

UNIVERSIDAD DE INVESTIGACIÓN DE TECNOLOGÍA EXPERIMENTAL YACHAY

Escuela de Ciencias Químicas e Ingeniería

Pre-feasibility study on the corrosion inhibitors production from Ecuadorian natural sources

Trabajo de titulación presentado como requisito para la obtención del título de Ingeniero en Polímeros

Autor

Ariel Cristóbal Miranda Contreras

Tutor:

Marvin Ricaurte, PhD

Co-Tutor:

Alfredo Viloria, PhD

Urcuquí, Noviembre 2021



SECRETARÍA GENERAL (Vicerrectorado Académico/Cancillería) ESCUELA DE CIENCIAS QUÍMICAS E INGENIERÍA CARRERA DE POLÍMEROS ACTA DE DEFENSA No. UITEY-CHE-2022-00011-AD

A los 18 días del mes de enero de 2022, a las 10:00 horas, de manera virtual mediante videoconferencia, y ante el Tribunal Calificador, integrado por los docentes:

Presidente Tribunal de Defensa	Dra. ORDOÑEZ VIVANCO, PAOLA ELIZABETH Ph.D.	
Miembro No Tutor	Dr. PALMA CANDO, ALEX URIEL , Ph.D.	
Tutor	Dr. RICAURTE FERNANDEZ, MARVIN JOSE , Ph.D.	

El(la) señor(ita) estudiante MIRANDA CONTRERAS, ARIEL CRISTOBAL, con cédula de identidad No. 0952387223, de la ESCUELA DE CIENCIAS QUÍMICAS E INGENIERÍA, de la Carrera de POLÍMEROS, aprobada por el Consejo de Educación Superior (CES), mediante Resolución RPC-SO-41-No.476-2014, realiza a través de videoconferencia, la sustentación de su trabajo de titulación denominado: Pre-feasibility study on the corrosion inhibitors production from Ecuadorian natural sources, previa a la obtención del título de INGENIERO/A DE POLÍMEROS.

El citado trabajo de titulación, fue debidamente aprobado por el(los) docente(s):

Tutor	Dr. RICAURTE FERNANDEZ, MARVIN JOSE , Ph.D.
Co - Tutor	Dr. VILORIA VERA, DARIO ALFREDO , Ph.D.

Y recibió las observaciones de los otros miembros del Tribunal Calificador, las mismas que han sido incorporadas por el(la) estudiante.

Previamente cumplidos los requisitos legales y reglamentarios, el trabajo de titulación fue sustentado por el(la) estudiante y examinado por los miembros del Tribunal Calificador. Escuchada la sustentación del trabajo de titulación a través de videoconferencia, que integró la exposición de el(la) estudiante sobre el contenido de la misma y las preguntas formuladas por los miembros del Tribunal, se califica la sustentación del trabajo de titulación con las siguientes calificaciones:

Тіро	Docente	Calificación
Tutor	Dr. RICAURTE FERNANDEZ, MARVIN JOSE, Ph.D.	9,7
Presidente Tribunal De Defensa	Dra. ORDOÑEZ VIVANCO, PAOLA ELIZABETH Ph.D.	9,7
Miembro Tribunal De Defensa	Dr. PALMA CANDO, ALEX URIEL , Ph.D.	9,0

Lo que da un promedio de: 9.5 (Nueve punto Cinco), sobre 10 (diez), equivalente a: APROBADO

Para constancia de lo actuado, firman los miembros del Tribunal Calificador, el/la estudiante y el/la secretario ad-hoc.

Certifico que en cumplimiento del Decreto Ejecutivo 1017 de 16 de marzo de 2020, la defensa de trabajo de titulación (o examen de grado modalidad teórico práctica) se realizó vía virtual, por lo que las firmas de los miembros del Tribunal de Defensa de Grado, constan en forma digital.

ARIEL CRISTOBAL MIRANDA CONTRERAS Fecha: 2022.01.20 17:43:27 -05'00'

MIRANDA CONTRERAS, ARIEL CRISTOBAL Estudiante

PAOLA ELIZABETH Digitally signed by PAOLA ELIZABETH ORDONEZ VIVANCO ORDONEZ VIVANCO Date: 202201.19 15:50:35 0:50:0

Dra. ORDOÑEZ VIVANCO, PAOLA ELIZABETH Ph.D. Presidente Tribunal de Defensa

MARVIN JOSE Finadocigidament por UMAIN RICAURTE FERNANDEZ final and a list for day for a Dr. RICAURTE FERNANDEZ, MARVIN JOSE , Ph.D. Tutor

> Hacienda San José s/n y Proyecto Yachay, Urcuquí | Tlf: +593 6 2 999 500 | info@yachaytech.edu.ec www.yachaytech.edu.ec





YEPEZ MERLO, MARIELA SOLEDAD Secretario Ad-hoc



Hacienda San José s/n y Proyecto Yachay, Urcuqui | Tlf: +593 6 2 999 500 | info@yachaytech.edu.ec www.yachaytech.edu.ec

AUTORÍA

Yo, **ARIEL CRISTOBAL MIRANDA CONTRERAS**, con cédula de identidad 0952387223, declaro que las ideas, juicios, valoraciones, interpretaciones, consultas bibliográficas, definiciones y conceptualizaciones expuestas en el presente trabajo; así cómo, los procedimientos y herramientas utilizadas en la investigación, son de absoluta responsabilidad del autor del trabajo de integración curricular. Así mismo, me acojo a los reglamentos internos de la Universidad de Investigación de Tecnología Experimental Yachay.

Urcuquí, Noviembre 2021

Ariel Cristóbal Miranda Contreras CI: 095238723

AUTORIZACIÓN DE PUBLICACIÓN

Yo, **ARIEL CRISTOBAL MIRANDA CONTRERAS**, con cédula de identidad 0952387223, cedo a la Universidad de Tecnología Experimental Yachay, los derechos de publicación de la presente obra, sin que deba haber un reconocimiento económico por este concepto. Declaro además que el texto del presente trabajo de titulación no podrá ser cedido a ninguna empresa editorial para su publicación u otros fines, sin contar previamente con la autorización escrita de la Universidad.

Asimismo, autorizo a la Universidad que realice la digitalización y publicación de este trabajo de integración curricular en el repositorio virtual, de conformidad a lo dispuesto en el Art. 144 de la Ley Orgánica de Educación Superior.

Urcuquí, Noviembre 2021

Ariel Cristóbal Miranda Contreras CI: 095238723

ACKNOWLEDGMENTS

First of all, I thank God for lending me life and fulfilling my professional dreams and aspirations. Furthermore, Yachay Tech University for opening the doors of its classrooms, and the teachers impart the necessary knowledge to each of its students.

In the same way, I thank each of the teachers and colleagues for sharing each anecdote, sadness, joy, and triumph achieved throughout my study journey.

I thank my tutor, Ph.D. Marvin Ricaurte, for his help during the development of my project and for constantly clearing my doubts and concerns that arose at work.

And finally, to my parents and siblings for being the fundamental pillar and inspiration to complete my higher studies, reflecting that every effort has its reward.

RESUMEN

El objetivo principal de este trabajo fue realizar un estudio de prefactibilidad de la producción de inhibidores de corrosión formulados a partir de fuentes naturales agroindustriales que se producen en el Ecuador, con el fin de reducir los problemas económicos actuales que presentan las industrias petroleras y de otros sectores, debido al alto costo de la limpieza de ensuciamiento en los intercambiadores de calor. Debido a que Ecuador es un país con una alta actividad agrícola, y con el fin de darles un valor agregado siguiendo los postulados de la economía circular, se realizó un estudio de mercado de los residuos del chocho, los extractos de la sangre de drago y de la cascara del banano, los cuales contienen compuestos orgánicos ricos en heteroátomos que podrían tener poder de inhibición. También para cada una de las fuentes naturales se buscó información sobre su cadena de valor, con el fin de saber el volumen de producción de los principios activos, lo cual nos ayudó a determinar la cantidad de materia prima que podemos disponer. Posteriormente, se propusieron diagramas de bloques de la transformación de cada materia prima en un inhibidor de corrosion. Gracias a datos experimentales que se obtuvieron en el laboratorio: identificación del tipo de solvente a emplear en la extracción, relaciones másicas, rendimiento, etc., se pudo hacer un estimado del escalamiento. Para el escalamiento de cada fuente natural, se logró estimar valores en el balance de masa, con el fin de obtener información sobre la cantidad de inhibidor a producir. Estos datos arrojados en cada balance de masa, se encontró que la extracción de la sangre de drago, es el más óptimo para una industrialización en comparación con los desechos del banano y el agua de desamargado del chocho, debido a que se encontró que la relación del producto final con respecto a la materia es de 1:1. Por lo que se decidió realizar un análisis económico de la industrialización formulación del inhibidor a partir de los extractos de la sangre de drago, para lo cual se hizo un balance de costos para la instalación de la planta, y se consideró que el precio del inhibidor de corrosion se vendería a \$70.41 por kilogramo, con esto se lograría tener la recuperación total de la inversión de cada mes y de la instalación se recuperaría en el primer año, lo que quiere decir que partir del año 2, ese costo de instalación se considera ganancia y se estima que es un valor aproximado a \$78,974 anuales. Por lo tanto, las estimaciones del análisis económico indica la rentabilidad del proyecto.

Palabras claves: inhibidor de corrosion, residuos naturales, rentabilidad, Ecuador.

ABSTRACT

The main objective of this work was to carry out a pre-feasibility study of the production of corrosion inhibitors formulated from natural agro-industrial sources that are produced in Ecuador to reduce the current economic problems presented by the oil industries due to the high cost of cleaning of fouling in heat exchangers. Because Ecuador is a country with high agricultural activity, and to give them added value following the postulates of the circular economy, a market study of lupine residues, extracts of dragon's blood, and banana peel, which contain organic compound rich in heteroatoms that could have inhibitory power. Also, for each of the natural sources, information was sought about its value chain in order to know the volume of production of the active principles, which helped us to determine the amount of raw material that we could have. Subsequently, block diagrams of the transformation of each raw material into a corrosion inhibitor were proposed. An estimate of the scaling could be made thanks to experimental data obtained in the laboratory: identification of the type of solvent to be used in the extraction, mass ratios, yield, Etc. For the scaling of each natural source, it was possible to estimate values in the mass balance in order to obtain information on the amount of inhibitor produced. These data thrown in each mass balance, it was found that the extraction of dragon blood is the most optimal for industrialization in comparison with the waste of the banana and the lupine debittering water because it was found that the relationship of the final product with respect to the raw matter is 1:1. Therefore, it was decided to carry out an economic analysis of the industrialization of the inhibitor formulation from the extracts of blood, for which a cost balance was made for the installation of the plant, and it was considered that the price of the inhibitor of Corrosion would be sold at \$ 70.41 per kilogram, with this it would be possible to have the total recovery of the investment for each month and the installation would be recovered in the first year, which means that from year 2, that installation cost is considered profit and it is estimated that it is an approximate value of \$ 78,974 annually. Therefore, the estimates of the economic analysis indicate the profitability of the project.

Keywords: corrosion inhibitor, natural waste, profitability, Ecuador.

TABLE OF CONTENTS

CHAPTER	R 1	1
1. INT	RODUCTION	1
1.1	Problem Approach	3
1.2	Objectives	3
1.2.	1 General Objective	3
1.2.	2 Specific Objectives	3
CHAPTER	R 2	4
2. BA	CKGROUND AND LITERATURE REVIEW	4
2.1 Co	prrosion inhibitors	4
2.2	Classification of corrosion inhibitors	5
2.2.	1 Anodic inhibitors	5
2.2.	2 Cathodic inhibitors	5
2.2.	3 Mixed inhibitors	6
2.3	Applications	6
2.3.	1 Fouling in heat exchangers	6
2.3.	2 Types of Fouling	7
2.4	Green inhibitors	8
2.5	Inhibitors of organic nature	9
2.6	Circular economy 1	0
2.7 extrac	State of the Art - Inhibitory efficiency of lupine, dragon's blood, and banana t11	1
2.7.	1 Lupine	1
2.7.	2 Dragon's blood1	3
2.7.	3 Banana 1	4
CHAPTER	3	6
3. ME	THODOLOGY 1	6
3.1	Market study 1	7
3.2	Traditional value chain analysis 1	7
3.3	Mass balance 1	8
3.4	Chain value definition 1	8
3.5	Process description 1	9
3.5.	1 Extraction Stage 1	9
3.5.	2 Stabilization Stage 1	9

3.5.3 F	Formulation of the inhibitor Stage	. 20
3.5.4 P	ackaging Stage	. 20
3.6 Feasil	pility economic	. 20
CHAPTER 4		. 22
4. RESULT	AND DISCUSSION	. 22
4.1 Lupin	e's production	. 22
4.1.1 I	upine debittering	. 23
4.1.2 P water (PB)	Proposed process for formulation of inhibition from lupine cooking D)	. 24
4.2 Drago	on´s blood	. 26
4.2.1 0	Obtaining Croton lechleri	. 26
4.2.2 P	Proposed value chain for the dragon's blood inhibitor	. 27
4.3 Banar	1a	. 29
4.3.1 0	Obtaining the banana	. 30
4.3.2 P	Proposed value chain for the banana inhibitor	. 30
4.4 Econo	omic analysis	. 33
4.4.1 C	COPEX	. 33
4.4.1.1	Equipment	. 33
4.4.1.2	Energy consumption costs	. 34
4.4.1.3	Inputs and raw materials	. 34
4.4.1.4	Plant maintenance	. 35
4.4.1.5	Employee salary	. 35
4.4.2 0	OPEX	. 36
4.4.2.1	Basic services	. 36
4.4.2.2	Installation and commissioning of the plant	. 36
4.4.2.3	Lease of space	. 37
4.4.2.4	Recovery and total investment	. 37
4.4.2.5	Profits	. 38
CONCLUSIONS	AND RECOMMENDATIONS	. 39
REFERENCES		. 40

LIST OF FIGURES

Figure 1. Representation of the action of a corrosion inhibitor on a metallic surface.	4
Figure 2. Fouling on the surface of the heat exchanger.	6
Figure 3. Structure of aminoamides	9
Figure 4. Chemical structure of the alkaloids presents in the extract of <i>Lupinous albus</i> L	. 12
Figure 5. Chemical structure of the alkaloids presents in the extract of <i>Lupinous albus</i> L	. 13
Figure 6. Project methodology diagram	. 16
Figure 7. Processes for the transformation of the inhibitor	. 19
Figure 8. Chocho producing provinces in Ecuador	. 22
Figure 9. Lupine debittering value chain	. 23
Figure 10. Transformation of Chocho to inhibitor	. 24
Figure 11. Dragon's blood producing area in Ecuador	. 26
Figure 12. Traditional value chain of the dragon's blood	. 26
Figure 13. Proposed value chain for the dragon's blood inhibitor	. 27
Figure 14. Banana production in Ecuador	. 29
Figure 15. Traditional value chain of the banana.	30
Figure 16. Proposed value chain for the banana inhibitor	. 31

LIST OF TABLES

Table 1. Natural products and their use in inhibiting the corrosion process 8
Table 2. Content of amino acids present in Chocho 11
Table 3. Percentages of alkaloids in the chocho. 12
Table 4. Hydroxycinnamic acids and flavanols in the peels of different bananaspecies15
Table 5. Sown area and lupine grain production 23
Table 6. Mass balance of lupine-based inhibitor production
Table 7. Mass Balance of Dragon's Blood Based Corrosion Inhibitor
Table 8. Banana peel corrosion inhibitor mass balance
Table 9. Inhibiting Power of Dragon's Blood 33
Table 10. Equipment costs 343
Table 11 Energy consumption 34
Table 12 Inputs and raw material
Table 13. Plant maintenance 35
Table 14. Employee salary
Table 15. Basic services
Table 16. Installation and commissioning of the plant 376
Table 17. Lease of space
Table 18. Recovery and total investment
Table 19. Profits

CHAPTER 1

INTRODUCTION

Currently, in the petroleum industries and other sectors occur fouling and scale formation during regular use of heat exchangers which produce high maintenance costs associated with cleaning these units. In general, special solvents, detergents, diluted, inhibited acids are used to clean this equipment. The corrosion inhibitors used here are made primarily from synthetic organic and inorganic compounds. (Otzisk, 2008).

In fact, the fouling that forms in the heat exchangers generates a significant decrease in the operating efficiency of the unit. In addition, the vast majority of national industries cause a significant loss of money, estimated at more than \$4.4 billion annually, it is also estimated that due to exchangers fouling losses, in industrialized nations, they are between 25% - 30% of their Gross domestic product (GDP). Consequently, approximately 15% of a plant's maintenance costs are due to fouling on the surface of heat exchangers, as this also includes production losses and cleaning costs for the removal of fouling deposits. Cleaning costs for each heat exchanger are estimated to be between \$40,000 and \$50,000. (Ibrahim, 2012).

There are two techniques to remove scale, such as mechanical and chemical cleaning. Mechanical cleaning has shown to have abrasion on metals, which gradually removes the material, reducing the useful life of the equipment, although it is respectful with the environment, unlike chemical cleaning that puts the health of workers at risk by handling chemical products. However, chemical cleaning is used more in the industry as it performs a uniform and thorough cleaning. For example: In a shell and tube heat exchanger, the shell side can only be chemically cleaned, while the tube bundle can be mechanically cleaned as long as the arrangement of the tubes provides enough space and access to interior (Müller, 2000).

Due to the problems that the currently used corrosion inhibitors have brought to the hydrocarbon industries, it is necessary to find inexpensive and environmentally friendly corrosion inhibitors. In recent years, scientists have discovered that plant extracts are biodegradable and contain renewable chemical compounds with excellent performance as inhibitors of corrosive processes. Furthermore, Benítez & et al (2014) said that, there are already higher plant-based corrosion inhibitors and algae that are used in the corrosion of metallic materials such as steel, zinc, and aluminum, depending on the medium that is both acidic and neutral.

Ecuador is a country with an important agricultural activity, which has its positive point, on the one hand, it helps the economy since it employs a large population of Ecuador (Pino & et al, 2018). On the other hand, seeing a large amount of demand for agricultural products in Ecuador, the waste that is produced daily is considerable. Therefore, thinking about reuse under the concept of circular economy and the postulates of green chemistry, in order to give added value to natural waste, in this way it would reduce the environmental pollution of these wastes and the risk for human health (Morocho, 2018).

Therefore, for natural sources to have added value, the extraction of these should be considered in complement with extracts of inedible plant species and little studied in Ecuador. For this reason, in the present work, it is proposed to study the pre-feasibility of the industrial-scale production of corrosion inhibitors from natural sources. Plant extracts of *Croton lechleri* (dragon's blood) will be studied, which is not edible and two natural residues such as the debittering water of *Lupinus mutabilis* (lupine) and *Musa acuminata* peel (banana). Therefore, this is not attentive against the food security of the country's population. These compounds are chosen because a multidisciplinary and interinstitutional group of researchers works at the laboratory scale to obtain and characterize plant extracts from these natural sources for their content of organic compounds rich in heteroatoms, which may have inhibiting power. In this way, with the help of their laboratory data and with bibliographic references, it could be chosen in such a way which of the 3 is more feasible to carry out an economic analysis for its industrialization, or in turn the 3 extracts.

1.1 Problem Approach

Oil industries often present fouling on their equipment, for which they need maintenance in certain periods, where corrosion inhibitors are used to clean them, whose inhibitors have a very high cost and they might be highly contaminating. That is why this work seeks to create a low-cost and environmentally friendly corrosion inhibitor, from natural waste, which is in accordance with the postulate of the circular economy.

1.2 Objectives

1.2.1 General Objective

To carry out a pre-feasibility study of the production of corrosion inhibitors from natural sources (Debittering water of lupine, banana peel, dragon's blood extracts).

1.2.2 Specific Objectives

- To identify the market study on the previously identified source, its conventional uses and the volume of production / consumption within Ecuador.
- To define scaling factors from experimental data obtained in the laboratory.
- To prepare a process block diagram with its respective mass balance, to keep track of all the substances that intervene in each process of the transformation of the raw material into the corrosion inhibitor.
- To carry out an economic analysis, where capital expenditure (CAPEX) and operational expenditures (OPEX) will be determined, such as plant implementation costs, and investment and profit recovery, which will determine the viability of the project.

CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 Corrosion inhibitors

A corrosion inhibitor is a chemical product that slows down the rate of corrosion. It is used in small concentrations on metal surfaces, creating a protective layer, which allows extending the useful life of the material (Figure 1). The use of corrosion inhibitors is of utmost importance in the hydrocarbon industries, as many of their devices are made of materials vulnerable to corrosion such as steel pipes, heat exchangers, boilers, among others. Its use helps for the anticipated maintenance of corrosion, it also implies a reduction in expenses due to equipment failures that corrode, because as corrosion increases, metallic structures can have total or partial failures. (Salazar ,2015)



Figure 1. Representation of the action of a corrosion inhibitor on a metallic surface. (Palou & et al, 2014)

Corrosion is defined as the deterioration of a mechanical material that is exposed to atmospheric and aqueous environments. It is caused by an electrochemical reaction. For corrosion to occur in a mechanical material, it must be in the presence of factors such as oxygen, temperature, and humidity. These cause the physical and chemical properties of the material to be affected (Shreir,2013). For example, iron is one of the metals that corrodes more quickly, while stainless steel is a combination of iron with several elements, it is slower to corrode and that is why it is used more frequently, but it is more expensive (Sato, 2011).

2.2 Classification of corrosion inhibitors

Corrosion inhibitors can be classified (according to their activity) into anodic, cathodic, and film formers that act in both types of reactions. According to their origin they are classified into organic and inorganic. (Chacón, 2016)

2.2.1 Anodic inhibitors

Anodic inhibitors are characterized by being inorganic substances, which form films on already corroded metal surfaces. They are also known as passivators because they reduce the rate of corrosion by delaying the cathodic reaction. These substances increase the electrochemical potential of the metal, giving it greater resistance to corrosion. (Viloria, 2019)

2.2.2 Cathodic inhibitors

Cathodic inhibitors are compounds that prevent reduction reactions from taking place, because they control the pH of the corrosive medium of the material. These compounds prevent the reduction of oxygen in alkaline environments, and prevent the reduction of hydrogen ions in acidic environments. (Chacón, 2016)

2.2.3 Mixed inhibitors

Mixed inhibitors are also known as synergistic effect inhibitors because they simultaneously act on the cathode and anode zones. These inhibitors are characterized by having two processes. (1) In the cathode zone, the objective is to reduce or slow down the corrosion rate in the mechanical material. (2) After this process, the anodic zone forms a coating on the oxide layer, however, its concentration is very low, unlike if it were acting alone. (Cabrera, 2006)

2.3 Applications

2.3.1 Fouling in heat exchangers

Fouling is defined as the accumulation of unwanted solid materials such as scale, algae or corrosion products on the surface of the heat exchanger (Figure 2). A heat exchanger is a device that serves to transfer heat from one fluid to another of lower temperature. The heat transfer occurs through a metal plate or tube, which allows the exchange between fluids without those fluids coming together. (Ibrahim, 2012)



Figure 2. Fouling on the surface of the heat exchanger. (Ibrahim, 2012)

The formation of fouling in the heat exchangers, can have a significant negative impact on the operating efficiency of the process units (Ibrahim, 2012). The main consequences of fouling in the exchangers are the following: the reduction of the cross-sectional area of the tubes or flow area, causing an irregularity in the surface and an increase in the pressure drop in the heat exchanger. These effects reduce the flow rate and create a big problem since this implies that there is a possibility that the heat exchanger could block (Río ,2011).

2.3.2 Types of Fouling

The fouling in the heat exchanger can be classified into 4 different types: chemical, biological, deposition or corrosion reaction. The main differences are due to various factors, including the operating condition. It is essential to distinguish in what type of incrustations we are, in order to apply the corresponding cleaning. (Jie & et al, 2009).

Biological: Biological fouling is defined as the accumulation of deposits of biological organisms on a metallic surface, such as algae, which grow within the fluid and settle. For the elimination of this fouling, the chemical cleaning or mechanical grinding process is used. (Jie & et al, 2009).

Chemical reaction: Chemical fouling is characterized by forming layers of dirt on the surface of the tube of heat exchangers, due to the chemical changes that the fluid undergoes due to high levels of temperature. Chemical cleaning or mechanical decalcification is used for the elimination of chemical fouling. (Jie & et al, 2009).

Fouling by deposition: Deposition fouling, also known as sedimentation fouling, is defined as the accumulation of solid particles suspended through the fluid that is deposited on the surface of a piece of equipment, where gravity is the primary mechanism that helps the deposition of the particles. One measure to minimize the effect of this fouling is to place the heat exchanger vertically, in this way the suspended solid particles are extracted by gravity. To eliminate fouling by deposition, mechanical cleaning is required by brushing or scraping. (Jie & et al, 2009).

Fouling by corrosion: Corrosion fouling is defined as the formation of an extra layer, which can often present increases in thermal resistance. As a preventive measure, use of stainless-steel materials should be used in the heat exchangers (304 or 316 stainless-steel tubes). (Jie & et al, 2009).

2.4 Green inhibitors

The hydrocarbon industries promote the use of renewable and environmentally friendly materials, which fits as a postulate of green chemistry. Different types of active ingredients in nature perform well in different chemical treatments in the hydrocarbon industry. Table 1, summarizes the active principles present in agricultural residues, as inhibitors of corrosive processes in the hydrocarbon industry (Viloria. 2014).

Table 1. Natural products and their use in inhibiting the corrosion proc	ss. (Viloria, 2014)
--	---------------------

Raw materials	Mechanism of action	Observations
	• Aloe vera gel: scale inhibitor.	• Multifunctional offshore treatment.
Aloe vera	 Aloe Vera Acibar: Hydrate Inhibitor. 	• Low CO2 content.
	• Suppression in the formation of	• The flower of the command,
	hydrates, as thermodynamic and	shell and seed with potential
	kinetic inhibitors.	use in the inhibition of
		hydrates in expansion
Care to the		processes of extraction of
		liquids from natural gas.
Mango peel and seed		• Active principles: Phenols
		and polyalcohols.

The Ecuadorian agricultural sector plays an important role in the national economy, which has been evidenced throughout the economic and social history of the country. Currently, 95% of the domestic demand for food consumed by Ecuadorians is covered by the agricultural sector. The agricultural sector represents an average of 9% of the country's total GDP, generates employment for 25% of the economically active population, after oil, it is the main source of income of dollars and foreign exchange from exports and its contribution to the trade balance it is highly favorable. (Iturralde, 2017).

2.5 Inhibitors of organic nature

Organic-based inhibitors aim to form a protective organic layer on the metal surface and are widely used in the hydrocarbon industries. Commonly used organic inhibitors are primary and polysubstituted monoamines, diamines, amides, polyamines, polyphenols, imidazolines, and quaternary ammonium compounds. Primary and polysubstituted monoamines are responsible for varying the pH of the medium and are classified as neutralizing amines (Figure 3). Organic corrosion inhibitors act by absorbing ions or molecules on the surface of a metal, the addition of this to the electrolyte of an iron / acid system inhibits the rate of reduction of hydrogen, blocking anodic and/or cathodic reactions (Vergara, 2018).

NH.

Figure 3. Structure of aminoamides (Vergara ,2018).

Corrosion inhibitors can be broadly classified by their chemical nature and mechanism of action. These inhibit corrosion through interaction with the metal surface, corrosion products, and by rectifying the environment. In acid cleaning of heat exchangers where fouling is present, which generates a decrease in the efficiency of the equipment, neutralizing organic inhibitors, such as, morpholine, cyclohexamine, dodecyl amine, are commonly used (Sánchez. 2004).

Green inhibitors are in accordance with the principles of the circular economy because they aim to give added value to natural waste since by not being used, they could cause a risk to nature.

2.6 Circular economy

The circular economy is defined as a production and consumption model that involves recycling, reuse, and reduction of natural resources, in order to maintain their usefulness and value at all times. The circular economy seeks to redefine the growth of the traditional economy, to provide a better service to the community. This idea arises from the industrial revolution since these companies have created many products, which are consumed and then discarded, generating the pollution in the environment. (Morocho, 2018).

Promote the recycling of the waste in households and institutions responsible for the implementation of sustainable policies. In Ecuador, the circular economy model is promoted through programs aimed at raising awareness about this waste (Ellen, 2020). An alternative to valorize waste is to use it as an active principle of natural origin for the formulation of corrosion inhibitors. Which will be used in the inhibition of acid corrosion, in the chemical cleaning of heat exchangers of admiralty brass (material of greater relevance in hydrocarbon refineries).

Next, we will see the state of the art of the 3 natural sources, where the principles of the circular economy are clearly reflected, and emphasis is placed on the content of polyphenols that these have since these could have inhibiting power.

2.7 State of the Art - Inhibitory efficiency of lupine, dragon's blood, and banana extract

2.7.1 Lupine

Lupine (*Lupinus mutabilis* Sweet), is an erect herbaceous legume with robust, somewhat woody stems that reach a height of 1.8 to 2 meters. It is grown mainly between 2000 and 3000 meters high, in temperate and cold climates. Its distribution goes from Colombia to the north of Argentina, the crop is of importance only in Ecuador, Peru and Bolivia (Tapia, 2019). (Tables 2 and 3) Lupine debittering is a process that is carried out so that the lupine can be in optimal consumption conditions for humans. In this process of cooking the lupine, multiple amino acids and alkaloids are obtained, which are of interest for this research since they could be used as neutralizing corrosion inhibitors. (Rodriguez, 2009).

Amino acids	Lupine
Isoleucine	274
Leucine	449
Lysine	331
Methionine	47
Cystine	87
Phenylalanine	231
Tyrosine	221
Threonine	228
Tryptophan	110
Valine	252
Arginine	594
Histidine	163
Alanine	221
Aspartic acid	685
Glutamic acid	1372
Glycine	259
Proline	257
Serine	317
Total amino acids	6051
Total Essential Amino Acids	2183

Table 2. Content of amino acids prese	ent
in Lupine. (Rodriguez, 2009)	

Alkaloids	Percentage %
Lupanin	60
13-Hydroxylupanin	15
Sparteine	7,5
4-Hydroxylupanin	9
Isolupanin	3

Table 3. Percentages of alkaloids in lupine. (Rodriguez, 2009)

No information has been found in the literature on the study of *Lupinus mutabilis* Sweet as corrosion inhibitors, however, information has been found on corrosion inhibitors based on extracts of different species of the genus Lupinus. *The Lupinus varius* L. belonging to the legume family, it was used as an inhibitor of aluminum corrosion in alkaline solution. (Irshedat & et al, 2013) (Abel-Gaber & et al, 2009). The extract of Lupine (*Lupinous albus* L.) was evaluated as a corrosion inhibitor of steel in an aqueous solution of 1 M sulfuric acid and 2 M hydrochloric acid by potentiodynamic polarization techniques and electrochemical impedance spectroscopy, and an inhibitor efficiency of 86.5 %, where the alkaloids sparteine, lupanin, and multiflorine are the active compounds responsible for this effect. (Figure 4)



Figure 4. Chemical structure of the alkaloids presents in the extract of *Lupinous albus* L. (Abel-Gaber & et al, 2009).

2.7.2 Dragon's blood

Dragon's blood (*Croton lechleri*), is a latex, found in the Amazon rainforest in South America, especially in Bolivia, Colombia, Ecuador and Peru, and that reaches between 10 and 20 meters in height. It is used in products to treat diarrhea, wounds, tumors, stomach ulcers, herpes infection, itching, pain, and swelling from insect bites, and other conditions. (Jones, 2003) Dragon's blood has 2 active principles that could be used in the formulation of the corrosion inhibitor, such as tannins and alkaloids (see the Figure 5). The regeneration of the *Croton lechleri* tree is 1 and 2 cm per year, and they grow in sunny environments with light shadows (King & et al, 2020).



Figure 5. Chemical structure of the alkaloids presents in the extract of *Lupinous albus* L. (Abel-Gaber & et al, 2009).

There are no reports of evaluation of dragon's blood or resin from the *Croton lechleri* Müll tree in the literature as a corrosion inhibitor. However, there are examples of extracts from other species of the genus *Croton* (family Euphorbiaceae) evaluated as inhibitors. *Croton cajucara* Benth extracts were tested for the inhibition of corrosion of carbon steel in a saline medium, it was dissolved in a microemulsion system and in dimethylsulfoxide, which resulted in efficiencies of 93.84% and 64.73%, respectively. This difference is due to the fact that the microemulsion allows better adsorption of the extract. The structure of the extract is rich in hydrophobic compounds (cleodane-type diterpenes) and hydrophilic compounds (isoquinoline-type alkaloids) (Felipe et al. 2013).

2.7.3 Banana

Banana (*Musa acuminata*) is a fruit that grows in tropical and subtropical regions, the largest banana producers in the world are India, China, Ecuador, Brazil, Colombia and Venezuela. Bananas have benefits for human health, all parts of the plant are used as fruits, peel, stem, pseudostem, bulb, flowers, leaves and sap for the treatment of many diseases such as fever, cough, bronchitis, dysentery, allergies, sexually transmitted infections, among others. It also has pharmacological activities as an antioxidant, antidiabetic, immunomodulator, hypolipidemic, anticancer, antimicrobial and anti-HIV. The edible part of the banana provides energy, vitamins and minerals in appreciable quantities, contributing to the daily requirements of vitamin C, Potassium, Magnesium and Boron (Mathew et al, 2017).

In other *Musa* species, more than 40 phenolic compounds have been identified that can be classified into hydroxynazimic acids and flavanols (Table 4) (Vu & et, 2018). Being a rich source of natural antioxidants, the use of its extract can be considered as a friendly option as a corrosion inhibitor, it is reported that banana flower extracts have been shown to have an inhibitory effect in acidic media on tempered steel. (Gunavathy & et al, 2013). Therefore, it can be considered a good inhibitor of metal corrosion in acidic media, thanks to its compounds containing oxygen and nitrogen atoms, which are efficient as corrosion inhibitors. (Kavitha & et al. 2014).

Table 4. Hydroxycinnamic acids and flavanols in the peels of different banana species (Vu & et al, 2018)

Phenolic compounds	Varieties	Quantity
Hydroxycinnamic acids:		
Ferulic acid	Red Yade (AAB)	$11.9 \pm 1.2 \mu g/g DM$
Ferulic acid-hexoside	Red Yade (AAB)	29.9 ± 7.6 µg/g DM
Triferuloyl-dihexose	Red Yade (AAB)	$30.9 \pm 3.4 \mu g/g DM$
p-cumaric acid methylester	Musa sapientium ^a	4.28 ^b
Caffeic acid-hexoside	Red Yade (AAB)	$7.1 \pm 1.6 \mu g/g DM$
Sinapic acid	Red Yade (AAB)	$3.7 \pm 0.4 \mu\text{g/g DM}$
Sinapic acid-hexoside	Red Yade (AAB)	$16 \pm 4.4 \mu\text{g/g DM}$
Flavonols:		
Rutin	Red Yade (AAB)	482 ± 206 µg/g DM
Quercetin- deoxyhexose-hexoside	Red Yade (AAB)	$75.2 \pm 14 \mu g/g DM$
Quercetin -7-rutinoside	Cavendish (AAA)	$8.78 \pm 0.15^{\circ}$
Quercetin -3-rutinoside	Cavendish (AAA)	$29.87 \pm 0.07^{\circ}$
Quercetin-3/7-rutinoside-3/7-rhamnoside	Cavendish (AAA)	$12.91 \pm 0.14^{\circ}$
Kaempferol-deoxyhexose-hexoside	Red Yade (AAB)	35.5 ± 4 µg/g DM
Kaempferol-3-rutinoside	Red Yade (AAB)	173.9 ± 50 µg/g DM
Kaempferol-3-rutinoside	Cavendish (AAA)	$12.35 \pm 0.20^{\circ}$
Kaempferol-7-rutinoside	Cavendish (AAA)	$4.12 \pm 0.01^{\circ}$
Kaempferol-3/7-rutinoside-3/7-rhamnoside	Cavendish (AAA)	$5.32 \pm 0.10^{\circ}$
Isorhamnetin-3- rutinoside	Red Yade (AAB)	139 ± 73 μg/g DM
Isorhamnetin-3-rutinoside	Cavendish (AAA)	$1.31 \pm 0.09^{\circ}$
Myricetin-deoxyhexose-hexoside	Red Yade (AAB)	114 ± 27 μg/g DM
Myricetin-3-rutinoside	Cavendish (AAA)	$22.50 \pm 0.50^{\circ}$
Laricitrin-3-rutinoside	Cavendish (AAA)	$2.22 \pm 0.05^{\circ}$
Syringetin-3-rutinoside	Cavendish (AAA)	$0.63 \pm 0.01^{\circ}$

Knowing the phenolic compounds from natural sources gives us an indication of the opportunity represented by the valorization of the same corrosion inhibitor formulations, with this we follow the principles of green chemistry and the circular economy. In addition, this product would have an advantage in the market with respect to common inhibitors, because it is a green inhibitor and because it is food waste, the price would be lower. So now we will see the methodology to carry out the industrialization of inhibitors based on natural sources, in order to know if the project is viable.

CHAPTER 3

METHODOLOGY

First, a market study was carried out in order to know the natural sources (*Croton lechleri, Lupinus mutabilis Sweet*, and *Musa acuminata*), their conventional uses and the volume of production / consumption within Ecuador. An analysis of the traditional value chain of natural sources was also carried out, to know the stage where it is produced and the associated volume of the inedible source or agricultural residue, for the formulation of the corrosion inhibitor. Then, a process block diagram (DBP) was drawn up in order to identify stages by stages of the formulation of the inhibitor from the active principles, where the extraction of the extract is considered the critical stage for the industrialization of the process. Finally, a feasibility study was carried out to indicate the profitability of the project. In Figure 6 you can see a diagram of the methodology that is considered to be carried out in the project.



Figure 6. Project methodology diagram

<

3.1 Market study

Market study is defined as the collection and analysis of data on a certain product, in order to understand how it works in the market. This study allows us to stay on the sidelines and be updated on new trends, expectations, and customer needs. (Aaker, 1998). Therefore, the market study is of great importance for this project and allows us to know its profitability.

Given that this project is characterized by the industrialization of this raw material as corrosion inhibiting agents, the market study was used to determine the production volume of the raw materials (Lupine, dragon's blood and banana), in order to know the balance of availability of raw materials in Ecuador. A bibliographic search was also carried out on the provinces that produce the crudest materials since, if industrialized, the plant would be located as close as possible to where it is produced. This would reduce the costs of moving the raw material to the plant, for example, fuel from the truck that brings the raw material.

3.2 Traditional value chain analysis

The value chain consists of the description of activities necessary for the creation of a product or service. The objective of this model is to increase production efficiency, with the least possible expense, in order to provide a quality product to the customer. The value chain begins with the raw material, then it is processed and ends until the distribution of the finished product. (Porter, 2004). A bibliographic review was carried out for the identification of the traditional value chain of agricultural residues such as Lupine, dragon's blood and banana, a distinction was made in the stage where the active principles of interest that have the inhibitory capacity would come out.

Meetings were held with different groups of researchers to obtain information on the experimental data obtained in the laboratories on the power of inhibitors from natural sources, also to obtain a mass ratio, the solvent applied in the extraction and, among others, with the in order to use them as scaling factors. Also, know the processes they use to obtain the corrosion inhibitor.

3.3 Mass balance

The mass balance was carried out in order to obtain vital information on the processes involved in the proposed block diagram for the production of corrosion inhibitors from natural sources. For this, few data were used that were obtained through bibliographic references. Besides, this technique allows to know how much mass there is of each compound in each of the streams involved in the proposed system.

To obtain the mass balance, concepts of thermodynamics and basic knowledge of the principles of chemical engineering were applied. The calculation basis is the amount of raw material that will be used to start the process, this value is chosen arbitrarily to facilitate the required calculations and on which other variables or extensive resulting magnitudes are linked. The data that were used in the stages to determine the mass balance of each current, either input or output, were the following (Couper & et al, 2005):

- Mass relationships between compounds
- Process efficiency
- Percentage of losses of liquid, solids, or global
- Recovery percentage
- Unit conversion

3.4 Chain value definition

A process block diagram is used to indicate how a certain product is manufactured, specifying the raw material, the process quantity, and the way the finished product is presented. First, the value chain and the mass balance must be defined to obtain the final product, the block diagram. This makes it possible to identify the number of products that will be carried out based on the amount of raw material that is considered adequate to satisfy the demand for the product. (Borrás and et al, 2021).

A process block diagram was developed for the formulation of the inhibitor from the proposed natural resources. This is in order to propose the processes that would be involved in the transformation of the raw material into a corrosion inhibitor. A bibliographic search of similar processes was carried out in order to propose the most feasible stages, with which it would be possible to industrialize.

3.5 Process description

The diagrams with the proposals for the transformation of the natural resource into a corrosion inhibitor are detailed, in which the stages of extraction, stabilization, formulation of the inhibitor, and packaging are generally considered (Figure 7). It is also important to mention the equipment that will be used in each stage, in order to know the number of inputs to be used, which will allow us to carry out an economic study of the process that can be carried out.



Figure 7. Processes for the transformation of the inhibitor

3.5.1 Extraction Stage

The extraction step is a unit operation that is used to separate a compound of interest, which is in a reaction mixture, for which the use of a solvent is required. Extraction stage is considered the operation unit most critical in all process for the project. For the extraction is required to choose the most adequate extraction agent that allow to get the major amount of the active principle and that can be profitable. (Couper & et al, 2005).

3.5.2 Stabilization Stage

The stabilization stage is a unit operation that is used to avoid the alteration of natural compounds. The stabilization stage is proposed for our block diagram because they are natural sources that are exposed to deterioration by various factors such as temperature, air, light, humidity, etc. There are some mechanisms for stabilization such as cold storage, avoiding contact with the sun, using stabilizers, inert atmosphere, among

others. You must choose the most effective method for each raw material and the most profitable. (Couper & et al, 2005).

3.5.3 Formulation of the inhibitor Stage

The formulation of the inhibitor is a process that serves so that the product maintains its inhibitory properties, and is achieved by adding an additive. The additive will facilitate or improve its production or conservation process. In addition, this process allows the product to obtain a texturization, which makes the product more profitable.

3.5.4 Packaging Stage

The packaging stage is the final process for the distribution of our obtained product, which would be the corrosion inhibitor. At this stage, it is necessary to know which is the most feasible way for the commercialization of this product so that the product is in its optimal conditions for its respective use. There are different ways in which it can be marketed such as cans, gallons, barrels, and others. And it also depends on the type of packaging, in which you can choose between amber glass, plastic, metallic, etc. All this must be taken into account for each of the natural sources and that it guarantees the lowest possible expenditure and with the best quality. (Couper & et al, 2005).

3.6 Feasibility economic

The economic analysis is carried out in order to better make the decision on whether the project is viable for industrialization (Boulding, 1941). To do this, an economic feasibility study is carried out whose function is to determine the profitability of the project over time. To obtain this information, an analysis of the expenses and profits obtained from the operation of the plant was carried out, where the following parameters are detailed:

- The selling price of the corrosion inhibitor per kg.
- Direct costs: Cost of raw materials and supplies, workers, installation and commissioning, electrical consumption of equipment, cost of equipment, among others.
- Indirect costs: Basic services, and rent.

The following chapter details the results for each raw material, the production in Ecuador, and from this to know if it is convenient to carry out the economic analysis of its production as a corrosion inhibitor.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Lupine's production

Figure 8 and Table 5 show us the production of lupine in Ecuador, where the area planted and production of lupine grain are observed, which shows that the province of Cotopaxi is the most productive lupine and that it is also produced in Imbabura, but to a lesser extent. (Jacobsen, 2002). With this, we can determine where the lupine's cooking water will collect the highest point that can be reused for the commercialization of inhibitors based on natural products.



Figure 8. Chocho producing provinces in Ecuador (Jacobsen, 2002).

	Sown a	rea (Ha)	Production (Tm.)			
Province	Alone	Associated	Alone	Associated		
Cotopaxi	1.940	1.198	291	36		
Chimborazo	1.112	212	172	13		
Pichincha	450	161	76	*		
Bolivar	279	26	88	*		
Tungurahua	232	27	66	*		
Imbabura	176	130	16	*		
Total	4.189	1.754	709	49		

Table 5. Sown area and lupine grain production (Jacobsen, 2002).

4.1.1 Lupine debittering

For debittering process that is commonly carried out in Ecuador, it is shown in Figure 9, where we will focus on our product of interest which are amino acids and alkaloids, this will be released during cooking. These components are present in the inhibitors based on natural products. (Abdel & et al, 2009)



Figure 9. Lupine debittering value chain (Abdel & et al, 2009)

4.1.2 Proposed process for formulation of inhibition from lupine cooking water (PBD)

To carry out the block diagram of the process (Figure 10), scale factors had to be used, such as mass ratios of the Lupine compounds, also efficiencies of the equipment used in the stages, and volume of solvents and additives to be used for this process transformation as a corrosion inhibitor.



Figure 10. Transformation of Chocho to inhibitor

Process description

In #1 stream, 1000 kg of raw material enters, which the cooking water from the lupine, after this stream enters the filtration stage in order to decrease the water, after this, two streams come out, one of waste # 10 and # 2 stream that is sent to the vacuum concentration process, in order to reduce excess water in our raw material, and # 3 stream that contains the concentrate and # 11 stream is obtained. which is the collected water. This # 3 stream is sent to the extraction process, where a # 8 stream with the extraction

agent enters and #4 stream is obtained, it contains a mixture of alkaloid compound, water and the extraction agent, and also a waste # 12 stream later # 4 stream.

Once the extract is obtained, it is taken to the stabilization stage, where it is stored and it is suggested to cover it so that it is not contaminated with the environment, where a stream of water # 13 and # 5 stream that contains our product of interest come out. Once our extract is stabilized, the stream is sent to the inhibitor formulation process, where it is necessary to add # 9 stream with a chemical additive, where we obtain # 6 stream, which contains our corrosion inhibitor. And finally, this # 6 stream enters the inhibitor packaging process, where we obtain stream # 14 of losses, and # 7 stream of corrosion inhibitor ready for commercialization.

Base	1000.000	kg												
	Feed	Filtration	Concentration	Extract	Stabilization	Additive	Inhibitor	Extraction agent	Aditiive	Waste-Filtration	Waste, concetration	Waste, extraction	Waste, stabilization	Losses, packing
Cooking water (kg)	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#13	#14
Alkaloid compounds (kg)	34.615	25.269	25.017	20.013	19.813	19.813	19.764	-	-	9.346	0.253	5.003	0.200	0.050
Organic compounds (kg)	115.385	84.231	84.020	83.958	83.958	83.958	83.748	-	-	31.154	0.211	0.063		0.210
Water (Kg)	850.000	807.500	161.500	153.425	149.589	149.589	149.215	-	-	42.500	646.000	8.075	3.836	0.374
Extraction agent (Kg)	-	-	-	54.107	21.643	21.643	21.589	1082.147	-	-	-	1028.040	32.464	0.054
Aditive (Kg)		-	-	-	-	1.375	1.372	-	1.375	-	-	-	-	0.003
Total (Kg)	1000.000	917.000	270.537	311.503	275.003	276.378	275.687	1082.147	1.375	83.000	646.463	1041.180	36.500	0.691
Alkaloid (%)	3.462	2.756	9.247	6.425	7.205	7.169	7.169	-	-	11.260	0.039	0.481	0.548	7.169
Water (%)	85.000	88.059	59.696	49.253	54.396	54.125	54.125	-	-	51.205	99.928	0.776	10.509	54.125

 Table 6. Mass balance of lupine-based inhibitor production

In Table 6, it can be seen that in # 7 stream the inhibitor is obtained, with a proportion of alkaloid of 7.17% and water of 54.12%, so the inhibitor obtained is aqueous due to its high-water content.

4.2 Dragon's blood

In Ecuador, the plant species known as dragon's blood occurs in tropical and subtropical areas. In Ecuador, *Croton Lechleri* is cultivated for the production of latex. In Figure 11, the green area of the map of Ecuador is the area where the dragon's blood trees are grown, which occur on the flanks of the Eastern Cordillera and in the Amazon. (Botanicus, 2007). Thus, it is known from where we can obtain our raw material for the transformation to corrosion inhibitor.



Figure 11. Dragon's blood producing area in Ecuador. (Quiliano & et al, 2010)

4.2.1 Obtaining Croton lechleri

To obtain latex from dragon blood, the knockdown method is commonly used to obtain all dragon blood from the tree. The production volume of *Croton Lechleri* is directly proportional to the diameter of the tree, which means that the more diameter the tree has, the more dragon blood is obtained (Quiliano & et al, 2010). In Figure 12, we can see the traditional value chain for obtaining *Croton Lechleri*, which from 1000 dragon's blood trees are obtained from 4000 liters of final product, it will serve as raw material for transformation into a corrosion inhibitor.



Figure 12. Traditional value chain of the dragon's blood. (Quiliano & et al, 2010)

4.2.2 Proposed value chain for the dragon's blood inhibitor

The block diagram proposed for dragon's blood (Figure 13) was made with data obtained in the laboratory by a group of researchers, where they gave us data that could be scaled such as the ratio of alkaloids: organic, percentages of liquid losses, or solid in the stages, solvent ratio.



Figure 13. Proposed value chain for the dragon's blood inhibitor

Process description

For the corrosion inhibition transformation process from dragon's blood, 1000 kg is proposed as a calculation basis. In # 1 stream, 1000 kg of raw material enters, after this it is sent to # 2 stream which is the sieving stage in order to eliminate solid waste, the product obtained is transferred to # 3 stream, to the alkalization stage, where 52.72 kg of 90% potassium hydroxide (KOH) is added, this stage is done with the objective of reducing the amount of acid in the solution, and with this, we increase the pH of the solution, which wants say we increase alkalization.

Then this stream enters the critical stage of the proposed process, the extraction stage, where it is carried out by the solvent extraction process, where the solvent is added, 2,618 kg of chloroform, from this stage 3 streams are obtained output, # 9 stream of the extract, which continues to preserve the compounds of medicinal interest, # 8 stream of the solid residue, and # 4 stream of the refining, in which 254 kg of alkaloids are obtained, which is our product of interest due to its high degree of inhibition. Due to this, # 4 stream is sent to the chloroform recovery stage, in order to reuse the solvent and minimize capital and operating costs associated with the extraction system, and this is achieved by means of heat obtains two output streams, # 7 stream that enters the extraction stage as recirculation and # 5 stream, where we obtain our crude product with less chloroform.

Base	kg	1000.000												
	Feed	Sieving	Alkalization	Refined	Crude product	Inhibitor	Chloroform recovery	Solid waste	Extract	KOH	Chloroform	Make up	Aditive	Sieved residue
Sangre de drago (Kg)	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11		#12	#13
Alkaloid compounds (kg)	268.571	261.857	261.857	254.863	248.491	248.491	6.372	5.237	1.757	-	-	-	-	6.714
Organic compounds (kg)	671.429	654.643	654.643	641.528	625.490	625.490	16.038	13.093	0.022	-	-	-	-	16.786
Water (Kg)	50.000	48.750	48.750	47.773	46.579	46.579	1.194	0.975	0.002	-	-	-	-	1.250
Solid (tree bark)(Kg)	10.000	1.180	1.180	1.156	1.127	1.127	0.029	0.024	0.000	-	-	-	-	8.820
KOH(Kg)	-	-	52.714	51.658	50.367	50.367	1.291	1.054	0.002	52.714	-	-	-	-
Chloroform (Kg)	-	-		2565.696	51.314	51.314	2514.382	52.363	0.088	-	2618.147	78.840	-	-
Aditive (Kg)	-	-				0.512							0.512	-
Total (KG)	1000.000	966.430	1019.144	3562.675	1023.368	1023.880	2539.307	72.746	1.870	52.714	2618.147	78.840	0.512	33.570
Alkaloid (%)	26.857	27.095	25.694	7.154	24.282	24.270	0.251	7.199	93.945	-	-	-	-	20.001
Water (%)	5.000	5.044	4.783	1.341	4.552	4.549	0.047	1.340	0.087	-	-	-	-	3.724

Table 7. Mass Balance of Dragon's Blood Based Corrosion Inhibitor

Finally, the crude product that we obtain in # 5 stream, passes to the stabilization stage, where a # 12 stream enters, with 0.512 kg of paraben, this in order to prevent the proliferation of fungi, bacteria, and yeasts, elements that could cause the deterioration of our final product, after this, we obtain # 6 stream, which is our final product, 1,023 kg of corrosion inhibitor, which gives a 1: 1 ratio with respect to the amount of raw material, This inhibitor is stored in steel barrels, ready for marketing. In Table 7, it can be seen that in # 6 stream, the corrosion inhibitor is obtained with a proportion of 24.28% alkaloids and 4.5% water.

4.3 Banana

The production of the banana (*Musa acuminata*) species in Ecuador is the productive engine of the economy since it is one of the most exported agricultural products. In Ecuador, the most banana-producing provinces are: El Oro, Guayas, and Los Ríos (Unda,2020). In Figure 14, it shows the areas of hectares planted and harvested with bananas in Ecuador, where it is observed that in the province of Los Ríos most of the Banana is obtained, and if the project is carried out, this will be the location of the inhibitor plant, in order to obtain the raw material more easily.

Figure 14. Banana production in Ecuador (Unda, 2020).

4.3.1 Obtaining the banana

In Figure 15, we can observe the traditional chain of banana production in Ecuador, where after being sent for sale, they generate solid waste, in which there is interest due to the phenolic content it contains, so it could be used to give an economic valuation. (Unda, 2020).

Figure 15. Traditional value chain of the banana. (Unda, 2020).

4.3.2 Proposed value chain for the banana inhibitor

As in the previous cases, data from the laboratory were also used, in order to make the block diagram (Figure 16) and be able to scale the processes, mass relationships, efficiencies, residue ratio, solvent ratio, among others, were used.

Figure 16. Proposed value chain for the banana inhibitor

Process description

For the proposed block diagram of the transformation of the banana peel into a corrosion inhibitor, several stages are proposed and with the help of data obtained from the laboratory by the members of the research group, it was possible to arrive at an estimate of the production of the inhibitor. First, in # 1 stream, 1000 kg of raw material enter, after this, it is taken to the drying stage, in order to reduce the volume of water, so that from this stage 2 streams leave, the # 11 stream, which deposits the liquid residue, and # 2 stream that follows in our main process, and this enters the grinding stage, to reduce the average volume of solid particles in the sample, and two streams also exit per stage, # 12 stream, where there are small losses, and # 3 stream, where we obtain our powdered product.

Now, # 3 stream is sent to the essential part of the process, which is the extraction stage, which requires the use of a solvent, for which a # 8 stream with a hydroalcoholic mixture enters, and in this stage the stream 2, # 10 stream which is a solid residue, and # 4 stream where we obtain our extract, which contains our product of interest, due to its

inhibitory power, because this extract has part of the chloroform present, # 4 stream is carried to the alcohol recovery stage, where # 7 stream is obtained which is entered again into the extraction stage, in order to reduce costs, also from this stage # 5 stream is obtained that carries our product of interest and which is taken to the stabilization stage, where 0.046 kg of paraben is entered through # 9 stream, in order to prevent the proliferation of fungi and bacteria, and from here # 6 stream is obtained, where 92 are found, 65 kg of inhibitor corrosion, in which it is ready for sale, as can be seen in Table 8, that the final product of # 6 stream, has a ratio of 0.663% phenolics and 82.714% water, making it a water-based corrosion inhibitor.

Base	kg	1000.000											
	Feed	Drying	Grinding	Extract	Crude product	Inhibitor	Alcohol recovery	Make up	Hydroalcoholic	Aditive	Solid waste	Drying Waste	Grinding losses
Banana peel (Kg)	#1	#2	#3	#4	#5	#6	#7		#8	#9	#10	#11	#12
Phenolic compounds (kg)	34.615	32.971	32.312	0.646	0.614	0.614	0.032		-	-	31.665	1.644	0.659
Organic compounds (kg)	115.385	109.904	107.706	2.154	2.046	2.046	0.108		-	-	105.552	5.481	2.198
Water (Kg)	850.000	8.500	8.330	766.399	76.640	76.640	689.759	108.647	798.406	-	40.337	841.500	0.170
Etanol (kg)	-	-	-	890.397	13.356	13.356	877.041	60.219	937.260	-	46.863		-
Paraben (Kg)	-	-	-	-	-	0.046	-			0.046	-		-
Total (KG)	1000.000	151.375	148.348	1659.596	92.656	92.703	1566.940	168.866	1735.666	0.046	224.417	848.625	3.028
Phenolic (%)	3.462	21.781	21.781	0.039	0.663	0.662	0.002		-	-	14.110	0.194	21.781
Water (%)	85.000	5.615	5.615	46.180	82.714	82.673	44.020		46.000	-	17.974	99.160	5.615

Table 8. Banana peel corrosion inhibitor mass balance

For the economic analysis, it was only carried out for the natural product that has the best characteristics to be elaborated as a corrosion inhibitor, because dragon's blood has a 1: 1 ratio of the final product with respect to the input raw material such as It was seen in the mass balance of Table 7, it can also be said that the group of researchers from the CEDIA group have achieved a better result from the point of view of inhibition efficiency with a chloroform extract of dragon's blood (<70 ppm) reaching more or less 50%, and with the extracts obtained with the other vegetables, a maximum of 35% was reached (see Table 9).

	Ecorr (V)	IE%
0.5 M HCl (White)	-0.183	0
0.5 M HCl + 500 ppm Croton lecheri (lyophilized)	-0.202	28.94
0.5 M HC1 + 500 ppm Lupinis mutabilis	-0.19	34.36
0.5 M HC1 + 500 pp, Musa acuminata	-0.183	27.02
0.5 M HCl + <70 ppm Croton lecheri (chloroform extract)	-0.211	50.49

Table 9. Inhibiting Power of Dragon's Blood

4.4 Economic analysis

For the viability of the project, a load of 1000 kg of dragon blood extract per month is considered as the first point, with a production of 1023 kg of corrosion inhibitor, and it is considered that the plant works 8 hours a day from Monday to Friday, that gives 50 Kg / day. And to know the initial investment that is needed for industrialization, the costs of machinery, electricity, basic services, workers, among others, are considered.

4.4.1 COPEX

4.4.1.1 Equipment

The equipment proposed in the Figure 13, for the proposal of the dragon's blood as a corrosion inhibitor, where it will be used that equipment will guarantee a good production of the inhibitor. In Table 10 it shows the equipment that will be used with their respective prices, since they are prices from China, it is estimated that shipping to Ecuador would cost twice each equipment.

Equipment							
Description	Quantity (#)	Price (\$)	Total (\$)				
Filter	1	2,000	2,000				
Tank with agitator	2	2,500	5,000				
Extractor	1	15,000	15,000				
Total	4	19,500	22,000				
Ecuador cost	4	39,000	44,000				

Table 10. Equipment costs

4.4.1.2 Energy consumption costs

Because this equipment consumes a large amount of energy, it is considered an important expense for the implementation of the plant. Table 11 shows the total monthly and annual cost of the equipment.

Energy consumption							
Fauinment	Energy consumption	Monthly energy consumption (kw/ b)	Monthly	Annual cost (\$)			
Equipment			τυσι (φ)	Annual Cost (\$)			
Filter	1.1	264	26.14	313.64			
Tank with agitator	2.25	540	53.46	641.52			
Extractor	20	4800	475.2	5,702.4			
Total	23.35	5604	554.80	6,657.55			

Table 11. Energy consumption

4.4.1.3 Inputs and raw materials

By means of references, the prices of the inputs and the material to be used were found as seen in the proposed diagram in Figure 13. Table 12 shows the total cost of inputs and raw materials used in the process, and these costs are monthly what is spent per load.

Inputs and raw materials							
Description	Price per kg (\$)	Amount (kg)	Total (\$)				
KOH, potassium hydroxide	109	52	5,668				
Chloroform	10	2,000	2,0000				
Paraben	4	0.51	2.048				
Dragon's blood	18.18	1,000	18,180				
Cost total	141.18	3,052.51	43,850.048				

Table 12. Inputs and raw material

4.4.1.4 Plant maintenance

It is estimated that the maintenance cost is 20% of the equipment costs and that such maintenance is carried out every month, in order to prevent equipment failures and have better efficiency, and therefore improve the quality of the product. Table 13 shows annual maintenance costs.

Plant maintenance				
Description	Annual expenditure	Annual expenditure		
Maintenance	20	8,800		

4.4.1.5 Employee salary

In the plant it is required to have workers for each area, in order to control the process, so it is estimated that 5 employees are needed with a salary of 800 per person. Table 14 shows the total expenses for payments to workers.

Т	able 14. Employee salary
	Employee salary

Employee salary				
Description	Amount	Reference salary	Total	
Workers	5	800	4,000	

4.4.2 **OPEX**

4.4.2.1 Basic services

Table 15 shows the basic services that meet the needs of workers and equipment in the plant.

Basic services			
Service	Monthly cost (\$)		
Water	50		
Light	80		
Cellphone	40		
Internet	130		
Total (\$)	300		

Table 15. Basic services

4.4.2.2 Installation and commissioning of the plant

For the installation of the equipment and start-up, it is estimated that it will cost approximately 40% of the total equipment. Table 16 shows the total cost of equipment installation including equipment costs.

Installation and commissioning of the plant		
Installation and commissioning of the plant (%)	40	
Installation and commissioning of the plant (\$)	17,600	
Acquisition costs (\$)	44,000	
Total annual costs, acquisition and commissioning (\$)	61,600	

Table 16 Installation and commissioning of the plant

4.4.2.3 Lease of space

The location of the plant must be in the Amazonian part of Ecuador, because the raw material is nearby, which in this case is the dragon's blood. Table 17 shows an estimate of the cost of rent that is needed for industrialization.

Table 17. Lease of space

Lease of space		
Service	Monthly cost (\$)	
Lease	500	

4.4.2.4 Recovery and total investment

Table 18 shows the total expenses of the plant for each month, and the price of the inhibitor is analyzed in order to cover the monthly expenses of the plant, the expense of the installation and set-up of the plant is recovered the first year. Also, it is considered that the income of the plant is paid taxes, which according to the Internal Revenue Service (SRI) are 22%. (Rivadeneira, 2017).

Recovery and total investment		
COPEX		
Electricity (\$)	1,664.40	
Workers (\$)	4,000	
Supplies (\$)	43,850.05	
Maintenance (\$)	733.34	
OPEX		
Lease of space (\$)	500	
Installation and commissioning (\$)	5,133.34	
Basic service	300	
Total monthly investment (\$)	56,181.10	
Proposed price of inhibitor per kg (\$)	70.41	
Monthly incomes (\$)	72,027.06	
Taxes (%)	22	
Taxes (\$)	15,845.95	
Total monthly recovery	56,181.10	

Table 18. Recovery and total investment

4.4.2.5 Profits

Table 19 shows the profit of the plant from the second year of service, because in the first year, the costs for installation and commissioning of the plant equipment are recovered, this would be a fixed profit per year, which is assumes \$ 78,974.36 would be earned annually. This means that the project turns out to be viable.

Profits				
	Monthly (\$)	Annual (\$)		
Year 2 profit, annual fixed profit	6,581.20	78,974.36		

Table 19. Profits

CONCLUSIONS AND RECOMMENDATIONS

- The industrialization of the corrosion inhibitor from dragon's blood turns out to be viable and with fixed profits from the second year of service.
- The corrosion inhibitor is intended to be used in the hydrocarbon industries for chemical cleaning.
- Current industries are looking for sustainable and environmentally friendly projects, in order to reduce pollution, and the corrosion inhibitors proposed from dragon's blood would preserve these postulates, for which there should be a welcome in the market.
- The plant would be located in the Ecuadorian Amazon and for every 1000 kg of raw material there would be a monthly production of 1023 kg of corrosion inhibitor.
- It is recommended that in jobs similar to this, more research is done on economic problems that the hydrocarbon industries have, in order to transform natural residues into necessary products for the industries.

REFERENCES

Aaker, D. A., & Day, G. (1998). Investigación de mercados. *México DF., México, MC Graw Hill, Interamericana de México SA, Tercera edición, Segunda edición en español.*

Abdel-Gaber, A. M., Abd-El-Nabey, B. A., & Saadawy, M. (2009). The role of acid anion on the inhibition of the acidic corrosion of steel by lupine extract. *Corrosion science*, *51*(5), 1038-1042.

Almeida Cuastumal, J. L. (2015). Evaluación del rendimiento de cuatro ecotipos de chocho (Lupinus mutabilis), en el Centro Experimental San Francisco, en Huaca– Carchi (Bachelor's thesis).

Astillo-Quiliano, A., & Domínguez-Torrejón, G. (2010). Evaluación de la producción de látex de sangre de grado (Croton lechleri) en función al diámetro y cuatro periodos de precipitación en poblaciones naturales de Ucayali, Perú. *Ecología Aplicada*, *9*(2), 61-69.

Benítez, L. P. T., Castellar, P. J. M., Percy, E. D. A., & Bravo, M. J. B. (2014). Uso de extractos de plantas como inhibidores de corrosión. *Informador técnico*, 78(2), 155-164.

Botanicus. (September 14, 2007). Botanicus Blog. Retrieved on August 31, 2021, from http://www.botanicus.org/NameSearch.aspx

Boulding, K. E. (1941). Economic analysis. Harper and brothers Publishers, London.

Cabrera, R. P. (2006). Protección contra la corrosión mediante el empleo de inhibidores. *Revista Peruana de Química e Ingeniería Química*, 9(1), 25-32.

Caicedo, C., & Peralta, E. (2001). *El cultivo de chocho Lupinus mutabilis Sweet: Fitonutrición,* Enfermedades y Plagas, en el Ecuador.

Chacón, V. L. G. (2016). Eficiencia de un inhibidor verde extraído de cáscara de manzana mediante el sistema soxhlet en la corrosión del acero 1018 en medio ácido.

Couper, J. R., Penney, W. R., Fair, J. R., & Walas, S. M. (2005). *Chemical process* equipment: selection and design. Gulf professional publishing.

Ellen Macarthur Foundation, 2020, Retrieved from: https://www.ellenmacarthurfoundation.org/circulareconomy/what-is-the-circulareconomy

Felipe, M. B. M. C., Silva, D. R., Martinez-Huitle, C. A., Medeiros, S. R. B., & Maciel, M. A. M. (2013). Effectiveness of Croton cajucara Benth on corrosion inhibition of carbon steel in saline medium. *Materials and Corrosion*, *64*(6), 530-534.

Fiallo Iturralde, J. I. (2017). *Importancia del sector agrícola en una economía dolarizada* (Bachelor's thesis, Quito).

Fombuena Borrás, V., Cardona Navarrete, S. C., & Domínguez Candela, I. (2021). Diagramas de flujo: aplicación de diagramas de bloques en Ingeniería Química.

Gunavathy, N., y Murugavel, S. C. 2013. "Studies on corrosion inhibition of Musa acuminata flower extract on mild steel in acid medium". Asian Journal of Chemistry 25 (5): 2483–90. <u>https://doi.org/10.14233/ajchem.2013.13415</u>.

Ibrahim, H. A. (2012). Fouling in heat exchangers. MATLAB-A fundamental tool for scientific computing and engineering applications, 3, 57-96.

Irshedat, M. K., Nawafleh, E. M., Bataineh, T. T., Muhaidat, R., Al-Qudah, M. A., & Alomary, A. A. (2013). Investigations of the inhibition of aluminum corrosion in 1 M NaOH solution by Lupinus varius l. Extract. *Portugaliae Electrochimica Acta*, *31*(1), 1-10

Jacobsen, S. E. (2002). Cultivo de granos andinos en Ecuador: Informe sobre los rubros quinua, chocho y amaranto. Editorial Abya Yala.

Jie, L., Lailing, H., & Duomin, L. (2009). Fouling and Cleaning of Heat Exchanger [J]. *Guangdong Chemical Industry*, *1*, 57-58.

Jones, K., 2003. Review of Sangre de Drago (Croton lechleri) - A South American Tree Sap in the Treatment of Diarrhea, Inflammation, Insect Bites, Viral Infections, and Wounds: Traditional Uses to Clinical Research. Journal of Alternative and Complementary Medicine, vol. 9, no. 6, pp. 877-896. ISSN 10755535. DOI 10.1089/107555303771952235.

KAVITHA, V, et al. 2014. "Evaluation of Daucus Carota Aerial Extract as Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Medium". International Journal of Research in Advent Technology 2 (7): 146–54. King, S. R., Martin, M. L., Fonseca, R., Fonseca, M. P., Diaz, C. G. L., & Valles, K.G. (2020) Sustainable Harvesting of Dragon's Blood (Croton lechleri) in Peru.Retrieved from: www.herbalgram.org

Machuca Rivadeneira, M. D. (2017). Análisis del impuesto a la renta y la cultura tributaria de los contribuyentes en el Ecuador.

Mathew, N. S., & Negi, P. S. (2017). Traditional uses, phytochemistry and pharmacology of wild banana (Musa acuminata Colla): A review. *Journal of ethnopharmacology*, *196*, 124-140.

Morales, E. L. Á., Córdova, S. A. L., Bravo, M. L. S., & Macías, B. L. C. (2020). Evaluación socioeconómica de la producción de plátano en la zona norte de la Provincia de los Ríos. *Journal of business and entrepreneurial studie*, *4*(2).

Morocho, F. R. A. (2018). La economía circular como factor de desarrollo sustentable del sector productivo. *INNOVA Research Journal*, *3*(12), 78-98.

Müller-Steinhagen, H. (Ed.). (2000). *Heat exchanger fouling: mitigation and cleaning techniques*. IChemE.

Otzisk, B. (2008). Chemical cleaning and degassing refinery equipment. *Petroleum technology quarterly*, *13*(1), 77.

Palou, R. M., Olivares-Xomelt, O., & Likhanova, N. V. (2014). Environmentally friendly corrosion inhibitors. *Developments in corrosion protection*, *19*(1), 431-432.

Pino, S., Aguilar, H., Apolo, A., & Sisalema, L. (2018). Contribution of the agricultural sector to the economy of Ecuador. Critical analysis of its evolution in the period of dollarization. Years 2000-2016. *Espacios*, *39*(32), 7.

Porter, M. (2004). Cadena de valor. México: Editorial CECSA.

Quelal Tapia, M. B. (2019). *Estudio de la comercialización del chocho desamargado* (*Lupinus mutabilis Sweet*) *en el Distrito Metropolitano de Quito* (Master's thesis, Universidad Andina Simón Bolívar, Sede Ecuador).

Raichev, R., Veleva, L., & Valdez, B. (2009). Corrosión de metales y degradación de materiales. *Editorial UABC*, 155-170.

Río Calonge, B. (2011). *Eliminación del Biofouling en intercambiadores de calorcondensadores que minimicen el impacto ambiental en el medio marino*. Universidad de Cantabria.

Rodriguez; L. Evaluación "in vitro" de la Actividad Antimicrobiana de los Alcaloides del Agua de Cocción del Proceso de Desamargado del Chocho (Lupinus mutabilis Sweet), Trabajo especial de Grado Previo a la Obtención del Título de Bioquímico Farmacéutico, Escuela Superior Politécnica del Chimborazo. Riobamba-Ecuador 2009.

Salazar-Jiménez, J. A. (2015). Introducción al fenómeno de corrosión: tipos, factores que influyen y control para la protección de materiales. *Revista Tecnología en Marcha*, 28(3), 127-136.

Sanchez, M. Aplicación de Técnica Electroquímicas en la Evaluación de Inhibidores de Corrosión usados en la Industria Petrolera, Universidad de los Andes, Tesis de Doctorado, 2004, Merida-Venezuela, http://bdigital.ula.ve/storage/pdftesis/postgrado/tde_arquivos/27/TDE-2008-1 114T17:05:27Z-64 /Publico/sanchezmiguelIparte.pdf

Sato, N. (2011). Basics of corrosion chemistry. *Green corrosion chemistry and engineering: opportunities and challenges*, 1-32.

Shreir, L. L. (Ed.). (2013). Corrosion: corrosion control. Newnes.

Unda, S. B. (2020). Relación de la cadena de valor y de servicios ecosistémicos del banano y plátano ecuatoriano. *Revista Metropolitana de Ciencias Aplicadas*, *3*(3), 174-182.

Vergara Estupiñán, O. C. (2018). Inhibidores de corrosión eficientes a temperaturas por encima del ambiente.

Vu, H. T., Scarlett, C. J., & Vuong, Q. V. (2018). Phenolic compounds within banana peel and their potential uses: A review. *Journal of Functional Foods*, *40*, 238-248.