose is:

- Transport the driver.
- Transport a person with a motor disability in a back seat or transport people who do not have a disability (assistant person).
- To tow a person in a wheelchair with the person on board.

Figure 2 shows the infrastructure and the routes between the different buildings within the UPG.

#### Box 2

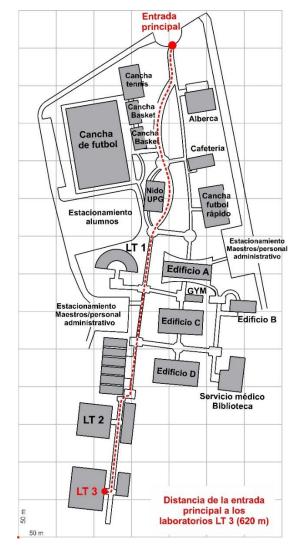


Figure 2

Layout of the Polytechnic University of Guanajuato with example of a longer route. [3]Design of an electric vehicle for people with handicap

# Methodology

The project will be developed by converting a bicycle into a hybrid tricycle based on a Mercurio Victoria R700 bicycle as shown in figure 3.

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# Box 3



Figure 3

Base bike for conversion to electric tricycle

Source: Own authorship

The development of the hybrid tricycle design was based on the methodology proposed in Figure 4, which is based on descriptive methods and design processes.

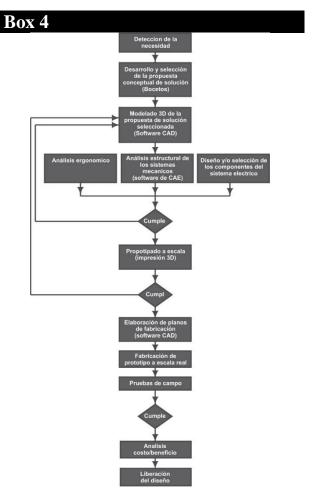


Figure 4

Design methodology

Source: Own authorship

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RENIECYT-CONAHCYT: 1702902 ECORFAN® All rights reserved. In order to detect the needs, first of all, a survey was carried out through a digital platform, which was sent to potential users, giving the following results as shown in Figure 5.

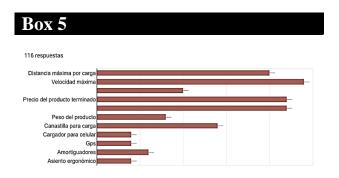


Figure 5

Detection of needs

Source: Own authorship

# List of requirements

In order to establish the limits according to the requirements, a list of requirements will be made. Among the most important limits are cost, size or weight of the tricycle, performance, legal or safety requirements, among others. The following table 1 shows the detailed requirements and specifications of the proposed hybrid tricycle.

# Box 6

# Table 1

Identifying needs

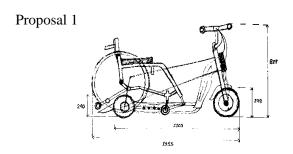
Requirements	W o D
1. Ergonomics	
- Comfortable seating.	$\mathbf{W}$
- People with mobility problems should have easy	$\mathbf{w}$
access to the rear seat.	
<ul> <li>Supportive supports with locks.</li> </ul>	$\mathbf{w}$
Functional features	
- Easy coupling.	$\mathbf{w}$
- Ability to tow a wheelchair.	W
- Stability while driving.	$\mathbf{w}$
<ul> <li>Auxiliary accessories for mobile phone.</li> </ul>	D
<ul> <li>Adjustable arms for towing any type of wheelchair.</li> </ul>	W
Control system	
<ul> <li>Reliable when operating the hybrid tricycle.</li> </ul>	$\mathbf{w}$
- Simple configuration.	D
Mode of operation	
- Manual.	W
- Electric, electronic.	W
Power generation	
- Human propulsion.	$\mathbf{w}$
<ul> <li>Battery charging system.</li> </ul>	$\mathbf{w}$
- Battery electric system.	W
<ol><li>Power transmission</li></ol>	
<ul> <li>Pedal, gear and chain system.</li> </ul>	W
<ul> <li>Propulsion by electric motor.</li> </ul>	W
<ol> <li>Working conditions</li> </ol>	
- Frequent use.	D
- Reliable.	W
4. Weight	
- Gross vehicle weight 300 kg.	D
- Towing capacity 120 kg.	W
<ol><li>Dimensions</li></ol>	
- 4000 mm x 1200 mm x 1100 mm	D
3. Maintenance	
<ul> <li>According to hours of use.</li> </ul>	D
<ul> <li>Easy to replace commercially available parts.</li> </ul>	$\mathbf{w}$

Mendoza-Derramadero, José De La Cruz, Mandujano-Nava, Arturo, Chihuaque-Alcantar, Jesús and Paz-Cabrera, Mauro. [2024]. Design of a High Performance Hybrid Tricycle (THAR) to assist people with motor disabilities. Journal Renewable Energy. 8[20]-1-7: e40820107.

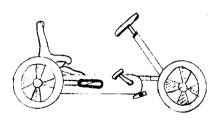
#### **Generation of alternatives**

For the conceptual design of the hybrid tricycle proposal, sketches were made of the configurations to solve the needs detected, these sketches are shown in figure 6.

# Box 7



Proposal 2



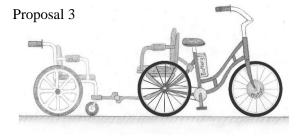


Figure 6

Proposals for conceptual designs.

Source: Own authorship

# Technical and economic evaluation of proposals

Identifying the essential criteria to meet the specifications obtained in the survey, the economic aspect, easy manufacturing, easy maintenance and with arms adaptable to any wheelchair, are the most influential factors in the definition of the design of the hybrid tricycle since it is required to have sufficient pulling power combined with the autonomy by battery charge, one of the difficulties is that the electric motors and batteries that are capable of achieving these characteristics require a higher electrical voltage and amperage, which influences the cost of the hybrid tricycle.

Consequently, the proposals are evaluated on a scale of 1 to 10, where 10 is satisfactory compliance with the criteria to be evaluated; in addition to applying a three-level weighting known as the influence factor, where 1 is important, 2 is very important and 3 is essential. See tables 2 and 3.

# Box 8

Table 2

Technical assessment

	Evaluation criteria	Weighting (Wi)	Alternative 1	Alternative 2	Alternative 3	Ideal option
1	Ergonomics	3	7	5	8	10
2	Functionality features	2	7	6	10	10
3	Control system	3	8	8	8	10
4	Mode of operation	3	9	7	9	10
5	Power generation	3	8	8	7	10
6	Power transmission	3	9	9	9	10
7	Operating conditions	2	9	7	7	10
8	Weight	3	8	8	9	10
9	Dimensions	1	8	7	9	10
10	Maintenance	2	6	8	8	10
		TOTAL = Σ (Wi X Pi)	199	184	209	250
		Technical coefficient = Total score / Perfect score	0.796	0.736	0.836	

Source: Own authorship

# Box 9

Table 3

Economic evaluation

	Evaluation of alternatives	Weighti ng (Wi)	Alternati ve 1	Alternati ve 2	Alternati ve 3	Ideal optio n
1	Operation	3	6	7	8	10
2	Manufacturi ng	2	7	6	7	10
3	Materials	3	8	8	8	10
4	Maintenanc e	2	7	7	9	10
5	Power generation	3	8	8	8	10
	$TOTAL = \Sigma$ (Wi X Pi)		94	95	104	130
	Coeficiente económico = Puntaje total / Puntaje perfecto		0.723	0.731	0.8	

Source: Own authorship

The best choice is one that not only has the most appropriate technical and economic factors, but also maintains a balance between the two. Therefore, the indicated project will be developed based on the first option as shown in the graph (see figure 7).

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# **Box 10**



Figure 7

Technical and economic balance

Source: Own authorship

#### Results

By applying the design methodology it was possible to obtain the virtual prototype of a hybrid tricycle based on the choice of one of the proposals put forward. The selected vehicle seeks to integrate the necessary elements to meet the technical and economic requirements of the project versus the comparison of the other proposals that were not selected. Using CAD design as a tool, a virtual model was designed, as shown in figure 8.

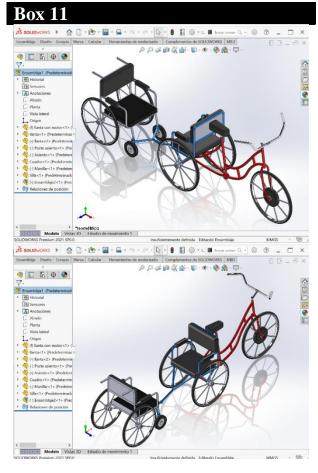


Figure 8

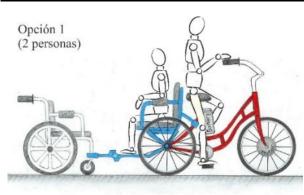
Design of virtual model of proposal 3 in CAD software Source: Own authorship

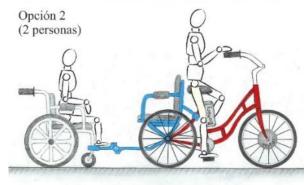
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This prototype has basically three sections, the first one is for the driver, the second one can be used to transport a person with motor disabilities or a carer and the third one is a coupling system to attach a wheelchair and transport a third person occupying the attached wheelchair as shown in figure 9. This can be used in two modes, either by human propulsion or in electric mode, both using chain and sprocket for power transmission. This is in order for the hybrid tricycle to behave efficiently and effectively as shown in figure 10.

# **Box 12**





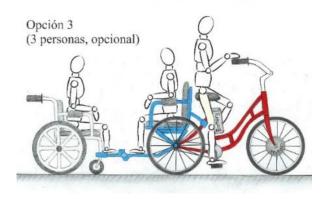


Figure 9

Options for use of the hybrid tricycle

Source: Own authorship

Mendoza-Derramadero, José De La Cruz, Mandujano-Nava, Arturo, Chihuaque-Alcantar, Jesús and Paz-Cabrera, Mauro. [2024]. Design of a High Performance Hybrid Tricycle (THAR) to assist people with motor disabilities. Journal Renewable Energy. 8[20]-1-7: e40820107.

# **Box 14**



Figure 10

Rendering of virtual model of proposal 3 in CAD software

Source: Own authorship

# **Conclusions**

The development of the virtual prototype proposed in this work seeks to optimise with a passenger configuration that adapts to the needs of two possible general scenarios that people with motor disabilities may present, where one of these scenarios is when the person with motor disabilities can have control of their body structure (from the waist up), i.e. can maintain a stable composure, the second scenario is when a person who has motor disabilities but does not have control of their body structure and therefore requires a person to accompany them with the function of taking care of their transfer when using this transport system.

The selected proposal is in its design phase; subsequent work will include the development of a physical prototype to scale using additive manufacturing, in order to identify areas of opportunity in the actual manufacture of this proposal. It is very satisfying to contribute with this type of alternative solutions to be applied for the benefit of our society with motor disabilities, thus contributing to a better quality of life in terms of mobility.

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It was decided to work on this type of vehicle because of the importance and the impact it has on people with motor disabilities because it represents a great satisfaction for the authors. More work will be done in terms of future manufacturing and assembly, and better integration with the ramp to achieve the main objective and offer more functional alternatives with the ramp.

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Integration of green technologies for the generation of electric energy using microgenerators and atmospheric batteries in the irrigation district #043 Alejandro Gascón Mercado, Canal Centenario, State of Nayarit

Integración de tecnologías verdes, para la generación de Energía Eléctrica utilizando Microgeneradores y Baterías Atmosféricas en el Distrito de Riego #043 Alejandro Gascón Mercado, *Canal Centenario Estado de Nayarit* 

Jaime-Navarro, Agustín\*a, Bonilla-Alejo, Sergio Raúl<sup>b</sup> and Rodríguez-Rodríguez, Joel<sup>c</sup>

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#### **CONAHCYT classification:**

Area: Engineering

Field: Technological sciences Discipline: Electric technology

Sub-discipline: Microelectronics and alternative technologies

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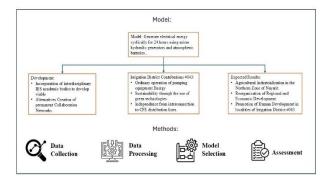
Received: January 17, 2024 Accepted: December 31, 2024



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#### Abstract

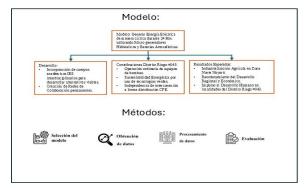
The project integrates the start-up of two modules: #1.- A revolutionary mechanical, hydrokinetic microgenerator that converts more than 50% of the slow flow of water into electrical energy, used in Irrigation District #043 in the State of Nayarit, Mexico, feeding three centrifugal pumps that operate with three-phase 10 Hp motors in each pump; module: #2.- It is proposed to carry out hydraulic works including elevated dams, where large quantities of water are momentarily stored, creating conditions for it to operate as an atmospheric battery and maintain the continuous operation of a generator driven by a Francis turbine with a continuous capacity of 0.25 to 0.5 MW at 60 Hz for a range of 8 hours. The sum of the two operating modules are called: Microgenerator Group and Pumping with Atmosphere Battery, being possible to triple the sum of the two modules through an arrangement to sustain a load of 0.25 a 0.5 Megawatts for a 24 hr cycle, exploring the increase in the number of microgenerators and consequently modify if necessary the capacity of the elevated dam, the general conditions of use and exploitation consider that it is not necessary to interconnect to the public state transmission network called Federal Electricity Commission (CFE). Achieving the sustainable operation of a new regional development engine that takes advantage of green energy in a cyclical manner.



Slow movement of the water, combination of technologies, microgenerator group, atmospheric battery and Economics Development

#### Resumen

El proyecto integra la puesta en marcha de dos módulos: #1.- Un microgenerador mecánico, hidrocinético revolucionario que convierte más del 50% del paso lento del agua en energía eléctrica, aprovechados en el Distrito de Riego #043 en el Estado de Nayarit México alimentando a tres bombas centrifugas que operan con motores trifásico de 10 Hp/s. para cada bomba; módulo: #2.- Se propone realizar obras hídricas incluyendo diques elevados, donde se almacenan momentáneamente grandes cantidades de agua, creando condiciones para que opere como una batería atmosférica y mantenga la operación continua de un generador impulsado con turbina Francis con capacidad continua de 0.25 a 0.5 MW. a 60 Hz por un rango de 8 horas. La suma de los dos módulos operando, se denominan: Grupo Microgenerador y Bombeo con Batería Atmósfera, siendo posible triplicar la suma de los dos módulos mediante un arreglo para sostener una carga de 0.25 a 0.5 Megawatts por un ciclo de 24 hrs., explorando el aumento del número de microgeneradores y en consecuencia modificar de ser necesario la capacidad del dique elevado, las condiciones generales de uso y aprovechamiento consideran que no es necesario interconectarse a la red pública de transmisión estatal denominada Comisión Federal de Electricidad (CFE). Logrando la operación sustentable de un nuevo motor de desarrollo regional que aprovecha energías verdes de una manera cíclica.



Movimiento lento del agua, combinación de tecnologías, microgenerador hidráulico, batería atmosférica y desarrollo regional

**Citation:** Jaime-Navarro, Agustín, Bonilla-Alejo, Sergio Raúl and Rodríguez-Rodríguez, Joel. [2024]. Integration of green technologies for the generation of electric energy using microgenerators and atmospheric batteries in the irrigation district #043 Alejandro Gascón Mercado, *Canal Centenario*, *State of Nayarit*. Journal Renewable Energy. 8[20]-1-6: e50820106.



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#### Introduction

Our passage as humankind on planet earth will record a high level of pollution by the year 2023. The prevailing way of life due to the application of the linear economy method continues to generate deterioration of the environment: damage to the ozone layer, increase of the carbon footprint and depletion of natural resources due to human activity. The increase in temperature has changed normal climate cycles, causing serious damage to biodiversity with climatic implications: hurricanes, severe droughts impacting watersheds, lakes and rivers, some have declared water in Mexico emergencies similar to other places globally.

Leading these environmental improvement efforts is the UN through the governments of the world with the 2030 Agenda and the 17 Sustainable Development Goals, seeking to change the way electricity is generated and consumed, the impact of the transition from petrol cars to hybrid and/or electric cars to establish new ways to promote human mobility. All other human activities imply further changes in the consumption of other natural resources: water and air.

With this frame of reference, the present research developed by the members of the multidisciplinary academic body of the Technological University of Nayarit<sup>[1]</sup> ITCAR<sup>[2]</sup> (Technological Innovation in Environmental Sciences and Renewable Energies) is identified. During the period 2022 - 2024, a formal investigation was established that has taken as its starting point the chapter entitled: 'Characterisation of Potential Clean Energy Generators in the State of Nayarit, to elaborate the Energy Transition Matrix 2020-2050'[3].

This course is directed towards hydroelectric microgeneration of electrical energy, with exploitation of slow water flows in streams, rivers and canals. In Mexico, and especially in the Nayarit Territory, there is a large capacity of hydrological resources that can be used throughout the year.

Below is an illustration of the availability of surface water in Nayarit, a water basin with its rivers and canals with a potential for microgeneration of electrical energy calculated at 2,491 MW/Hra (Microgeneration by rivers and water runoff) including dams of 4,314 GW/Hra (Microgeneration by rivers and water runoff). See (Fig.1).

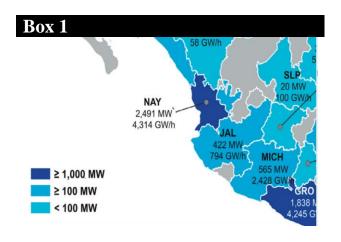


Figure 1
Capacity in MW and GW. of electricity generation in Nayarit, by means of hydropower potential

Subsequently, the focus was to study and select the type of microgenerator already tested with the best results and adapted to rivers and canals, particularly the irrigation District Canal No.043. Thus, after several months and experiences in communities of Navarit as Santa Cruz de Miramar, where with the few resources available. the 'Rio El Naranjo' characterised, with possibilities of using a helical screw, which has been developed in Spain and is for sale, costs were obtained only. In the months of May and July 2024, after the PRIMSO call of the Government of the State of Nayarit, through the COCYTEN (Council of Science and Technology of the State of Nayarit), assigned economic resources to this research work specifically to be designed and potentially selected to be implemented in the irrigation district NO. 43 Alejandro Gascón Mercado. After analysing the characteristics and measurements of the canal or irrigation district No.45, the best option was the WATEROTOR Microgenerator, a device that harnesses the kinetic energy of slow moving water to generate electricity. It works by means of a rotor or turbine that is installed in water currents, such as rivers or canals, to convert the constant flow of water into rotational movement.

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The WATEROTOR is an efficient and sustainable solution for generating energy in areas where there is access to water resources. Moreover, its environmental impact is relatively low, as it does not require reservoirs or large infrastructures, as in traditional hydroelectric plants. This technology can be especially useful in rural or isolated communities that do not have access to conventional electricity grids. The WATEROTOR microgenerator will be the means to generate enough electrical energy to power 3 three-phase 10 Hp pumps. Each one with its own pumping pipe work to fill in a manner. cyclical an elevated (ATMOSPHERIC BATTERY), which will be calculated to sustain for 8 hrs. With a constant generation capacity of 0.25 to 0.5 MW/Hra. At 60 Hz. Without interconnection to C.F.E. (Electricity supply company)

# Methodology

The challenge begins with the selection of the type of microgenerator that will adapt to the measurements of channel 043 (See fig.2) in question and whose capacity is in the range of 10 to 50 KW/Hra. at 60 Hz. Three-phase, which does not use fossil fuels or chemicals that pollute the atmosphere.

This microgenerator is ideal for this type of canal, which met the expectations of this project, after an analysis and which makes perfect use of the kinetic energy of slow moving water flows and which adapts to the measurements of the irrigation district in question.

It was the WATEROTOR microgenerator that works efficiently at water velocities as low as 3.2 km/h (0.9 m/s), ideal for the 'Irrigation District 043, Canal Centenario located in the state of Nayarit'. Below is an image of the selected Microgenerator. The design of the WATEROTOR is totally underwater, that is to say it is submerged in water, easy to install and uninstall, totally mobile.

# Box 2



Figure 2
Waterotor Microgenerator for slow water flow.
MODULE 1

It is observed that the selected microgenerator, with the function of electrically feeding groups of 3 three-phase pumps of 10 hp's each. So that through pipes properly calculated to fill the elevated dam (element considered in the Atmospheric Battery) MODULE 2. That contains, the quantity of cubic meters necessary to, in turn, manage to maintain an electric generator of 0.25 to 0.5 MW. working in a range of 8 to 24 hrs.

At this stage, it is worth mentioning that with the resources allocated to this project, from the PRIMSO call of the Government of the State of Nayarit, through COCYTEN (Council of Science and Technology of the State of Nayarit). A photometric study of the terrain (8 kilometres of the canal, irrigation district 043) will be carried out using a photometric drone. This will be used to define the places where the best conditions for the installation of the microgenerators can be found.

On the other hand, the aforementioned pumping equipment will have hydraulic works to raise the water to an elevated dam. Strategically placed in a place close to the canal.

From the above, it is required to build a hydroelectric work of pipe that will gradually decrease diameter from the high dam to the entrance snail to the body of a structure with Francis turbine, which with sufficient force moves the shaft of an electric generator with a capacity of 0.5 MW/Hra. And the output of the generator is considered to be 0.5 MW. Return the water to the canal or irrigation district again.

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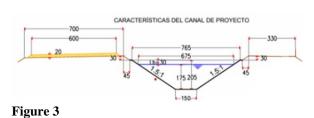
Based on the characteristics and geometry of the irrigation district, Alejandro Gascón Mercado. Where these measurements are the basis for selecting the WATEROTOR microgenerator.

Below are the measurements of the geometry of the Irrigation District #043.

The centennial canal has a trapezoidal channel, with the following measurements

- Channel Width = 2.40 mts.
- Slope Distance = 1.75 mts.
- Total Channel Height = 3.50 mts.
- Flow Depth = 3.00 mts.

# Box 3



Cutting of the Centenario Canal, Irrigation District #043, Alejandro Gascón Mercado

The geometry of the channel determined the measurements of the depth and width of the base of the channel. And it was this data that determined the size and kilowatt capacity of the WATEROTOR microgenerator. That if they coincide with the KW. That are required for the group of pumps proposed in this research work.

The use of sustainable energy and natural environments, are a source of inexhaustible and affordable energy where there is no direct damage to the environment, plus the prototypes do not have a footprint or carbon footprint to obtain electricity. Another important point is to take advantage of the resources offered by the State of Nayarit, as is the Centenario a left bank channel without operating, the main source is the fall and the energy provided by the flow and velocity of natural water in a specific geographical space, where a study conducted that affects the agricultural sector, rural economy, this channel will be used as the natural source of hydraulic energy to be potential energy and / or electricity.

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# Box 4



Figure 4

Geographical location of Margen Derecho "Distrito de Riego #43, Alejandro Gascón Mercado." from QGIS

The 2,047 hectares of the localities El Tambor and Corral de Piedra, both located in the Municipality of Santiago Ixcuintla Nayarit Mexico, are highlighted in blue. Surveys will be carried out with a Drone Photometric along the Irrigation District #043. The purpose is to know the topographic features associated with the area of influence of the Centennial Canal, to determine the best locations of the microgenerators for electricity generation.

QGIS software was used to process the field photometric information to generate numerical elements.

For the generation of illustrations of mechanical components, as in the case of the proposed microgenerator, the Solid Works platform was used.

# Box 5



Figure 5

Illustration of Proposed Microgenerator Generated in Solid Works

Jaime-Navarro, Agustín, Bonilla-Alejo, Sergio Raúl and Rodríguez-Rodríguez, Joel. [2024]. Integration of green technologies for the generation of electric energy using microgenerators and atmospheric batteries in the irrigation district #043 Alejandro Gascón Mercado, Canal Centenario, State of Nayarit. Journal Renewable Energy. 8[20]-1-6: e50820106.

This proposal brings together a green, friendly environmentally means microgeneration of electricity and is combined with an atmospheric battery. To which is added a hydroelectric type work with a Francis turbine of special dimensions for a generator of 0.25 to 0.5 MW, to take advantage of the fall of water from a height of more than 7 mts. to 10 mts. with a dam of more than 180 cubic metres. With a potential to sustain the production of electrical energy for almost 10 hours of generation. The combination of modules 1 and 2 of this project, as well as the hydroelectric work required, can be replicated several times along the canal or irrigation district No. 043, and the 2 modules and the hydroelectric work can be sized according to the needs in target generation capacity. According to what can be invested and the electrical load that needs to be fed. A versatile and sustainable design can be considered, taking into account the following aspects listed, in order to be successful when implemented in the field:

On the initial route of 9 kms. of the trajectory of the Irrigation District #043 considered in the terms of reference of the call PRISMO 2024, using as a means of support overflights with the use of a Drone that uses a photometric camera. The intention is to have clarity of the real and existing topography in the canal area; by identifying the available elevations and in case of not having natural elevation elements, then we will proceed to suggest the construction of elevated dams as water reservoirs and/or some type of project available in CONAGUA<sup>1</sup>.

# Box 6



Figure 6

Topographic Profile, Zona Canal Centenario State of Nayarit

- For the operation of the modules: Microgenerator + Gravity Pump, it is necessary to have structures that allow the temporary storage of water at a height of 7 to 10 mts. with variable capacities that allow the calculated electricity generation.
- The generation of sustainable electrical energy considers it fundamental not to pollute and to be a green energy proposal with moderate investment, with the potential to achieve a great social impact in the region where Irrigation District #043 is located.
- The system of microgeneration and generation with hydroelectric work with capacities in the range: 0.25 to 0.5 MW/hra. does not consider being interconnected to the Public Networks of the CFE, being used 100% in the area of the Irrigation District #043.

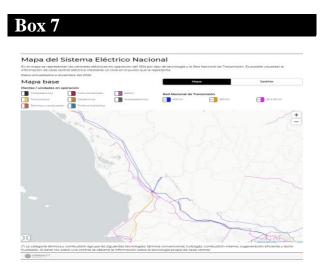


Figure 7
Public Networks CFE, State of Nayarit

It is necessary to manufacture a series of components that, when installed in the areas identified for generation, allow the purification and, if necessary, diversion of: waste, suspended solids and other agents present on the water surface that affect the operation and rotation of the microgenerator rotor. Allowing ordinary operation with a low level of scheduled preventive/corrective maintenance.

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<sup>&</sup>lt;sup>1</sup> Topographic identification of the study area Mapa topografico Nayarit, altitud, relieve (topographic-map.com https://es-mx.topographic-map.com/map-xnm57/Nayarit/?center=21.75775%2C-105.05703&popup=22.18168%2C-109.76786&zoom=13

Benefits with high social impact are contemplated for the northern region of Nayarit, by achieving production in the generation of electricity in the range: 0.25 to 0.5 MW of continuous three-phase type available in a minimum range of 10 hours extended to 24 hrs, it is possible to consider the following goals:

- Attract foreign investment to global companies, by means of different agreements, with differentiated and attractive regulated prices in peso tariffs per KW/Hra consumption.
- 2Through being able to increase the pumping of water over long distances from the canal, it is feasible to consider increasing the number of hectares that will become potential generators of crops in the region. With low cost electricity in pesos. Causing new lands to abandon the temporary use and to be adhered to the new Irrigation District #043. As a strategy to ensure food security for the national population.
- Strengthening the generation of jobs, with better remuneration, as a strategy to retain the migration of young people, due to the fact that they cannot find employment in their area of origin.

Low-cost electricity, aimed at developing micro-enterprises in each of the communities, to give added value to their crops (dehydrating, canning, etc.), promoting national sales and export abroad with higher profit margins.

We identified the potential to boost the local economy by extending the initial surface area by 24,000 hectares of irrigated land in the northern zone along the municipalities: Santiago, Tuxpan, Ruiz and Rosamorada with electricity availability along the 58 Kms. of the Centennial Canal 365 days a year.

Laying the foundations for attracting investment and the establishment of global companies. The present implementation presents the feasibility of being able to be replicated in the states where its hydrological characteristics allow it, at least the following are identified:

# Box 8



Figure 8

Surface Water Availability Summary in Mexico

The integration of a model to attract foreign investment, promoting the empowerment of the countryside and the promotion of growth in these regions, is a matter of another type of scope, and in this sense the detonating and articulated role that the availability of electricity can play when considering regional development strategies is emphasised.

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8[20]1-5: e60820105

Article

Comparison of *Canna indica*, *Pontederia sagittata* and *Heliconia rostrata* as phytoremediator species in the treatment of gray water in Úrsula Galván, Ver.

Comparación de Canna indica, Pontederia sagittata y Heliconia rostrata como especies fitorremediadoras en el tratamiento de aguas grises en Úrsulo Galván, Ver.

Acosta-Cadenas, Montserrat<sup>a</sup>, Jimenez-Flores, Juana Fabiola<sup>b</sup>, Utrera-López, Daniel<sup>c</sup> and Arellano-Montero, Edgar Javier<sup>d</sup>

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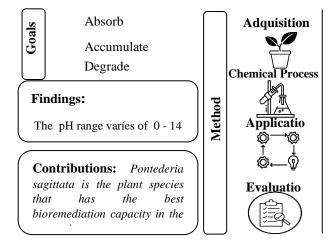
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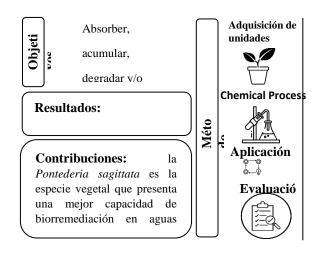
#### Abstract

Artificial wetlands began to be used as tools for wastewater treatment. It was found that these could be built following the same operating principle as natural wetlands, which since they existed have fulfilled the function of storing and purifying wastewater. In some studies, the species: \*Canna indica, \*Pontederia sagittata and \*Heliconia\* spp. have shown potential for contaminant removal. Due to the high demand for these plants as phytoremediation species, several studies have evaluated the role of Heliconia in wastewater remediation, finding positive effects in bioremediation (Ascuntar and Toro 2007, \*Gómez and Segura 2008, \*Gutiérrez 2009, \*Sandoval 2009, \*Peña et al., 2011). Pontederia cordata has a root system, which has microorganisms associated with it that favors the purifying action of aquatic plants, retaining heavy metals (Cd, Hg, As) in their tissues. In addition, it removes some organic compounds, such as phenols, formic acid, dyes and pesticides, and reduces levels of BOD5, COD and suspended solids. (Celis et al., 2005). The species Canna indica is considered an effective plant for phytoremediation due to its physiological and morphological properties.



#### Resumen

Los humedales artificiales, empezaron a ser utilizados como herramientas para el tratamiento de aguas residuales, se encontró que estos podían ser construidos siguiendo el mismo principio de funcionamiento de los humedales naturales, los cuales desde que existen, han cumplido la función de almacenar y purificar el agua. En algunos estudios, las especies: Cama indica, Pontederia sagitata y Heliconia spp. han mostrado potencial para la remoción de contaminantes. Debido a la alta demanda existente alrededor de estas plantas como especies fitorremediadoras, Diversos estudios han evaluado el papel de la Heliconia en la remediación de aguas residuales encontrando efectos positivos en la biorremediación (Ascuntar y Toro 2007, Gómez y Segura 2008, Gutiérrez 2009, Sandoval 2009, Peña et al., 2011). Pontederia cordata posee un sistema de raíces, que tienen microorganismos asociados a ella que favorece la acción depuradora de las plantas acuáticas, retienen en sus tejidos metales pesados (Cd, Hg, As). Además, remueve algunos compuestos orgánicos, tales como fenoles, ácido fórmico, colorante y pesticidas, y disminuye niveles de DBO5, DQO y sólidos suspendidos. (Celis et al., 2005). La especie Cama indica es considerada una planta eficaz para la fitorremediación por sus propiedades fisiológicas y morfológicas.



Humedales articiales, aguas grises, Canna

Artificial wetlands, grays water, Canna

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Article

#### Introduction

Currently, we are facing a crisis due to water scarcity in different communities, as population growth in the area brings with it increased demand for drinking water and increases water pollution (Rhodes, 2019). Water pollution is an environmental challenge that affects the quality of life of all people. Among the various sources of contamination, we have graywater, which is generated by domestic activities, being very common represents a great concern due to the impact on human health and the aquatic ecosystem.

The main contaminants in graywater are nitrogen and phosphorus, organic compounds, fecal coliform bacteria, organic matter, among many others (Jiménez, et al., 2010). In Mexico in 2012, urban centers discharged approximately 7.3  $\text{km}^3$  (equivalent to 229.73  $\text{m}^3/\text{s}$ ) of wastewater. At the federal entity level, those that in 2012 generated the largest municipal water discharges were the state of Mexico (24.22 m<sup>3</sup>/s), Federal District (21.96 m<sup>3</sup>/s) and Veracruz (16.08 m<sup>3</sup>/s), which together accounted for 27.1% of the national volume generated. For this reason, it is necessary to look for alternatives to help us solve this problem in a sustainable manner. Artificial wetlands began to be used as tools for wastewater treatment, it was found that they could be built following the same principle of operation of natural wetlands, which since they exist, have fulfilled the function of storing and purifying water. These wetlands consist of an intermediate ecosystem, between aquatic and terrestrial, in which three important elements interact: water, soil and macrophytic plants. During this interaction, several biological processes occur, which allow obtaining better quality water at the outlet of the system (Zarate, 2001). This is presented as a sustainable strategy for graywater treatment, using aquatic plants to absorb, accumulate, degrade and/or transform the pollutants present. In some studies, the species Canna indica, Pontederia sagittata and Heliconia spp. have shown potential for the removal of pollutants.

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Pontederia spp. as a phytoremediation plant

Valdivia, G. 2019 in the work "Efficiency of *Eichhornia crassipes* (mart.) Solms laub - pontederiaceae and nasturtium officinale w.t. aiton - brassicaceae in the removal of dbo5 and dqo from the effluent of the wastewater treatment plant of celendín", mentions that Pontederia cordata has a root system, which has microorganisms associated with it that favors the purifying action of aquatic plants, retaining heavy metals (Cd, Hg, As) in their tissues. In addition, it removes some organic compounds, such as phenols, formic acid, dyes and pesticides, and decreases levels of BOD5, COD and suspended solids (Celis et al., 2005).

Studies of Canna indica as a phytoremediation plant

The same author mentions that the Canna indica species is considered an effective plant for phytoremediation due to its physiological and morphological properties. For Cheng et al. (2007) it is a species of the Cannaceae with high resistance to stress due to the presence of heavy metals, as well as a high potential for their degradation.

A study by Aguiar & Castillo (2019) points out the possibility of using the vegetative species Achira for the purification of water bodies and consequently improve water quality. In addition, achira according to (Caguana, 2018), presents other uses, in human food, animal feed and for the production of industrial starch and the preparation of noodles.

A study conducted by Quezada et al., (2012) called "Natural remediation to complete the purification of chromium (VI) in tannery effluents". He established the following results (C. indica) showed that, from the analysis of plant tissue, it was demonstrated that chromium, regardless of its oxidation state in solution, (III) or (VI), is stored in greater proportion in the root, reaching concentrations above 3,000 mg/kg (dry weight). Also (Wang LK, Shammas NK, Hung YT, 2010) mentions that C. indica has been used to treat the waters of the Yangtze River, China where the efficiency of this plant in the elimination of chromium in water is proven (Quezada, R et al., 2012) (Quezada, R et al, 2012). Likewise, contaminated water in the Zhujiang River (Guangzhou) was treated with a floating system of this species.

Acosta-Cadenas, Montserrat, Jimenez-Flores, Juana Fabiola, Utrera-López, Daniel and Arellano-Montero, Edgar Javier. [2024]. Comparison of *Canna indica*, *Pontederia sagittata* and *Heliconia rostrata* as phytoremediator species in the treatment of gray water in Úrsula Galván, Ver. Journal Renewable Energy. 8[20]-1-5: e50820105.

# Methodology

Plastic containers were lined with a black plastic bag to prevent water leakage, this ensures that it is possible a single water outlet that can be collected, then proceeded to cut 4 pieces of hose of 25 cm each, these hoses so that water can reach the receiving containers, A piece of hose was wrapped with an edge of insulating tape, this had the function of providing a relief in the hose, when introducing the hose through a hole in the container this relief allowed a pressure that prevented the exit of the hose and water.

#### Box 1

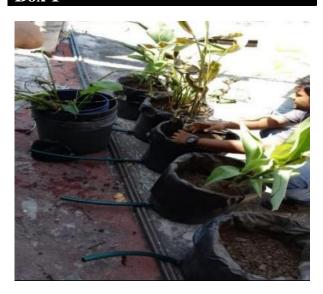


Figure 1
Installation of wetlands

The plastic containers were then filled with the substrate. Two different calibers were used for the first layer of gravel, one of 4-5 cm and the other of 2 cm. We placed 6 centimeters of fine gravel, 8 centimeters of sand after another 8 centimeters of gravel, the vegetal component was placed and then the last layer of soil was placed between 8 centimeters. The plastic containers were placed in a row and at the same level, and then the collection trays were placed.

# Box 2



Figure 2
Greywater treatment plants

# Box 3

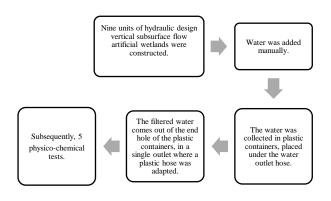


Figure 3
Graywater treatment process

# Results

#### pH test

Hydrogen potential (pH) is used to determine whether water is acidic or alkaline. The pH range varies from 0 to 14 standard units (S.U.), where 7 is neutral. A pH below 7 indicates acidity, while a pH above 7 indicates a basic or alkaline condition. The pH is expressed in logarithmic units and each whole number represents a 10-fold change in the acidity or alkalinity of the water. Water with a pH of 5 is ten times more acidic than water that has a pH of 6. Because chemicals can affect pH, pH is an important indicator of water that changes from a chemical standpoint (Perez, R, 2017).

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Pollution can change the pH of water which, in turn, can harm the organisms living there. Table 1 shows the pH values obtained when entering through the wetland, as well as the values obtained when having been 24 hours inside the wetland.

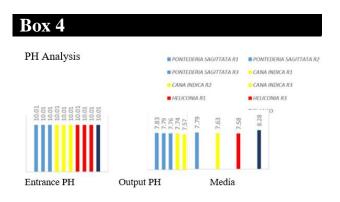


Figure 4
Hydrogen Potential

Considering the hydrogen potential readings obtained from the water samples, we can say that the heliconia is the one that manages to reduce the hydrogen potential of the treated graywater the best.

# Hardness test

It is a chemical characteristic of water that is determined by the content of carbonates, bicarbonates, chlorides, sulfates and occasionally calcium and magnesium nitrates. Hardness is undesirable in some processes, such as domestic and industrial washing, causing more soap to be consumed, as insoluble salts are produced. In boilers and water-cooled systems, it causes scaling in pipes and a loss in heat transfer efficiency.

It also imparts an undesirable taste to drinking water. Large amounts of hardness are undesirable for the reasons stated above and must be removed before water is suitable for use in the beverage, laundry, metal finishing, dyeing, and textile industries (Romero J., 1999).

Hardness is measured in CaCO<sub>3</sub> and according to each limit is considered from soft to very hard water as shown in Table 1.

# Box 5

## Table 1

Classification of water according to its total hardness

Hardness	Definition
0 - 75	Soft Water
75 - 150	Little Hard Water
150 - 300	Hard Water
> 300	Very hard water

Five different physicochemical tests were performed on the treatment to compare the efficacy of each species. The results are shown in the table:

#### Box 6

Table 2

	Parameters				
Treatment	pН	D	CE	SD	SS
Pontederia S.	7.79	287	1.06	0.04835	1.30988
Canna I.	7.63	628	3.03	0.08320	0.84949
Heliconia R.	7.58	532	2.44	0.05869	0.67410
Target	8.28	520	1.19	0.05834	1.39291
Gray Water	10.0	0	33.3	1.71411	12.2377

Results of physical-chemical analysis (pH, hardness, electrical conductivity, suspended solids, dissolved solids).

Heliconia spp. reduced the pH of the water up to 24.26%, with 7.58, complying with the regulation of 6.5 to 8.5 according to Delgado, J. in 2021. It is also the most effective in reducing suspended solids, leaving them at 0.67%, the variations that occurred in the other species may be due to environmental factors and wetland conditions (Delgado, J. 2021).

Pontederia sagittata decreased water hardness to 287 mg CaCO $_3$ /L and significantly reduced electrical conductivity to 1.06  $\mu$ S/cm. Based on Morales et al., 2019, plant components tolerated and absorbed soluble salt ions by adhering them to their tissues without affecting growth.

As for dissolved solids resulted in 0.0483 mg/L. according to Buitrón, A., 2024, it is below the established norm, indicating that a considerable proportion of dissolved solids could be effectively controlled by the implemented treatments.

#### **Conclusions**

According to the tests carried out, it can be concluded that the *Heliconia rostrata* species presented a better capacity to reduce the hydrogen potential in graywater. On the other hand, the *Pontederia sagittata* species decreased water hardness, which indicates a better performance of the plant, and also gave positive results in the conductivity analysis, i.e., it has great potential for the removal of salts present in gray water and finally it was the species that obtained the best performance in the removal of dissolved solids in water. Overall, *Pontederia sagittata* is the plant species with the best bioremediation capacity in graywater.

More research should be done on the physicochemical analysis of artificial wetlands. Consider the use of *Pontederia sagittata* and *Heliconia rostrata* for graywater treatment. It is proposed to continue monitoring and optimizing the system.

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Sólidos totales y disueltos (TSS y TDS) - Parámetros de calidad del agua | Hach. (2015).Hach.com.

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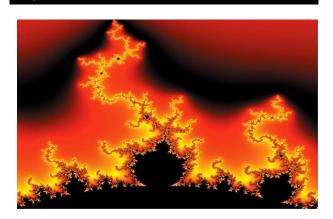


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