|  |  |
| --- | --- |
| cetlogo ***CHEMICAL ENGINEERING TRANSACTIONS***  ***VOL. , 2023*** | A publication of  aidiclogo_grande |
| The Italian Association  of Chemical Engineering  Online at www.cetjournal.it |
| Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš  Copyright © 2023, AIDIC Servizi S.r.l. **ISBN** 978-88-95608-98-3; **ISSN** 2283-9216 | |

Life cycle analysis for the selection of entrainer for candelilla wax extraction

Andres Mares-Valenzuelaa, Nancy Medina-Herreraa, Carlos Escamilla-Alvaradob, Guillermo Martínez-Ávilaa, Romeo Rojas-Molinaa

aUANL, Facultad de Agronomía, Francisco I Madero s/n, Ex-Hacienda del Cañada, General Escobedo, N.L., 66050, Mexico.

bUANL, Facultad de Ciencias Químicas, Av. Universidad s/n, Cuidad Universitaria, San Nicolás de los Garza, N.L., 66455, Mexico

nancy.medinahr@uanl.edu.mx

Abstract

The present study analyzes the environmental implications of the use of citric acid and sulfuric acid for the extraction of wax from the candelilla plant using gate-to-gate LCA methodology and two methods, Eco-Indicator99 and ReCiPe. The extraction process uses sulfuric acid since last century with no improvements so far. Despite this, candelilla wax is highly valued in the market and used in several industries. Midpoints and endpoints indicators were selected due to operational implications, soil, freshwater, and human health damage are the principal topics. Calculations about emissions and resources were fixed from field and laboratory data for the inventory and computed with SimaPro software for both scenarios. Results show that, for most of the categories, citric acid has a higher impact because its production process has a greater environmental effect. Thus, there is a trade-off for using citric acid as a substitute for sulfuric acid.

* 1. Introduction

Candelilla wax comes from the plant *Euphorbia antisyphilitica,* it grows in the Chihuahua’s Desert region. The wax comes from the lipidic cover of the stems created by the plant as a defense mechanism against dehydration. Usage of candelilla wax has been recorded from pre-hispanic Mexico, it was extracted in clay containers and used to cover bowstrings to make them resistant to temperature changes, and for decorative purposes. Nevertheless, the production process and its commercialization started in the first decade of 1900 with the establishment of a protocol (Ochoa-Reyes et al. 2010). In that region, wax commercialization is a unique source of income for several families.

Candelilla wax is used in different industries for its physical and chemical properties in cosmetics formulation, and in chewing gum production for flavor conservation properties and plastic appearance (Rojas Molina et al., 2011). There are many other applications including lubricants, adhesives, crayons, etc. Télles-Pichardo et al (2013) and Saucedo-Pompa et al. (2009) investigated candelilla wax as an edible coat in fruits for its conservation and protection against some fungal invasion in papaya and avocado, their results proved an improvement in shelf life. Candelilla wax has been classified as safe for use in the alimentary industry by the U.S. Food and Drug Administration, European Food Safety Authority, and The Food and Agriculture Organization.

According to Hodge and Sineath (1956), the candelilla extraction process starts with the hand-picking of the plant. The plant is collected in bundles of around 30 kg that are transported to the processing site. Around 3.96L of sulfuric acid is added for each 45 kg of candelilla plant in a steel container named “paila” whose capacity is around 500L. In the “paila”, water is heated to boiling point using an exhausted plant from a previous batch. Then, sulfuric acid is added to the solution and the fresh plant is introduced to the process. Then, a Fisher esterification occurs due to the presence of sulfuric acid, and the wax is formed as greyish foam that floats on the surface. The foam is separated from the aqueous solution using a punctured shovel and then conveyed to a metal barrel. In the barrel, organic and aqueous phases separate for decantation. After this, the aqueous phase is drained at the bottom of the barrel retrofitted to the “paila” and the organic phase is transported to another barrel until the amount collected is enough for primary refining. The exhausted plant in the paila is transferred out and left to dry by the sun. After this another batch started within the paila. At the end of the day, after five or six batches the organic phase in the storage barrel is reheated to separate impurities by adding 1.8L of sulfuric acid and is left to cool down after night. Once the wax is solidified, the impurities are removed with a knife, and the remaining acidic water in the barrel is discarded to the ground (Ochoa-Reyes et al., 2010). Even though sulfuric acid has a good yield, it has negative environmental effects caused by its incorrect management and endangers people. Several accidents occur principally by human error within the process. Therefore, there are efforts to substitute the use of sulfuric acid.

There are some investigations to improve the process and reduce human error and risk. León-Zapata (2008) through lab essays demonstrated that citric acid was the most promising substitute among other organic acids due to wax’ yield and purity closest to sulfuric acid. This method was replicated for different laboratory characterization protocols of candelilla with promising results. Aranda-Ledesma (2022) evaluation was made with citric acid at 1% v/v with a 2.8% of performance per batch compared with León-Zapata (2008) with 4% at 1M. When a process is changed several factors should be examined to avoid negative effects.

Chomkhamsri et al. (2011) defined Life Cycle Thinking (LCT) and Life Cycle Assessment (LCA) as a science-based evaluation method whose goal is to give information to make better decisions for the environment. LCT is important when the evaluation is expected to conclude in changing one product to another in a process or an alternative process is proposed, to avoid environmental burden shifting, preventing the creation of new problems trying to solve another. Every LCA is unique considering no situation happens the same way, but this analysis generates valuable information about a certain product and a general panorama of all implications for the environment (Lee et al., 1995). If a change in the setup is made, new results may be reflected in the impact categories chosen, therefore a clear idea of the goals is needed, so the variables and the system limits looking for reliable results (Ekvall and Weidema, 2004).

There are different LCA methods, the selection depends on the known system information, and the impacts to be analyzed. Every method has measurements and focuses on different areas of study. Thus, results might be biased because of the parameters. Some authors recommend using more than one method to have a complete view of the process evaluated and have concrete conclusions. The most recognized methods are CML, Eco-Indicator, TRACI, ReCiPe, and IMPACT (Cavalett et al., 2013). Methods of LCA are based on using two different indicators: midpoints and endpoints. Midpoint effects are measurable on specific impact categories and have a direct impact on the environment. While endpoints are focalized on the damages caused by these indicators, fundamentally they are divided into three: Human Health, Ecosystem Quality and Resources, and are measured in generic units because of the combination of specific impact categories. Usually, midpoint characterization has lower uncertainty than endpoint characterization (Schenck and White, 2014).

Until the authors’ knowledge, there are no studies performed to evaluate the environmental impact of candelilla wax, so the indicators chosen were considered relevant based on the nature of the process and the principal affectations to land air and human health. Wax’ trade is essential in the communities, and efforts have been done in order to preserve the plant and be overexploited making the process sustainable. Following that path, the objective of the present study is to evaluate the environmental impact of both citric and sulfuric acid.

* 1. Methodology

The methodology proposed by Schenck and White (2014) was followed to perform the LCT. This methodology has four phases: goal and scope definition, inventory analysis, impact analysis, and interpretation. The data was computed with SimaPro software version 9.2.0.2 to analyze both scenarios sulfuric and citric acid. The methodology is based on ISO standards guaranteeing optimization points in different phases in the LCA of the process. LCA is part of different environmental management techniques developed as risk evaluations and environmental audits.

2.1. Goal and Scope Definition Phase

For the goal scope and definition phase, it was considered only the resources used in the production of the cerote (the product of the first step of wax refining). The secondary refining was not considered. The LCA was carried out as a gate-to-gate approach, since the candelilla plant grows in the desert no additional resources are used, the transportation distances change according to the availability of the plant and are the same in both scenarios, so it was not considered in the inventory. One of the major goals was the improvement of the extraction process of the candelilla wax from the fresh plant, substituting sulfuric acid.

The methods selected for this study are Eco-Indicator 99 and ReCiPe. The eco-indicator 99 is based on three damage categories previously mentioned, considering different midpoint indicators. The perspective selected was holistic, and this resulted in a balance of short- and long-term damage. The impact categories selected were Ecotoxicity, Acidification/eutrophication, Respirable inorganics, Carcinogens, and Climate change. It is important to notice that the categories that have not been selected for presentation still affect the values of the endpoint categories. For ReCiPe, the selected impact categories were Terrestrial Ecotoxicity, Freshwater Ecotoxicity, Human Carcinogenic Toxicity, Human Non-Carcinogenic Toxicity, Global Warming, Terrestrial Acidification, and Water Consumption.

2.2. Inventory Analysis Phase

The data for the process with citric acid inventory was taken from experiments carried out in San Jerónimo, a community in Zacatecas, México. For the process with sulfuric acid, the information was fixed from Hodge and Sineath (1956) and Ochoa-Reyes et al. (2010). For the citric acid, the information was obtained from Aranda-Ledesma et al. in 2022 and Bautista-Hernández et al. in 2021 in laboratory evaluations. Some calculations were needed in order to complete the inventory, such as the amount of exhausted plant used to boil water and heat the cerote in the refining. Candelilla’s physicochemical characteristics have never been assessed so all specific data like specific heat were made considering wood with 10% of humidity as candelilla, along with combustion emissions like CO, CO2, CH4, particulate matter, and organic carbon. Sulfuric acid fogs and its chemical compounds, SO3 and H2SO4, were also calculated considering the heat, the boiling point, and the volatile proportion of these compounds at the specific temperature. Once the inventory was completed, SimaPro is used to compute both methods, the functional unit selected was 1130 kg of candelilla processed in 5 batches of 226 kg which is what is usually processed on a labor day.

* 1. Results and Discussion

The results are presented by the type of method selected and impact categories according to the process, emissions, and possible affectations.

* + 1. ReCiPe Results

The results in Figure 1 show that citric acid has a greater impact on terrestrial ecotoxicity, human non-carcinogenic toxicity, and human carcinogenic toxicity than sulfuric acid. Regarding terrestrial ecotoxicity, the process that contributes most to the process according to the inventory in SimaPro is citric acid production generating 201,157.46 kg of 1,4-DCB than sulfuric acid, toxicity caused by 1,4-DCB has been evaluated in rats and mice, and showed affectation in kidney and liver at 3,000 mg/m3 (Meek et al., 1994). The same study presented exposition to this compound increased the incidence of neuropathy. For Global warming, citric acid produces 258,228.323 more kg of CO2 eq resulting in a greater contribution to Global warming and its proven effects like heat-trapping and contribution to respiratory disease from smog and bad air quality. The only category where sulfuric acid impact is higher than citric acid is in freshwater ecotoxicity, for 16,337.59 kg 1,4-DCB, due to superficial and underground water contamination from contaminated soil. Even when sulfuric acid has a lower affinity to the soil, citric acid usage generates the double of SO2 eq causing greater terrestrial acidification. T(see b) in Figure 1).

|  |  |
| --- | --- |
|  |  |

Figure 1. Results of ReCiPe a) Midpoint indicators in kg 1,4-DCB; b) other indicators.

* + 1. Eco-Indicator99

The midpoint indicators show that, for Ecotoxicity (Figure 2-part a)), the sulfuric acid scenario has a higher impact with values around 5,000 PDF\*m2yr, affecting every cycle on earth, since the disappearance of species causes ecological imbalances by altering trophic and ecological chains. In other categories, such as climate change, carcinogens, and respirable inorganics, the impacts of citric acid are higher, this is due to the production of citric acid contributing the most to these values for the carcinogens for all the residues produced in the process. Results of the last three categories are presented in DALY (Disability-adjusted life years), this measure shows the impact of health conditions to make quantifiable comparisons. The inventory from Climate Change (Figure 2 part b)) indicator shows that the principal contribution to this indicator comes from GHG released to the atmosphere as, CO2, N2O, and CH4. These gases are measured in DALY (Disability-Adjusted Life-Years). The carcinogens category was affected by arsenic in water, cadmium that affects the ground, and particulates < 2.5 in air, this specific indicator was affected for emissions to soil, water, and air, all higher values correspond to citric acid (Table 1). All units were DALY, as a direct reference of the effect in the Human Health endpoint indicator.

|  |  |
| --- | --- |
|  |  |

Figure 2. Eco-indicator 99 results a) ecotoxicity indicator b) other indicators

Table 1: Midpoint indicators inventory results for Eco-Indicator 99.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Indicator | Substance | Compartment | Unit | Citric acid scenario | Sulfuric acid scenario |
| Climate Change | Carbon dioxide, fossil | Air | DALY | 0.0571 | 0.0045 |
| Dinitrogen monoxide | Air | DALY | 0.0037 | 5.05x10-5 |
| Methane, fossil | Air | DALY | 0.0031 | 0.0003 |
| Carcinogens | Arsenic | Water | DALY | 0.0265 | 0.0140 |
| Cadmium | Ground | DALY | 0.0178 | 0.0001 |
| Particulates < 2.5 µm | Air | DALY | 0.0015 | 0.0001 |

For all three endpoint indicators citric acid has a bigger negative impact, almost 4 times more than sulfuric acid due to its production process. Resources indicator (Figure 3 part a)) is affected by the use of natural gas, values in the citric acid scenario were 109,673.15 MJ surplus compared to 48,386.13 MJ surplus for the sulfuric acid scenario. The second contribution is crude oil, followed by coal and copper, all values are higher for citric acid and are proportional to the natural gas values (Table 2). At endpoint Human Health (Figure 3 part b) the biggest contribution is particulates < 2.5, nitrogen oxides, both in air and arsenic in water. Values proportion variates in the citric acid scenario versus the sulfuric acid scenario (Table 2). The common characteristic of these values is that they are higher in the citric acid scenario. The principal contaminating processes were the transportation and heating with natural gas according to the contribution process comparison. Ecosystem Quality shows more species could be endangered due to citric acid production, considering the fraction of potentially disappeared species (PDF) (Figure 3 part c).

|  |  |
| --- | --- |
|  |  |
|  | |

Figure 3. Endpoint indicators for Eco-Indicator99 a) Resources, b) Human Health, and c) Ecosystem Quality.

Table 2: Endpoint inventory weighted for Eco-Indicator 99.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Substance | Compartment | Unit | Citric acid scenario | Sulfuric acid scenario |
| Gas, natural/m3 |  | MJ surplus | 109673.15 | 48386.13 |
| Oil, crude |  | MJ surplus | 79256.56 | 14708.33 |
| Coal, hard |  | MJ surplus | 11334.50 | 526.44 |
| Particulates, < 2.5 um | Air | kPt | 3.77 | 0.34 |
| Nitrogen oxides | Air | kPt | 2.18 | 0.29 |
| Arsenic | Water | kPt | 2.08 | 0.86 |

* 1. Conclusion

An LCA for candelilla wax’ extraction using two acids was carried out. From the results, it can be concluded that citric acid has a greater impact than sulfuric acid, due to its production mainly for processes like the transportation of raw materials and posterior transportation to the market. It is known that citric acid is produced principally from *Aspergillus niger* for the industrialized global market, which process has major challenges. One of the most studied is recovery from different technologies, trying to make more affordable and increase the recovery percentage. The most used technology is the calcium precipitation even when micelles removal is a problem that implicates an additional step to the process, increasing its residues and complexity. On the other hand, the production of sulfuric acid is standardized and well-established, all emissions have been regulated and modifications can be done easily due to the nature of the chemical process.

Workers’ risks of using sulfuric acid are higher when the infrastructure and working conditions are not ideal, even when using citric acid sets up a safer operation environment, its use has higher environmental effects yet when future emissions were excluded. In-site effects are presumable lower considering sulfuric acid’s high toxicity, the LCA is performed trying to avoid environmental burden shifting, in this case, higher emissions due to its production. Some actions need to be made to reduce environmental impact and protect candelilleros health. Making the citric acid process more efficient is one of the major opportunities for improvement, reducing emissions.

References

Agencia para Sustancias Tóxicas el Registro de Enfermedades. (2006). *ATSDR - Resumen de Salud Pública: Diclorobencenos*. www.atsdr.cdc.gov/es

Aranda-Ledesma, N. E., Bautista-Hernández, I., Rojas, R., Aguilar-Zárate, P., Medina-Herrera, N. del P., Castro-López, C., & Guadalupe Martínez-Ávila, G. C. (2022a). Candelilla wax: Prospective suitable applications within the food field. LWT, 159. https://doi.org/10.1016/J.LWT.2022.113170

Aranda-Ledesma, N. E., Bautista-Hernández, I., Rojas, R., Aguilar-Zárate, P., Medina-Herrera, N. del P., Castro-López, C., & Guadalupe Martínez-Ávila, G. C. (2022b). Candelilla wax: Prospective suitable applications within the food field. LWT, 159, 113170. https://doi.org/10.1016/J.LWT.2022.113170

Bautista-Hernández, I., Aranda-Ledesma, N. E., Rojas, R., Tafolla-Arellano, J. C., & Martínez-Ávila, G. C. G. (2021). Antioxidant activity of polyphenolic compounds obtained from Euphorbia antisyphilitica by-products. Heliyon, 7(4), e06734. https://doi.org/10.1016/J.HELIYON.2021.E06734

Cavalett, O., Chagas, M. F., Seabra, J. E. A., & Bonomi, A. (2013). Comparative LCA of ethanol versus gasoline in Brazil using different LCIA methods. International Journal of Life Cycle Assessment, 18(3), 647–658. https://doi.org/10.1007/s11367-012-0465-0

Chomkhamsri, K., Wolf, M.-A., & Pant, R. (2011). International Reference Life Cycle Data System (ILCD) Handbook: Review Schemes for Life Cycle Assessment. In Towards Life Cycle Sustainability Management (pp. 107–117). Springer Netherlands. https://doi.org/10.1007/978-94-007-1899-9\_11

Ekvall, T., & Weidema, B. P. (2004). System boundaries and input data in consequential life cycle inventory analysis. International Journal of Life Cycle Assessment, 9(3), 161–171. https://doi.org/10.1007/BF02994190

Hodge, W. H., & Sineath, H. H. (1956). The Mexican candelilla plant and its wax. Economic Botany, 10(2), 134–154. https://doi.org/10.1007/BF02985323

Lee, J. J., O’Callaghan, P., & Allen, D. (1995). Critical review of life cycle analysis and assessment techniques and their application to commercial activities. Resources, Conservation and Recycling, 13(1), 37–56. https://doi.org/10.1016/0921-3449(94)00016-X

León-Zapata, D., Fármaco Biólogo Página, Q., & Ángel De León Zapata, M. (2008). Mejoras tecnológicas al proceso de extracción de cera de candelilla.

Meek, M. E., Giddings, M., & Gomes, R. (1994). 1,4-Dichlorobenzene: Evaluation of Risks to Health from Environmental Exposure in Canada. Journal of Environmental Science and Health, Part C, 12(2), 277–285. https://doi.org/10.1080/10590509409373446

Ny, H., MacDonald, J. P., Broman, G., Yamamoto, R., & Robèrt, K. H. (2006). Sustainability constraints as system boundaries: An approach to making life-cycle management strategic. In Journal of Industrial Ecology (Vol. 10, Issues 1–2, pp. 61–77). https://doi.org/10.1162/108819806775545349

Ochoa-Reyes, E., Saucedo-Pompa, S., De la Garza, D., Rodríguez, R., Aguilar-González, C. (2010). Extracción tradicional de cera de candelilla Euphorbia antysiphilitica. Revista Acta Química de La Universidad Autónoma de Coahuila, 2(3). http://www.postgradoeinvestigacion.uadec.mx/AQM

Pizzol, M., Christensen, P., Schmidt, J., & Thomsen, M. (2011). Impacts of “metals” on human health: A comparison between nine different methodologies for Life Cycle Impact Assessment (LCIA). Journal of Cleaner Production, 19(6–7), 646–656. https://doi.org/10.1016/j.jclepro.2010.05.007

Renou, S., Thomas, J. S., Aoustin, E., & Pons, M. N. (2008). Influence of impact assessment methods in wastewater treatment LCA. Journal of Cleaner Production, 16(10), 1098–1105. https://doi.org/10.1016/j.jclepro.2007.06.003

Rojas Molina, R., Saucedo Pompa, S., De León Zapata, M. A., Jasso Cantú, D., & Aguilar, N. (2011). Pasado, presente y futuro de la candelilla. Revista Mexicana de Ciencias Forestales, 2(6), 7–18. https://doi.org/10.29298/RMCF.V2I6.571

Saucedo-Pompa, S., Rojas-Molina, R., Aguilera-Carbó, A. F., Saenz-Galindo, A., Garza, H. de La, Jasso-Cantú, D., & Aguilar, C. N. (2009). Edible film based on candelilla wax to improve the shelf life and quality of avocado. Food Research International, 42(4), 511–515. https://doi.org/10.1016/J.FOODRES.2009.02.017

Schenck, R., & White, P. (2014). *Environmental Life Cycle Assessment: measuring the environmental performance of products* (14th ed.). American Center for Life Cycle Assessment.

SEMARNAT-CONANP. (2015). Programa de Manejo Area de Proteccion de Flora y Fauna OCAMPO. *Secretaría de Medio Ambiente y Recursos Naturales; Comisión Nacional de Áreas Naturales Protegida*, *1*, 164.

Télles-Pichardo, R., Cruz-Aldaco, K., Ochoa-Reyes, E., Aguilar, C. N., & Rojas, R. (2013). *Edible Coatings of Wax and Polyphenols from Candelilla: An Alternative of Conservation of Papaya (Carica papaya L.)*. *5*(10).