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Supercritical Extraction of Essential Oils from Dry Clove: a Technical and Economic Viability Study of a Simulated Industrial Plant †

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Abstract: The supercritical fluid extraction (SFE) is a green methodology that allows the solvent to be easily removed by simply reducing the system's pressure or temperature. An interesting compound to be separated through SFE is the clove's essential oil, which contains 75.5% (m/m) of eugenol and shows many food and biomedical applications, like antibacterial and antifungal activities, and use as antioxidant, anti-inflammatory, and for asthma and allergy relief. Herein, we simulated the operation of a SFE plant with two 400 L-extractors using CO_2, and performed the economic analysis based on real purchase costs from large scale exportation suppliers. Our results show that this is not only a process that results in minimum harmless emissions, consuming low amounts of utilities; but it is also an investment with excellent economic indicators, which is viable even if there are increases of 56% on clove's purchase costs. A fixed capital expenditure (CAPEX) of 347,000 USD is required, leading to a high net present value (NPV) of 8,600,000 USD after the project's lifetime (40 years), with a payback of 18.67 years and internal rate of return (IRR) of 7.29%.

Keywords: Clove essential oil; supercritical fluid extraction; industrial plant simulation; technical-economic analysis.

1. Introduction

A supercritical fluid is a compound under conditions of temperature (T) and pressure (P) beyond its critical point (T_c, P_c), so that the liquid and vapor phases are indistinguishable [1]. The supercritical fluid extraction technology (SFE) presents remarkable advantages over the traditional extraction techniques: it allows the solvent to be easily removed by simply reducing the system's pressure or temperature; results in enhanced energetic efficiency; may proceed with minimal or even no amount of organic co-solvents; and results in minimum quantities of residues. Nowadays, it is employed to separate compounds from coffee, tea, and hop: they are extracted from solid matrices, and the supercritical fluid is used to solubilize the desired materials while filling the vessel [2]. The solvent flows inside the extractor, swelling its fixed bed and facilitating the mass transfer. In a second step, the pressure is reduced, with a consequent decrease of both the density of the solvent and of the solubility of the extracted compound, allowing for their easy separation. Finally, the solid residue (usually biomass) is removed from the extractor. One of the most used solvents for SFE is CO_2: it presents low toxicity and reactivity; is no inflammable; presents moderate T_c, P_c, and purchase costs; and results in no solvent residues in the equipment [3]. In turns, a relevant compound which may be separated through SFE is the essential oil from clove (*Eugenia caryophyllata*), composed of eugenol (75.5% in mass), eugenyl acetate (11.0%), trans-caryophyllene (12.1%), and α-humulene (1.4%). It presents antibacterial and antifungal activities; and may be used as antioxidant; anti-inflammatory; and for asthma and allergy relief [3]. In Brazil, its annual production estimated in 6000 ton/year, with 5000 ton/year are destined to exportation. However, there is still a need for technical and economic feasibility studies covering large-scale extraction plants (400 L-extractors) [4], so, we used the SuperPro Designer 10 (Intelligen) to simulate an industry working with two extractors. We also collected real purchase data from large-scale exporters of clove and its essential oil compounds; and from suppliers of pressurized CO_2 [5–10] and input these information into the simulator's database. Finally, we applied the Weighted Average Capital Cost (WACC) methodology to calculate the main investment indicators of the industrial SFE plant and to evaluate the viability of the process for different clove's purchase costs.

2. Simulation and Technical-Economic Model

We developed the simulation diagram that is shown on Figure 1. Two 400 L-extractors are charged with solid clove and then pressurized with CO_2. Two flash drums complete the system and allow the recovery of the oil compounds. We registered the following prices from large-scale exporters: 25.73 USD/kg (eugenol); 32.51 USD/kg (eugenyl acetate); 12.19 USD/kg (trans-caryophyllene); and 14.19 USD/kg (α-humulene) [6–9]. After that, we created a mixture ("clove oil") containing the abovementioned mass fractions [3]; and, finally, we created a second mixture ("solid clove"), comprised of "Biomass" (a solid from the database that represents the average information collected for different vegetable materials) and clove oil. Once the manufactures' guarantee an oil degree from 15 to 20% (m/m), the mean value of this range (17.5%) was took as the mass fraction of oil in this semi-solid mixture. The purchase cost, in turns, was defined as 0.64 USD/kg of dry clove [5]. The software does not provide an equipment model for SFE, so the extractor must be created from simpler equipment already present in it. For that, we created two extractors (E-101 and E-102) from batch stocking drums and added the following discrete unit operations: opening of the tank and charging with solid dry clove ("*Pull In*"); transferring of CO_2 from the previous streamlines ("*Transfer In*"); heating of the tank to the operation temperature ("*Heat*"); pressurization with the supercritical fluid ("*Pressurize*"); SFE ("*Extract*"); and discharging of: a light phase mainly composed of CO_2 and residual oil; a heavy phase enriched in oil; and the solid biomass that sedimented. The SFE cycle has duration of 210 min and must proceed at 150 bar and 40 °C [11]. Manufactures already provide the gas under this pressure and at 15 °C, eliminating the pressurization costs. For the minimum purchase of 100 cylinders (10L-cylinders, fabricated in accordance to ISO 9809-1:2019) the purchase cost is of 40 USD/cylinder [10]. Under 150 bar and 40 °C, the rate of mass of solvent per mass of solid feed (S/F ratio) in SFE must at least satisfy $S/F \geq 2$. For $S/F = 6.6$ (ideal ratio), the yield Y - defined as the ratio between the oil mass extracted and the maximum mass that could be extracted if infinitely high times and solvent amounts were given (i.e., extracted mass per total amount of oil in the dry clove) - is 90%. Moreover, under these conditions of P, T and S/F, the maximum fraction of CO_2 that may remain on the heavy phase at the exit of the extractor is of 2.2% of the total gas. This value was taken as the mass split to the bottom phase, simulating the worst conditions. For $P \geq 9$ MPa, only ~0.20% of the extracted oil mass remains in the light phase at the exit of the extractor, so this percent was took as the mass split of oil to the upper phase [4,11]. To keep the $S/F = 6.6$, we defined that the entrance of solid material in the 400 L-extractors should be directly proportional to what was empirically verified for a 1 L-process [11], so they are charged with 228 kg of solid clove and are submitted to 429.94 kg CO_2/h. After the extraction, the light phases are directed to an adiabatic flash drum for separating the CO_2 from the extracted compounds. At this stage, we reduced P to 80.64 bar (40 °C), since this condition allows the formation of a vapor phase comprised of only CO_2 (molar fraction of $0.997 \approx 1$) in equilibrium with a liquid phase containing a molar fraction of 0.6916 of CO_2 [3]. Then, a second adiabatic flash drum under atmospheric pressure (1.013 bar) fully separates the remaining gases from the oil phase. A heat-exchanger that guarantees the gases to flow into the extractors at 40 °C; and a CO_2 make-up entrance stream to compensate gas losses in the flash drums complete the simulation. We also limited the useful volumes to 90% of the total volume of each equipment.

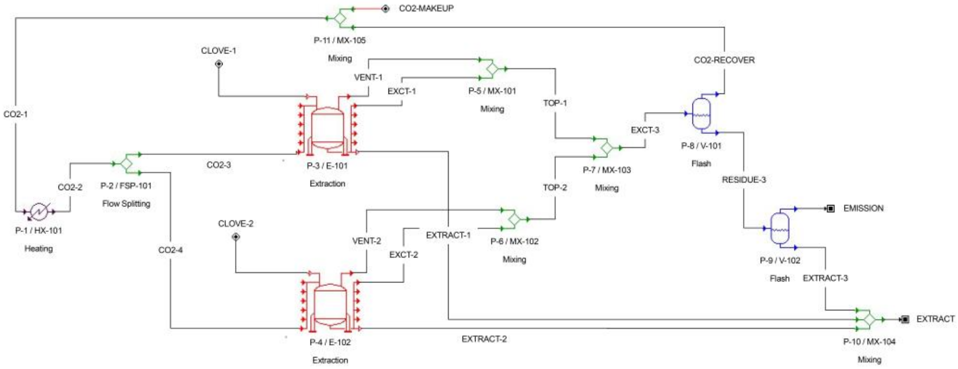


Figure 1. Simulation diagram developed in the SuperPro Designer 10 simulation interface.

The plant costs estimates were performed according to Turton's method, in which Equation 1 is frequently applied: FC_i represents the fixed capital that must be expensed for acquiring a given equipment; A_i is the capacity of the equipment in "i"-scale; and n is a cost exponent that ranges from 0.26 to 1.33 depending on the class of equipment, and that represents the economy of scale of the plant. Since many Chemical and Food Engineering equipment present $n \approx 0.6$, this value is frequently used to the estimative (six-tenths rule). The plant's Direct Fixed Capital (DFC, or Capital Expenditure, CAPEX) is estimated with basis on the Total Equipment Purchase Cost (PC). The PC is calculated as the sum of purchase costs of all equipment (estimated with Equation 1) with the costs related to equipment that are unlisted in the project, but which are relevant to real plant operation. The cost of unlisted equipment is estimated as 20% of the listed equipment costs. After that, it is possible to estimate the Project's Direct Cost (DC) as the sum of PC costs with costs of: process piping (estimated as 35% of PC); instrumentation (40% of PC); insulation (3% of PC); electrical facilities (10% of PC); buildings (45% of PC); yard improvements (15% of PC); auxiliary facilities (40% of PC); and installation of listed and unlisted equipment (50% of PC). Other important estimates are the Project's Indirect Costs (IC), sum between the engineering costs (25% of DC) and the construction costs (35% of DC); and the Other Costs (OC), calculated as the sum of contractor's fee costs (5% of the sum DC + IC) with the project's contingency budget (10% of the sum DC + IC). The DFC if finally given by the sum DFC = CAPEX = DC + IC + OC. Also, the Facility-Dependent Costs (FDC) are estimated as the sum of maintenance, depreciation, and miscellaneous costs comprised of insurance costs (estimated as 1% of DFC); local taxes (estimated as 2% of DFC); and factory expenses (5% of DFC). Other estimates performed are: laboratory quality control and quality assurance costs (15% of total costs related to the payment of factory operators); additional electricity (15% of the calculated electricity cost); and electrical power for unlisted equipment (5% of the calculated electricity cost) [12].

$$\mathrm{FC}_2 = \mathrm{FC}_1\left(\frac{\mathrm{A}_2}{\mathrm{A}_1}\right)^{\mathrm{n}} \qquad (1)$$

$$\mathrm{NPV} = (\text{Value at the end of year n})/(1+\mathrm{j})^{\mathrm{n}} \qquad (2)$$

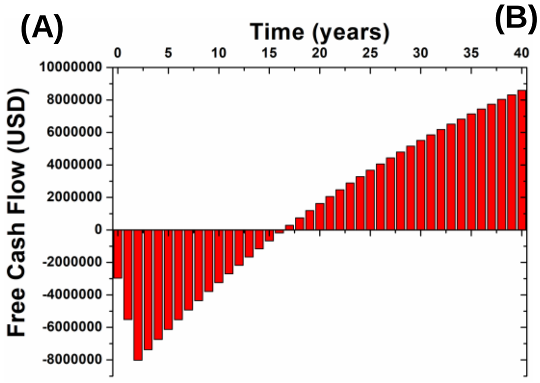
The evaluation of the investment feasibility involves the calculation of economic indicators: the Net Present Value (NPV) represents the real value of the general investment result after a defined period of time, which we took as the project's lifetime of 40 years. The NPV is calculated through Equation 3, where j is the rate of return or discount rate (minimum interest rate that makes one investment attractive) and n is the number of periods, in years. Basically, a higher NPV implies a better investment, since it directly represents the wealth generated. We also estimated a depreciation rate of 20% per year, which was linearly adjusted to the basic cash flow, and defined the rate of return as the Brazil's basic interest rate, 2.30% per year. The economic analysis was performed in accordance to the Weighted Average Capital Cost (WACC) methodology for evaluating the annual free cash flow (FCF) of the plant, which consists on evaluating the contribution of the debt costs (interest on the amount) and the return demanded by the shareholders for performing an investment (capital cost). A given investment is considered feasible if it results in a return superior than the debt and capital costs. For a total of 330 working days per year, the Operational Expenditure (OPEX) of the project was considered constant and equals to the sum of costs of: acquisition of raw materials; labor costs; utilities costs (cooling water, water steam, and electricity costs); and laboratory quality control and quality assurance costs. The plant construction period was defined as 30 months, whereas the plant start-up period was of 4 months, which are the standard of the SuperPro Designer 10 database. So, operational profits are obtained only after the initial 34 months, but we considered that the OPEX is incident from the first year. The main project parameters that we applied to the economic analysis are summarized on Table 1. Another important economic indicator is the "*Earnings Before Interest, Taxes, Depreciation and Amortization*" (EBITDA), which considers the net revenue discounted of the value expended on the production, stocking and commercialization. The WACC methodology discounts the depreciation effects from the EBITDA, and only cash flow expenses are considered for the discount of income tax, reducing the total amount of interest paid. We applied a standard income tax rate of 34% per year with no tax benefits. Finally, the annual net working capital necessary was considered constant and was estimated as 5% of the initial fixed capital investment [12].

Table 1. Main project operation parameters applied to the analysis.

Project Operation		**Reference**
Project Lifetime (years)	40	Software Standard (Database)
Plant Construction Period (months)	30	
Plant Start-up Period (months)	4	
Total Working Days (per year)	330	
Cost of Operational Labor (COL)	**Industrial Scale (400 L - Extractor)**	
Wage (with benefits, administration, supervision and supplies) (USD/h)	14.93	[13–15]
Workers per shift	3	[14–16]
Total Wage per year (USD/year)	1673956.00	
Cost of Utilities (CUT)		
Electricity (USD/kWh)	0.25	[13–17]
Cooling Water (USD/ton)	0.78	
Water Steam (USD/ton)	16.80	

3. Simulation Results and Economic Feasibility Analysis

The simulation results indicated that virtually all of the CO_2 may be recycled, leading to an almost null annual cost related to the purchase of this raw material. However, this is only an ideal situation, and the stocking of this gas is necessary for different reasons: our hypothesis was that the gas was supplied in cylinders under 150 bar, what is necessary for eliminating the costs of purchasing and operating a compressor; and it is necessary to have stocked gas for moments of: stopping; maintenance; and start-up of the plant; as well as for compensating losses from non-idealities not covered by the project. Then, we considered an annual minimum purchase allowed by the suppliers, 100 cylinders of 10 L under 150 bar, corresponding to 4,000 USD/year [10]. The equipment estimates, in turn, were performed for equipment fabricated in carbon steel (CS), or in stainless steel SS316 (only the two extractors). The free cash flow and the economic indicators are shown on Figure 2. We calculated that ~64.4% of the OPEX correspond to labor-dependent costs. Once we hypothesized that the plant must work with three operators, we estimated that the extra-investing in automation could drop the labor-dependent costs ~597,200.00 USD/year if there was only one operator directly working, a reduction of ~41.4% of the annual operating costs. We may notice that the payback period (the time necessary for the investment to pay itself) is slightly superior than the break even point (when the free cash flow reaches zero): 18.67 years for the payback, against 17 years for the break even. It is a consequence of defining an initial period for construction and start-up where we considered the OPEX was already present. On the other hand, the payback period is lower than half of the project's lifetime (40 years), and the operational profits after taxes are substantial (691,323.06 USD/year). The consequence is a high internal rate of return (IRR) of 7.29% per year. The IRR is the discount rate that a cash flow must present to equal the NPV to zero, so greater differences between the IRR and the minimum rate of return (2.30%/year) make an investment more attractive. The NPV also confirms that the investment has an outstanding capacity of generating wealth: the investment of 347,000 USD is converted into a NPV of ~8,600,000.00 USD after lifetime. Finally, it is important to verify the effect of different purchase prices on the economic indicators, once agricultural commodities (like clove) may be highly influenced by oscillations of the international markets. Therefore, we calculated the NPVs and the correspondent break even points for purchase costs of dry clove ranging from 0.05 to 1.12 USD/kg, verifying a linear decrease of the NPV with the clove's price: NPV (in USD) = -1,771,750,000,000.00 x (clove's purchase cost, in USD/kg) + 1,993,750,000,000.00, adjusted $R^2 \approx 1$; and a linear increase of the break even point until 0.70 USD/kg of clove, when its rate of grown suffers a substantial enhancement. Defining that the process is viable: if the NPV is higher than the CAPEX investment (i.e., the operating effectively generates wealth); and if the break even point is not superior than 75% of the project's lifetime, then the process is viable for clove costs until 1.00 USD/kg, an increases of 56.25% of its cost. In this limit situation (1.00 USD/kg), the NPV = 2,220,018.89 USD, and the break even occurs at 30 years.



(B)

Economic Indicators	
Investment (CAPEX) (USD)	347,000.00
Earns (USD/year)	3,663,042.18
OPEX (USD/year)	2,598,233.00
EBTIDA (USD/year)	1,064,809.18
Depreciation Rate (per year, linear)	20.00%
Net Working Capital (NWC) (USD/year)	17,350.00
Income Tax	34.00%
Operational Profits (after taxes, USD/year)	691,323.06
Net Present Value (NPV) (USD)	8,598,312.83
Discount Rate (per year)	2.30%
Internal Rate of Return (IRR) (per year)	7.29%
Discounted Payback Period (years)	18.67
Break Even Point (years)	17.00

Figure 2. (A) 40-years free cash flow; (B) main financial indicators of the SFE plant of Figure 1.

Enormous amounts of biomass (793,749.29 kg/year) are produced as residues. The average heat of combustion of other three vegetable species belonging to the same family as clove (*Myrtaceae*) which are present in Brazilian flora is 18.25 MJ/kg for the dry biomasses [18,19], and typically, 25% of this energy is effectively available for use [20]. So, the produced biomass represents a potential for the generation of 3.62 x 10^6 MJ/year, what could be applied to the generation of water steam for use on the heat exchanger or for the generation of electricity in turbines, reducing the OPEX of the plant, or could constitute a new source of revenue. Indeed, there is a growing market for the acquisition of wood pellets and for their use as energy source: by the end of 2019, the United Kingdom (UK) biomass boiler market that reached ~16,500 commercial and industrial systems (systems with capacity above 200 kW), and 12,700 domestic boilers installed and in operation. By April 2020, the UK imported 896,000 tons of wood pellets from 6 major countries (44,000 ton came from Brazil), an increase of 39.3% in relation to the 643,000 tons in April 2019. [21,22]. There is not a single supplier dominating the whole international market, representing an opportunity for new players.

4. Conclusions

The analysis and simulations show that the investment in an industrial plant for the supercritical extraction of the clove's essential oil compounds with CO_2 is very attractive. This oil presents many relevant food and biomedical applications, including: antibacterial and antifungal activities; and use as antioxidant and anti-inflammatory; and for asthma and allergy relief. The SFE is not only a green-process, but it also presents excellent investment indicators. The expenditure of

347,000 USD is converted into a NPV of 8,600,000 USD after the project lifetime, with a payback of 18.67 years, and the process is viable even if clove's purchase cost is increased by up to 56.25%.

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