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Techno-Economic Evaluation of the Production of Protein Hydrolysed from Quinoa (*Chenopodium quinoa* Willd.) Using Supercritical Fluids and Conventional Solvent Extraction †

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Abstract: The production of quinoa protein hydrolysate (QPH) using two technologies to extract the oil and separate the phenolic compounds (PC) prior to enzymatic hydrolysis were evaluated: (1) Supercritical fluid extraction (SFE), and (2) Conventional solvent extraction (CSE). The economic evaluation and sensitivity study was performed using SuperPro Designer® 9.0 software, quinoa grain batches of 1.5 kg (laboratory) and 2500 kg (industrial scale) were considered. The results revealed that SFE allows higher yields and separation of PC, however, Both processes are economically promising, especially when the QPH and by-products are produced in large scale and sold at the current market price.

Keywords: quinoa protein hydrolysate; bioactive peptides; supercritical fluids extraction; economic evaluation

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1. Introduction

Peru is the world's leading producer and exporter of quinoa (*Chenopodium quinoa* Willd.), however, around 91 % in FOB value exported is in the form of grain, 3.6% in flakes and 2.2% in flour [1]. The functional food market is constantly growing at a global level, which projected to reach US$ 280 billion by 2025 with an annual growth rate of around 8% [2], this reaffirms the importance of focusing efforts on the industrialization of functional foods and nutraceuticals from Peruvian biodiversity. Peptides have gained interest worldwide, due to their antioxidant capacity, which can be used as antioxidants in food, and also to reduce the risk of chronic diseases related to oxidative stress, additionally [3], recent research indicates that the peptides are important for the body's immune system against viruses [4].

However, there is a lack of information on the operating costs of production on an industrial scale of QPH [5]. The aim of this study was to compare the oil extraction yield, remaining phenolic compounds and quinoa protein hydrolysed (QPH) yield. Furthermore, an economic evaluation and sensitivity study was performed using SuperPro Designer® 9.0 software, quinoa grain batches of 1.5 kg (laboratory) and 2500 kg (industrial scale) were considered.

2. Materials and Methods

2.1. Experimental Process

The input parameters and process conditions were obtained from previous works [6], were used as input data for the model. The production of QPH, begins with the first stage, which is the extraction of saponins of the grains, saponins yield for each process was 0.31 g saponin/100 g (db), the second stage consists of the extraction of oil and phenolic compounds of the quinoa flour, which the bulk density was 450 kg/m^3, for CSE the parameters Solid/Solvent (petroleum ether) ratio was 1:3.33 for 19 h at 55 °C, the oil yield was 4.58 g fat/100 g (db); for SFE the operating parameters used were $P = 23$ MPa, $T_{reactor} = 55$ °C, and ethanol 7–8 g of quinoa/100 mL, CO_2 mass flow = 35 g/min and extraction time for 4 h, the oil yield was 6.30 g fat/100 g (db). The third step consisted in the extraction of the protein, proteins were precipitated at acid pH for 2 h at 50 °C, for SFE the protein yield was 11.94 g protein/100 g (db) and 11.74 g protein/100 g (db) for CSE, then the for step consist in enzymatic hydrolysis, using endopeptidase COROLASE 7089, the enzyme concentration was 4.2 UHb/g protein for 2 h, and QPH yield for SFE was 197.12 g hydrolyzed/100 g and 160.52 g hydrolyzed/100 g for CSE. The remaining phenolic compounds in QPH were evaluated by the determination of rutin equivalent, expressed as μg rutin/mL, achieving a higher purification in the process with SCF (16.15 ± 2.05 μg rutin/mL), compared to CSE (113.22 μg rutin/mL ± 8.13).

2.2. Scale-Up and Economic Evaluation of QPH Production

Is possible to scale the cost of equipment with the required capacity with Equation (1), in which C_1 represents the cost of equipment with capacity Q_1, in the same way C_2 is the cost of equipment with capacity Q_2 and n is the cost coefficient, the latter was obtained from literature and varies according to the equipment used [7,8]. According to the above, the Fixed capital investment (FCI) was calculated for both plants at a production scale of 2500 kg/batch as shown in Table 1.

$$C1 = C2\left(\frac{Q1}{Q2}\right)^{n}, \tag{1}$$

The cost of manufacturing (COM) can be determined as the sum of the three main components: direct costs, fixed costs, and general expenses. COM was estimated according to the methodology proposed by Turton et al. [8] by using Equation (2). According to Equation (2), the three main components are estimated in terms of five operational major costs: Fixed capital investment (FCI), Cost of raw material (CRM), Cost of labor (COL), Cost of utilities (CUT) and Cost of waste treatment (CWT), the economic parameters to determine the COM is shown in Table 1.

$$\mathrm{COM} = 0.304 \times \mathrm{FCI} + 2.73 \times \mathrm{COL} + 1.23 \times (\mathrm{CUT} + \mathrm{CWT} + \mathrm{CRM}) \tag{2}$$

The sensitivity study consisted of 16 scenarios, both for the industrial and laboratory scale, considering the sale of by-products such as saponins and oil, as shown in Table 2. Additionally, a regression was carried out to evaluate the influence of two input variables (productivity and hydrolysate yield) on two economic indicators: Cost of Manufacturing (CM) and Net Present Value (NPV). Finally, the statistical study consisted of evaluating the significance of COM and NPV at both industrial and laboratory scale, considering scenario 1–4 as group 1, scenario 5–8 as group 2, scenario 9–12 as group 3 and 13–16 as group 4. The COM was evaluated by one-way ANOVA followed by Tukey's post hoc test ($p < 0.05$) and the NPV was evaluated by nonparametric Kruskall-Wallis analysis for independent samples. ($p < 0.05$), analyzed using SPSS for Windows version 24.0 (SPSS, Inc., Chicago, IL, USA).

Table 1. Input economic parameters used for COM simulation.

Type of Cost	Laboratory Scale (1.5kg/batch)	Industrial Scale (2500 kg/batch)
Fixed Capital Investment (FCI)		
Conventional extraction	\$94,562.61	\$490,165.00
Supercritical extraction	\$249,698.88	\$10,268,219.25
Depreciation rate	10%/year	10%/year
Annual maintenance rate	6%/year	6%/year
Cost of operational labor (COL)		
Wage (\$/hour)	\$2.34	\$2.34
Number of workers per shift	2	6
Cost of Raw Material (CRM)		
Grains of quinoa	1567 \$/ton	1567 \$/ton
Industrial CO_2	0.033 \$/kg	0.033 \$/kg
Absolute ethanol	0.53 \$/kg	0.53 \$/kg
Petroleum ether	859 \$/t	859 \$/t
NaOH 1N	125 \$/t	125 \$/t
HCl 1N	41.37 \$/t	41.37 \$/t
NaOH 0.1N	120 \$/t	120 \$/t
Phosphate buffer	1160 \$/t	1160 \$/t
Endopeptidase COROLASE® 7089	27.73 \$	27.73 \$
Cost of utilities (COU)		
Electricity	0.1183 \$/kw	0.1183 \$/kw
Water	1.63 \$/t	1.63 \$/t
Cost of Waste Treatment (CWT)	100 \$/ton	100 \$/ton

Table 2. Cost of manufacture of QPH for both scales (laboratory=1.5 kg/batch and industrial 2500 kg/batch) evaluated.

Process-Plant-Scenario	Sale of Saponins	Sale of Oil	Productivity (ton/año)	COM (US$/kg)	CRM (%)	COL (%)	FCI (%)	CUT (%)	CWT (%)	GM (%)	ROI (%)	PBT (year)	VPN (at 7% interest) (US$)	Operating Cost (US$/year)	Revenues (US$/year)
SCF-L-1	Yes	Yes	162	2599.68	22.93	19.36	40.44	17.27	0.00	−1019.12	−33.86	NA	−3.470.000	421.000,00	37.000
SCF-L-2	Yes	No	162	2641.68	22.93	19.36	40.44	17.27	0.00	−1190.85	−34.40	NA	−3.512.000	421.000,00	32.000
SCF-L-3	No	Yes	162	2618.79	22.93	19.36	40.44	17.27	0.00	−1025.88	−33.88	NA	−3.472.000	421.000,00	37.000
SCF-L-4	No	No	162	2660.88	22.93	19.36	40.44	17.27	0.00	−1199.84	−34.43	NA	−3.514.000	421.000,00	32.000
SCE-L-5	Yes	Yes	35	4367.18	7.13	51.23	38.84	2.61	0.19	−1751.31	−36.63	NA	−1.305.000	151.000,00	7.000
SCE-L-6	Yes	No	35	4409.26	7.13	51.23	38.84	2.61	0.19	−2065.05	−36.99	NA	−1.315.000	151.000,00	6.000
SCE-L-7	No	Yes	35	4386.29	7.13	51.23	38.84	2.61	0.19	−1764.85	−36.64	NA	−1.305.000		7.000
SCE-L-8	No	No	35	4428.38	7.13	51.23	38.84	2.61	0.19	2089.35	−37.01	NA	−1.315.000	151.00	6.000
SCF-I-9	Yes	Yes	269,998	28.90	67.17	1.19	28.92	2.72	0.00	67.31	85.96	1.16	205.006.000	20.504.000	62.719.000
SCF-I-10	Yes	No	269,998	70.98	67.17	1.19	28.92	2.72	0.00	62.29	70.51	1.42	162.784.000	20.504.000	54.376.000
SCF-I-11	No	Yes	269,998	48.01	67.17	1.19	28.92	2.72	0.00	67.11	85.26	1.17	203.102.000	20.504.000	62.343.000
SCF-I-12	No	No	269,998	90.10	67.17	1.19	28.92	2.72	0.00	62.03	69.82	1.43	160.880.000	20.504.000	53.999.000
SCE-I-13	Yes	Yes	57,734	57.06	55.54	19.12	3.88	6.65	14.80	42.4	155.83	0.64	28.159.000	7.845.000	13.620.000
SCE-I-14	Yes	No	57,734	92.79	55.54	19.12	3.88	6.65	14.80	32.64	104.53	0.96	18.171.000	7.845.000	11.646.000
SCE-I-15	No	Yes	57,734	73.55	55.54	19.12	3.88	6.65	14.80	41.98	153.26	0.65	27.658.000	7.845.000	13.521.000
SCE-I-16	No	No	57,734	109.29	55.54	19.12	3.88	6.65	14.80	32.06	101.96	0.98	17.671.000	7.845.000	11.547.000

L: Laboratory; I = Industrial; SCF: Supercritical fluid; SCE: Solvent conventional extraction; COM: Cost of manufacturing; CRM: Cost of raw material; FCI: Fixed cost of investment; CUT: Cost of utilities; CWT: Cost of Waste Treatment, GM: Gross margin; ROI: Return of investment; PBT = Payback time; VPN = Value present net.

3. Results and Discussion

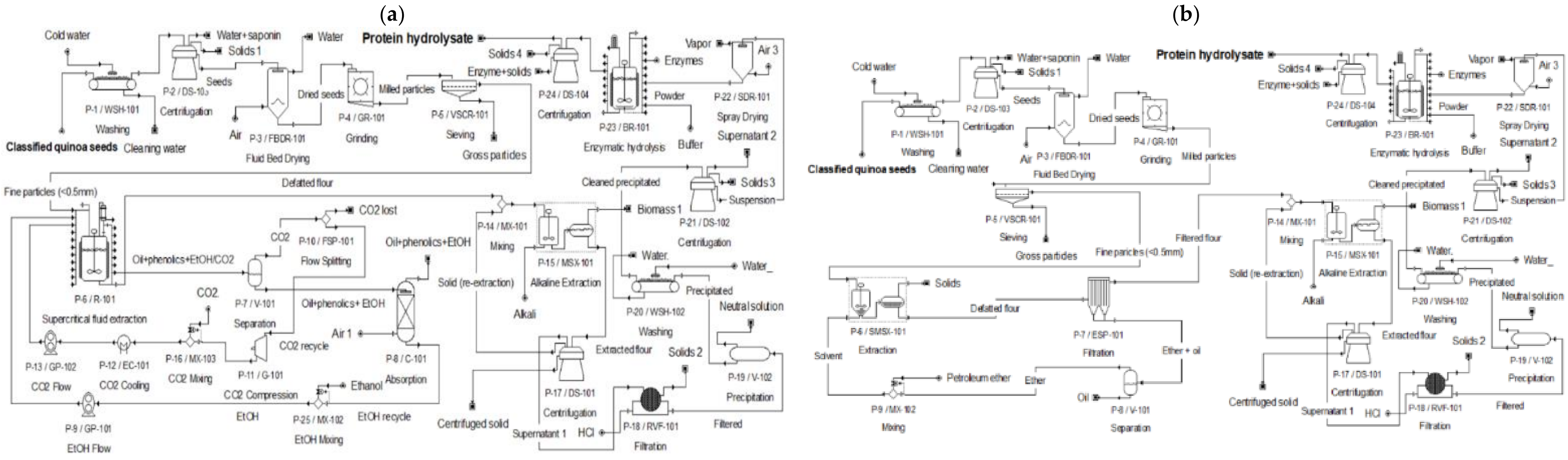
3.1. Scale-Up Process

For the scale-up process, it was assumed that the yield and QPH composition obtained at the laboratory scale would be similar to the those obtained at the industrial scale under the same processing shown in Table 1. Moreover, the financing of the scale-up process was not considered in this study. To perform the simulations was considered process operation of three daily shifts for 330 days per year, corresponding to 7920 h per year. Laboratory scale of 1.5 kg/batch of quinoa grain and industrial of 1500 kg/batch quinoa grain were considered. The mass of quinoa grain to be processed at each stage was calculated based on the volume of the extraction vessel and the bulk density of the material of 450 kg/m^3, thus determining the volume of the vessel of the SFE unit, obtaining the value of 4000 L and 15,000 L for the CSE, in the defatted stage respectively, the flow diagrams obtained with the simulator for both processes are as follows at the Scheme 1.

3.2. Economic Evaluation of QPH Production

The oil extraction yield with SCF is 37% higher than CSE, this is in agreement with other similar studies that report percentages higher than 89% of oil recovered using SCF [9,10], additionally, also confirming the feasibility of using SFE to obtain defatted quinoa as a raw material in food applications, free of solvent residues, and with a technological quality superior to that obtained by extraction with organic solvents [11]. The remaining phenolic compounds in QPH, with SCF process allows a higher degree of purification of the quinoa flour, reducing it by 85.84%, which, to date, no similar work has been reported. The QPH yield with SCF was 22% higher than that obtained with CSE, this may be due to the higher protein yield content reported in the previous research [6], and authors also report similar values [12,13].

For both cases, the scale-up reduced the COM, the COM was lower in SFE compared to CSE, US$ 90.10/kg and US$ 109.29/kg, respectively and higher net present value (NPV), US$ 205,006,000 and US$ 28,159,000 compared to CSE. The CRM is the most important at industrial scale for both processes, however, when using SCF it is higher by 20% compared to CSE, despite having constant raw material costs for both processes, whith defatted quinoa flour by SCF it increases from 6.06 to 85.23 considering CO_2 and absolute ethanol as important components in such variation. The sensitivity study considered the sale of by-products such as saponins and oil, The market price for QPH considered was of US$ 200/kg. The best scenario is when the sale of both by-products is included, the COM is reduced to US$ 28.90/kg (SFE) and US$ 57.06/kg (SCE), and profitability also improves. In addition, the significance the COM and NPV was statistically evaluated, there are no significant differences ($p<0,05$) on an industrial scale, between the two processes evaluated.



Scheme 1. Simulation flowsheet designed with SuperPro Designer 9$^{®}$ for the QPH production process using (**a**) SFE (**b**) CS.

4. Conclusions

The type of pretreatment with SFE and CSE applied to quinoa flour prior to enzymatic hydrolysis influences on the oil yield, remaining phenolic compounds and hydrolysate yield. The significance analysis of the factors considered shows that there is no significant effect on the COM and NPV of the QPH production at industrial scale between each technology; however, the pretreatment with SFE allows obtaining a lower COM and higher NPV, the sensitivity study and the evaluated scenarios show an additional income generated by the sale of by-products such as saponins and oils.

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References

1. Available online: Desenvolvimiento-Comercio-Exterior-Agroexportador-2020.Pdf (accessed on).
2. Alongi, M.; Anese, M. Re-Thinking Functional Food Development through a Holistic Approach. *J. Funct. Foods* **2021**, *81*, 104466. https://doi.org/10.1016/j.jff.2021.104466.
3. Wen, C.; Zhang, J.; Zhang, H.; Duan, Y.; Ma, H. Plant Protein-Derived Antioxidant Peptides: Isolation, Identification, Mechanism of Action and Application in Food Systems: A Review. *Trends Food Sci. Technol.* **2020**, *105*, 308–322. https://doi.org/10.1016/j.tifs.2020.09.019.
4. Galanakis, C.M.; Aldawoud, T.M.S.; Rizou, M.; Rowan, N.J.; Ibrahim, S.A. Food Ingredients and Active Compounds against the Coronavirus Disease (COVID-19) Pandemic: A Comprehensive Review. *Foods* **2020**, *9*, 1701. https://doi.org/10.3390/foods9111701.
5. Rueda, J.; Lobo, M.O.; Sammán, N. Changes in the Antioxidant Activity of Peptides Released during the Hydrolysis of Quinoa (Chenopodium Quinoa Willd) Protein Concentrate. *Proceedings* **2020**, *53*, 12. https://doi.org/10.3390/proceedings2020053012.
6. Olivera-Montenegro, L.; Best, I.; Gil-Saldarriaga, A. Effect of Pretreatment by Supercritical Fluids on Antioxidant Activity of Protein Hydrolyzate from Quinoa (*Chenopodium Quinoa* Willd.). *Food Sci. Nutr.* **2021**, *9*, 574–582. https://doi.org/10.1002/fsn3.2027.
7. Viganó, J.; Zabot, G.L.; Martínez, J. Supercritical Fluid and Pressurized Liquid Extractions of Phytonutrients from Passion Fruit By-Products: Economic Evaluation of Sequential Multi-Stage and Single-Stage Processes. *J. Supercrit. Fluids* **2017**, *122*, 88–98. https://doi.org/10.1016/j.supflu.2016.12.006.
8. *Analysis, Synthesis, and Design of Chemical Processes*, 5th ed.; Turton, R., Ed.; Prentice Hall International Series in the Physical and Chemical Engineering Sciences; Prentice Hall: Boston, MA, USA, 2018; ISBN 978-0-13-417740-3.
9. Wejnerowska, G.; Ciaciuch, A. Optimisation of Oil Extraction from Quinoa Seeds with Supercritical Carbon Dioxide with Co-Solvents. *Czech J. Food Sci.* **2018**, *36*, 81–87. https://doi.org/10.17221/122/2017-CJFS.
10. Benito-Román, O.; Rodríguez-Perrino, M.; Sanz, M.T.; Melgosa, R.; Beltrán, S. Supercritical Carbon Dioxide Extraction of Quinoa Oil: Study of the Influence of Process Parameters on the Extraction Yield and Oil Quality. *J. Supercrit. Fluids* **2018**, *139*, 62–71. https://doi.org/10.1016/j.supflu.2018.05.009.
11. Solaesa, Á.G.; Villanueva, M.; Beltrán, S.; Ronda, F. Characterization of Quinoa Defatted by Supercritical Carbon Dioxide. Starch Enzymatic Susceptibility and Structural, Pasting and Thermal Properties. *Food Bioprocess Technol.* **2019**, *12*, 1593–1602. https://doi.org/10.1007/s11947-019-02329-4.
12. Aluko, R.E.; Monu, E. Functional and Bioactive Properties of Quinoa Seed Protein Hydrolysates. *J. Food Sci.* **2003**, *68*, 1254–1258. https://doi.org/10.1111/j.1365-2621.2003.tb09635.x.

13. Abugoch, L.E.; Romero, N.; Tapia, C.A.; Silva, J.; Rivera, M. Study of Some Physicochemical and Functional Properties of Quinoa (*Chenopodium quinoa* Willd) Protein Isolates. *J. Agric. Food Chem.* **2008**, *56*, 4745–4750. https://doi.org/10.1021/jf703689u.