Recovery of bioactives from kānuka leaves using subcritical water extraction: Techno-economic analysis, environmental impact assessment and technology readiness level

Essien, Sinemobong O.; Udugama, Isuru; Young, Brent; Baroutian, Saeid

Published in:
Journal of Supercritical Fluids

Link to article, DOI:
10.1016/j.supflu.2020.105119

Publication date:
2021

Document Version
Peer reviewed version

Citation (APA):
Essien, S. O., Udugama, I., Young, B., & Baroutian, S. (2021). Recovery of bioactives from kānuka leaves using subcritical water extraction: Techno-economic analysis, environmental impact assessment and technology readiness level. *Journal of Supercritical Fluids*, *169*, Article 105119. https://doi.org/10.1016/j.supflu.2020.105119

Recovery of bioactives from kānuka leaves using subcritical water extraction: Techno-economic analysis, environmental impact assessment and technology readiness level

Sinemobong O. Essien[a], Isuru Udugama[b], Brent Young[a], Saeid Baroutian[a,1]

[a]*Department of Chemical and Materials Engineering, The University of Auckland, Auckland 1010, New Zealand*

[b]*Department of Chemical and Biochemical Engineering, Technical University of Denmark, Kgs. Lyngby, Denmark*

Abstract

The techno-economic feasibility (TEA), technology readiness level (TRL), and environmental impact of producing bioactive kānuka leaf extracts using subcritical water extraction (SWE) were assessed and compared to using conventional ethanol extraction (EE). Both SWE and EE had the same TRL value from the analysis. The TEA showed that though EE required more process units, the total capital expenditure for SWE was still 3% higher than for EE. However, the manufacturing and unit cost of production were NZ$4.49 million and NZ$ 2.14/kg for SWE and NZ$4.7 million and NZ$ 5.57/kg for EE, respectively. The net present value for SWE was twice the value for EE. Sensitivity analysis revealed that the raw materials cost and product sales price were the controlling factors for profitability. Kānuka extract production with SWE was more environmentally benign than EE. Overall, producing bioactive kānuka extracts with SWE had better profitability with a shorter payback time than EE.

Keywords: Techno-economic assessment; environmental impact analysis; subcritical water extraction; kānuka; technology readiness level

---

[1] Corresponding author: s.baroutian@auckland.ac.nz; +64 9-923-1424

1 Introduction

Subcritical water extraction (SWE) of secondary metabolites from plants is increasingly researched and published in the literature. In the last decade, numerous plant species have been associated with the subject of SWE. A discussion of the current developments in the application of SWE to plant bioactives recovery is detailed in Essien et al. [1].

Kānuka, *Kunzea ericoides*, is a plant that serves a variety of functions: the direct and indirect products of kānuka have shown significant immunomodulatory, anti-inflammatory, antimicrobial, and aromatherapeutic properties [2-4]. It can be used in the food industry as a plant extract-based food additive and colouring agent; in the cosmetic industry as an active ingredient; and in medicine as a natural health, super nutrition supplement [5]. All parts of this plant can be used because of its versatility.

It is clear from the literature that these properties are made possible by constituents known as bioactive compounds. These are extra-nutritional constituents of plants, like kānuka, small in quantity but with the ability to modulate cellular processes which result in the promotion of good health conditions. Their impact on human health is being studied intensively. Consequently, the demand for extraction of these bioactive compounds using green, environmentally benign technologies is rapidly growing. However, studies investigating the extraction of bioactive compounds from kānuka and its economic viability are still scarce in the literature despite the interest in these compounds as evident in the few research outputs.

SWE, also known as pressurized hot water extraction, is a green alternative proposed to feasibly replace conventional methods of extraction of polyphenols from plant matrices. Essien et al. [6] have reported experimental work that employed SWE to produce bioactive liquid extracts from kānuka leaves more efficiently than conventional EE. Besides efficiency, economic viability is a crucial consideration when designing and operating a plant that should be competitive in the current market. The market size of plant extract-based products and bioactive ingredients was estimated to have a cumulative annual growth rate (CAGR) of 16.5% [7]. This growing trend is driven mainly by a rise in trading and an interest in natural plant extracts as substitutes for synthetic preservation, herbal medicines, functional foods and food additives. Thus, a techno-economic assessment (TEA) is necessary for deciding the economic feasibility of upscaling a production process from the laboratory level to the industrial level to develop SWE of kānuka leaves.

Information on the techno-economic analysis of pressurized hot water extraction is relatively scanty and even so, is mostly focused on hydrothermal processing such as hydrothermal liquefaction, which is different from SWE in both its purpose and operating conditions. Moreover, there are no studies in the literature on techno-economic analysis of SWE for the recovery of polyphenols from kānuka. However, some studies have employed SWE for this purpose on other plant matrices as can be seen in Table 1.

Table 1: Selected techno-economic assessment on SWE

Author	Technology evaluated	Feedstock/extraction target	Basis for evaluation	Approach
Todd and Baroutian [8]	SWE, $SCCO_2$, solvent extraction	Grape marc/Bioactive phenolic compounds	Final liquid product yield	Literature data, economic, sensitivity, and environmental impact analysis
Asiedu et al. [9]	Subcritical water-based flash hydrolysis	*Scenedesmus obliquus*/ protein concentrate	Production capacity (protein concentrate per day)	Simulation, economic and sensitivity analysis.
Vardanega et al. [10]	SWE	Brazilian ginseng/Probiotic carbohydrates and β-ecdysone	Cost of manufacturing	Experimental, simulation, economic evaluation.
Zabot et al. [11]	SWE, sequential with $SCCO_2$	Rosemary leaves/Terpenoids and phenolic compounds	Plant capacity	Simulation, economic evaluation
This work	SWE, solvent extraction	Kānuka leaves/Bioactive polyphenol extracts	Plant throughput	Simulation, economic, sensitivity, TRL, and environmental impact analysis.

Thus, the novelty in the present work is that it evaluates the feasibility of scaling up production of bioactive liquid extracts from kānuka leaves using SWE technology and compares it to conventional solvent extraction with ethanol (EE). The technical maturity of the SWE is also investigated by way of a technology readiness level (TRL). The overarching goal is to present a techno-economic and environmental impact analysis at optimum conditions for a cost-effective kānuka bioactive extract production process. The rest of the paper is organised such that all the assumptions and activities carried out to achieve the aim of this study are presented first followed by a discussion and analysis of the outcomes of these activities.

2 Approach and methods

The focus of this assessment was on SWE and EE scenarios. Figure 1 shows the steps taken in the techno-economic and environmental impact assessment. These steps involved a technical analysis to determine the material and energy requirement, which were then used as inputs for the economic and environmental impact analysis. Computational software was utilised to achieve this goal and are mentioned in the relevant sections of the paper. The findings of the experiments in Essien et al. [6] provided the process parameters, conditions and yields that were implemented in the simulated kānuka extract production plant. The kānuka processing plant was assumed to operate at maximum capacity (100%) for 330 days per year [12, 13] with a lifetime of 10 years. The system boundary was defined from raw material (kānuka leaves) preparation up till the final product (liquid extract) collection.

2.1 Process simulation

The technical analysis focused on process variables such as the quantity of raw materials, energy consumption, processing time and yield. It involved model validation to ensure reliable modelling and simulation of the conceptual plant. Figure 2 shows the simplified process flow diagrams for SWE and EE. The downstream processing products from kānuka were studied as a liquid product.

The extraction of bioactive compounds from kānuka leaves can be modelled by several process simulators, e.g. Symmetry, HYSYS. In this paper, the extraction was modelled and simulated using Aspen Plus$^{®}$ v10 by Aspen Technology. To scale-up the extraction process, it was assumed that the performance (yield and composition of product) of the industrial scale unit is the same as that of the laboratory scale, and the operational conditions (temperature, solid-solvent ratio, pressure, time) are constant [14-16]. The extraction conditions for SWE were pressure 40 bar, temperature 170°C and those for EE were temperature 30°C and atmospheric pressure, 60% v/v concentration. Both processes were designed to operate in batch mode at a solid-solvent ratio of 15 g/L for 8 h per 5 days per week.

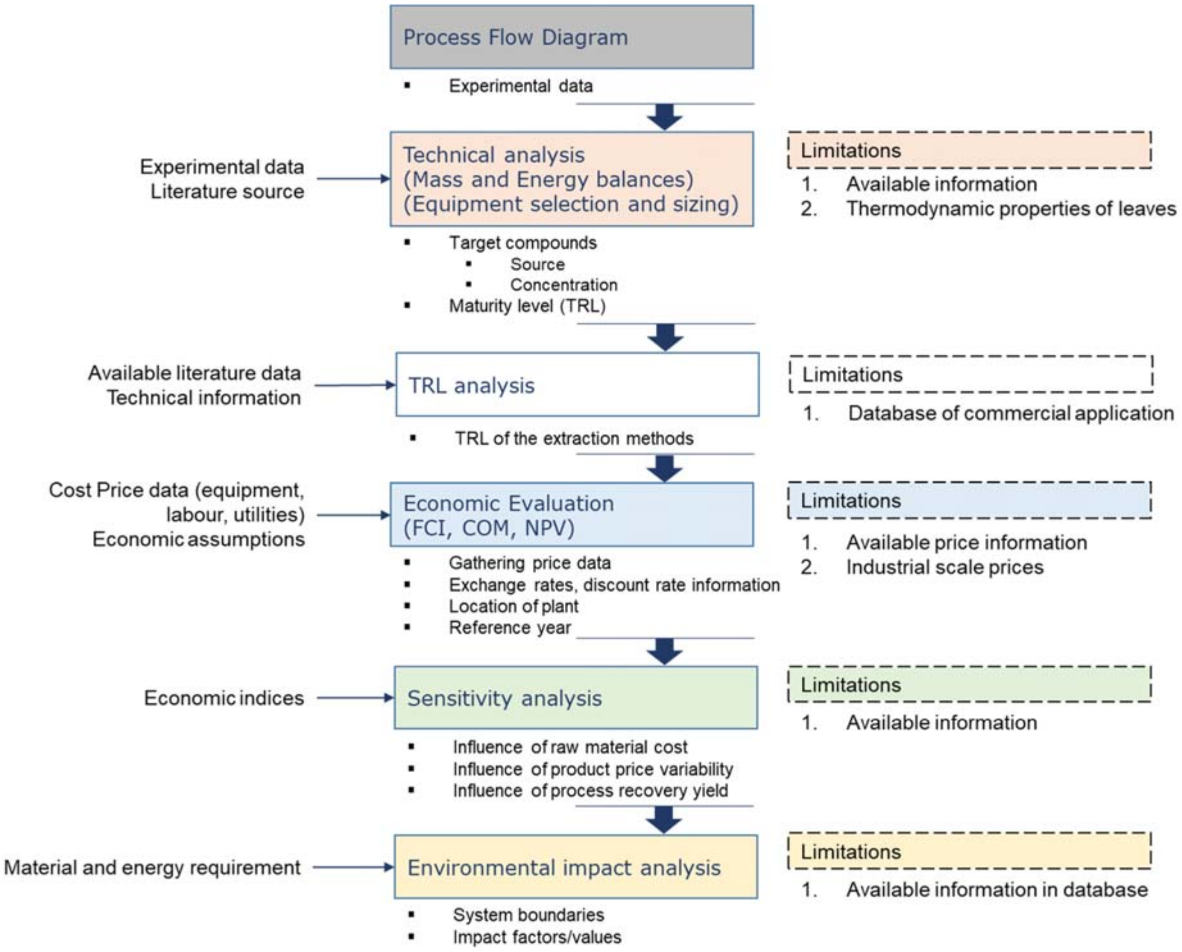

Figure 1: Flow chart showing the steps of the approach taken in this techno-economic assessment

The SWE vessel was modelled as a 1000 litre pressure vessel operating at 80% capacity to account for expansion due to overhead pressure changes. A fixed throughput of 32 metric tonnes/year (MT/year) dried kānuka leaves was obtained based on this assumption. The extraction vessel for EE was scaled to take up the same capacity as SWE for a fair comparison. Both processes were broken into unit operations and modelled as blocks in the software. The SWE time was 20 min, but an operating time of one (1) hour was used to account for idle time for loading, cooling, and unloading. The operating time including time for loading, cooling, and unloading was eight hours for EE. For a more eco-friendly and cost-effective process, downstream evaporation of the extraction solvent was assumed to separate ethanol from the extracted compounds, for recycling. The evaporator was modelled as a set of heat exchangers and flash tanks. A 5% loss of ethanol was assumed between the evaporator and the reuse of ethanol at an inlet temperature of 25°C [17].

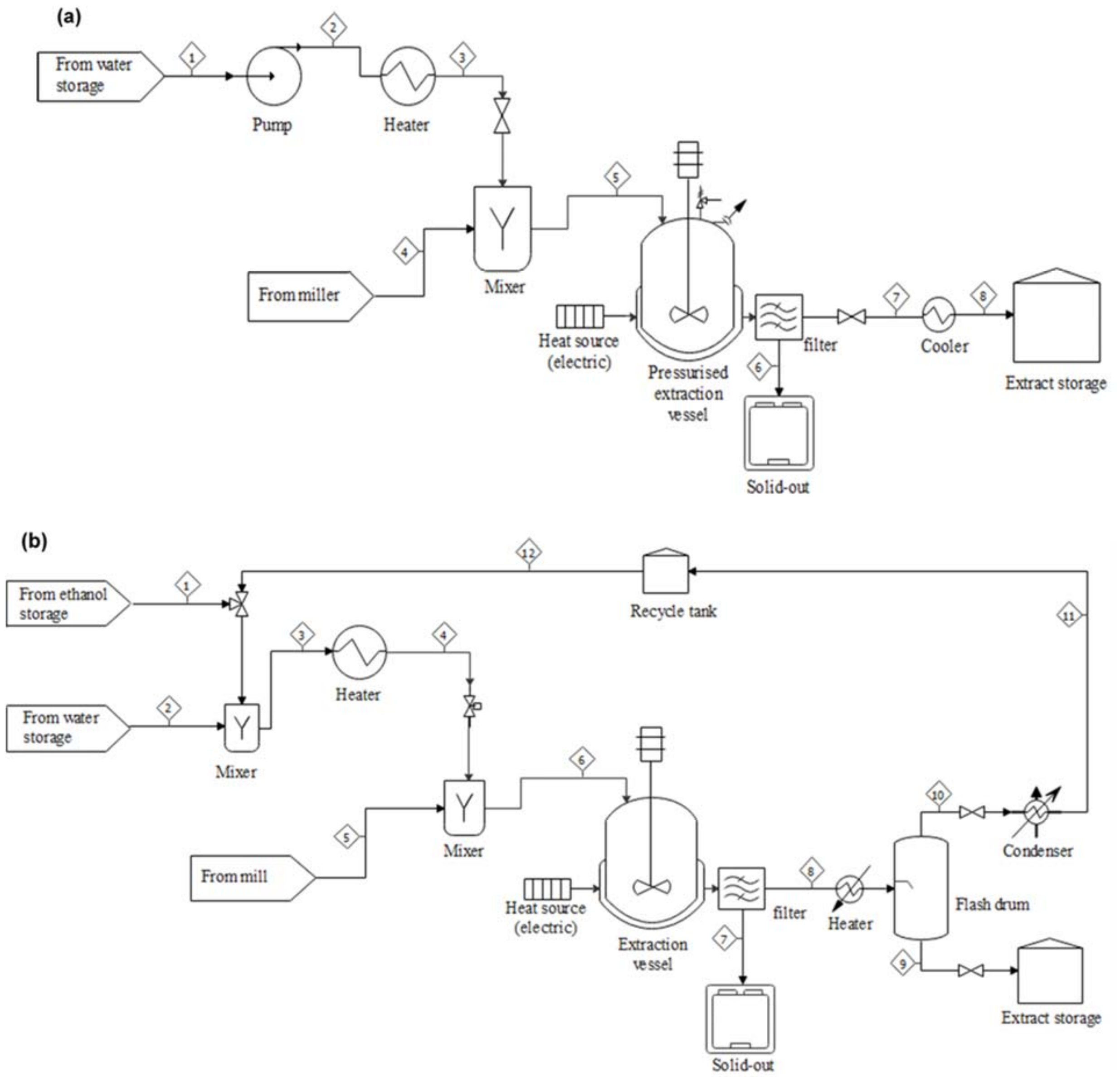

Figure 2: Simplified process flow diagrams of (a) subcritical water extraction (SWE) and (b) ethanol extraction (EE)

The thermodynamic method package “Wilson” was selected and used in estimating the process stream properties needed to solve the steady-state mass and energy balance. The Wilson model can handle any combination of polar and non-polar compounds, up to very strong nonideality [18]. The conundrum at this stage was adding kānuka leaves as a component for analysis in Aspen Plus. Kānuka is a lignocellulosic material, and these types of materials are comprised mainly of hemicellulose, cellulose and lignin as major components and extractives a minor component. However, these compounds are not present in the native Aspen Plus database, presenting another set of hurdles in the simulation. The missing component data were entered directly using data from the National Institute of Standards and Technology (NIST) ThermoData Engine and estimated using Aspen plus property estimation. Estimation was done based on functional groups contribution method [19] and some known physical properties. Owing to the complexity of kānuka leaves, the polyphenol content was represented by gallic acid (GA) which is widely used as a standard in quantifying total phenolic content in plant extracts, while cellulose represented the solute-free solid content. Like Mosca et al. [20], the initial polyphenol content in kānuka leaves was assumed to be 10% greater than the maximum extractable amount obtained using the extraction technique with the highest extraction yield. To ensure that the property method calculates the model properties accurately or to a minimum level of uncertainty, data regression of the minimum thermophysical properties required was performed. Literature references consulted for experimental data and in property estimation included external databases, chemical suppliers and publications [21-31]. Overall, the thermodynamic model accuracy was considered acceptable for a preliminary cost estimation study.

2.2 Technology Readiness Level (TRL)

The TRL assessment metric covers research, development and implementation/deployment of a given technology. The TRL 9-point metric, originally developed by NASA, rates the maturity stage of a given technology in an industrial setting. The lowest value, TRL 1, is given when the concept of the technology is still in the early stage of research, where all the basic principles have been observed and documented while the highest value is given to a technology that has been successful in an operational environment. A TRL number was assigned only after the descriptor of each level has been achieved [32]. The evaluation of the TRL based on these descriptors can be somewhat arbitrary, in particular where multiple processing technologies need to be evaluated in an early stage design setting and detailed analysis on a project is infeasible to perform. To this end, this work employed the TRL assessment framework outlined in Li et al. [33] to carry out this analysis.

Firstly, literature and an open internet search (to identify some of the commercial activities) was performed, and the results were divided into lab, pilot, and full-scale attempts. Commercial applications of these technologies accounted for the full-scale implementation. This initial classification allowed a TRL range of 1-3 to be assigned to all lab attempts while a TRL range of 4-6 and 7-9 was assigned to the pilot and full-scale applications, respectively.

Secondly, the TRL number for extraction technology (within the assigned range) was determined by a combination of process awareness (real understanding of the underlying process phenomena), technical “know-how” (ability to design, build and implement the process) and the number of applications where a similar implementation is available. The details of this final decision were taken as per Table 2 of Li et al. [33].

2.3 Economic assessment

The market potential of kānuka extract from SWE and EE were evaluated based on the current price trend. According to Náthia-Neves et al. [34], determination of economic viability of a process should be concerned about the performance, productivity and selectivity of the process. This, in summary, means the process that yields the maximum quantity of products, enriched with the compound of interest, at the shortest processing time and minimal manufacturing cost. Hence, the economic assessment was conducted by determining the total capital investment and production cost for each extraction scenario at optimum operating conditions.

2.3.1 Total capital expenditure (CAPEX)

Often in chemical process plants, the total capital expenditure (CAPEX) is based on the sum of working capital and fixed capital investment (FCI). Here, the FCI is a sum of the costs of purchased equipment and other direct and indirect expenses, which were estimated as factors of the total equipment purchase cost. The equipment sizes were determined from the mass balance, and their fob costs were obtained from a conceptual equipment cost databank [35] based on the size, process parameters, and material of construction. These fob costs were updated to the current year (2020) using the chemical engineering plant cost index (CEPCI) [36] and converted to New Zealand dollars (NZ$) as shown in Eq. 1. An exchange rate of 1.67 NZ$ per US$ was used. Due to the location of the plant, an additional 30% of the fob cost was added to get the installed equipment cost. The milling unit operation was not included in the simulation, but the cost of the mill was considered [12]. Lastly, the working capital, estimated as 5% of the fixed capital investment, was calculated and added to the FCI to obtain the CAPEX.

$$Cost_{2020} = Cost_{2014}\left(\frac{CEPCI_{2020}}{CEPCI_{2014}}\right)\left(1.67\,\frac{NZ\$}{US\$}\right) \tag{1}$$

2.3.2 Annual production cost

The annual production cost associated with the day-to-day operations, also known as the cost of manufacturing (COM), is a sum of variable and fixed production cost, and general expenses. It was calculated as a function of labour cost (COL), waste treatment cost (CWT), utility cost (CUT), raw material cost (CRM), and FCI using the detailed analytical cost estimation method [37]. The COL was the product of the number of operators per shift, and the hourly labour rate per operator. An additional 30% of the operating labour cost was added to cover benefits and leave packages. The life of the plant was assumed as 10 years with negligible salvage value. The CWT was the expenses incurred for the collection and disposal of the spent kānuka leaves as green waste. The CUT was directly related to the electricity consumed during extraction processes through heating, cooling, and pressurisation; the electricity demand to reduce the leaves to an average particle size of 0.85 mm was also included. For the CRM, the following components were considered: (i) cost of kānuka leaves; and (ii) cost of solvents (e.g. water and ethanol) used for the extraction. The cost of transportation to the processing plant was excluded from this calculation. The economic assumptions used for this assessment are listed in Table 2. The extraction processes were compared based on annual production cost per unit product, and per polyphenol content, that is the amount of NZ\$ needed for the production of 1 kg of extract (COM NZ\$/kg) and production of 1 kg of gallic acid (COM NZ\$/kg$_{GA}$).

Table 2: List of assumptions for the economic analysis of the subcritical water (SWE) and ethanol extraction (EE) of kānuka leaves product.

General	
	Reference year: 2020
	Plant operating life: 10 years
	Tax rate per year: 28%
	Inflation rate: 2% p.a.
	Exchange rate 1.67 NZ$/US$; 1.8 NZ$/EUR (May 2020)
	Operating time: 8 h per day, 330 days per year
	Construction period: 1 year
	Single Extraction train
Labour cost	
	1 eight-hour shift/day; 2 operators per shift, 5 shifts/week
	Labour cost: NZ$22 h^{-1} $worker^{-1}$
	Administrative and management cost: NZ$: 150, 000[*]
Fixed capital cost	
	Annual depreciation rate; 10%. Straight-line method
	Resale value, land prices not included
Waste treatment	
	Solid waste collection and disposal: NZ$111.10 per tonne
Utilities cost	
	Electricity: NZ$0.17/kWh[†]
Raw materials	
	Cost of kānuka leaves: NZ$50/kg
	Cost of ethanol: NZ$5.6/L[‡]
	Cost of water: NZ$1.55/$m^3$[⁑]

[*] [8]; [†] Commercial rate estimate for 2019 [38]; [‡] [39]; [⁑] [40]

2.3.3 Revenue generated and profitability analysis.

The revenue generated from sales of the value-added products was a function of the recovery efficiency, quantity of phenolic compounds in the final products, and sale price. Laboratory results were scaled-up under the criterion mentioned in section 2.1 to obtain the quantity of product. It was challenging to get the sales price for the extracts obtained from kānuka leaves since they are not yet commercialised. Hence, the product price was derived by gathering easily accessible cost information on commercial liquid bioactive products characteristics to the extracts in this study. These products' prices varied with the amount of bioactive compound in the products. Therefore, the sales price was given as NZ$/mg of polyphenol content, and for conservative analysis of the process, a low sales price was adopted.

To evaluate the profitability (and hence the economic feasibility) of the two extraction processes, economic investment indicators like Operating Margin (OpM), Net Present Value (NPV), Return on Investment (ROI), and Payback period (PBP) were calculated using Eq. 2 – 5, respectively [13, 41, 42]. These are some of the main profitability factors often reported in the literature regarding the techno-economic subject matter. A discount rate of 15% was assumed for the calculation of the NPV of SWE and EE.

$$OpM\ (\%) = \frac{Operating\ earnings}{Total\ revenue} \tag{2}$$

$$NPV\ (NZ\$) = \sum_{t=1}^{n} \frac{R_t}{(1+i)^t} - CAPEX \tag{3}$$

$$ROI(\%) = \frac{Annual\ net\ profit}{Total\ capital\ investment} \tag{4}$$

$$PBP\ (yrs) = \frac{Total\ capital\ investment}{Annual\ net\ profit} \tag{5}$$

where R_t =net cash inflow- cash outflow during a single period *t;* *t* = number of time periods; *i* = discount rate.

2.4 Sensitivity analysis

Due to the uncertainties surrounding the market value of kānuka leaves and sales price of the product, a sensitivity study was carried out exploring the impact of market price scenarios on COM and NPV. The goal was to examine the influence of the cost inputs assumed in this techno-economic evaluation on the output responses, and the range of these variations. The parameters varied over a range, and the outcomes were presented by assuming that all other factors remained mostly constant. Like the product sales price, the cost price for dry kānuka leaves was obtained from similar products in the market. Seven cost price values were assessed for the dry leaves (NZ$ 15 to NZ$ 100/kg). The sales price of the liquid extract ranged from NZ$ (0.001 to 0.01)/mg_{GA} though the market price may be higher than reported. A similar approach was published in Náthia-Neves et al. [34] for Genipap extracts and Zabot et al. [43] for onion peels. The total capital investment, COM, and NPV as a function of the plant capacity for SWE were also assessed.

2.5 Environmental impact analysis

The potential environmental impacts (PEI) of recovering value-added product from kānuka leaves using SWE and EE techniques were analysed using the Waste Reduction (WAR) Algorithm [44, 45]. Developed by the US Environmental Protection Agency (EPA), this algorithm is a tool aimed at minimising the PEI of a process by evaluating the effect that a material or process will have if it were emitted into the environment. The PEI was measured by eight impact categories, namely human toxicity potential by ingestion (HTPI), terrestrial toxicity potential (TTP), human toxicity potential by exposure (HTPE), aquatic toxicity potential (ATP), global warming potential (GWP), ozone depletion potential (ODP), photochemical oxidation potential (PCOP), and acidification potential (AP). The first four impact categories are local toxicological impacts, while the last four are global atmospheric impacts. The weighted sum of the individual impacts gave the total impact per kilogram of products. The Aspen Plus mass and energy balance results were the inputs to this tool, and energy was assumed to be supplied by natural gas. A gate-to-gate approach was used with the system boundary defined around the processing facility. The greenhouse gas (GHG) emission was also calculated using default effective emission factors of 56,100 kg CO_2-eq per TJ of natural gas as a fuel source.

This assessment is per the 2006 IPCC guidelines for National GHG inventories [46]. A similar approach can be found in Daza Serna et al. [47], Moncada et al. [48] and Ravber et al. [16].

3 Results and discussion

3.1 Process modelling

The simulation flowsheet representing SWE and EE are shown in Figure A.1. The models provided insights to not only the extract yield and the energy consumption but also the complexity of the process. Pressurisation was not included/required in EE, which should have made it the simpler of both methods; however, the need to recover and reuse the solvent added extra process units. The estimated energy consumption when considering the overall process was higher for EE than for SWE, even though EE was the least energy-intensive process when taking the system boundary around the extractor (Table 3). On the other hand, recycling of solvent was not required in SWE due to the solvent used, albeit, the high pressure and high-temperature operation posed more health and safety issues than EE. Bioactive product yield for the conventional EE process (4 MT/year) was lower than the observed for SWE (5 MT/year). The key reason for the lower productivity is its long extraction period, up to 8 h, to process the same amount of raw materials processed in one hour by SWE. As a result, fewer batches are processed throughout the year by EE, and a smaller yield of extracts are obtained.

Table 3: Electricity demand for the two extraction scenarios

	Subcritical water extraction	Ethanol extraction
Feedstock pre-treatment (kW)	145	145
Solvent preparation (kW)	147	2
Extraction/collection (kW)	229	322
Ethanol recovery (kW)	-	328
Total electricity (kW)	521	797
Electricity demand (kWh) per kg feed	31	54
Power consumption, kWh/kg product	252	506

3.2 TRL analysis

To evaluate the TRL of SWE and EE technologies, a literature review (including a patent search and a general web search) was conducted. The results obtained were categorised into instances where SWE and EE were employed in lab-scale, pilot-scale and full-scale applications related to plant-based extractions. The results obtained are shown in Figure 3.

Analysing the information recorded in Figure 4 shows that there are thousands of lab-scale examples of both SWE and EE. EE is a well-established technology; it is simple, low cost and has been used from time immemorial, so it is no surprise that lab to full-scale application returns high numbers. SWE, on the other hand, is a relatively new technique. Experimentally, except for [6], no one has done anything on kānuka using SWE. Nevertheless, technology-wise, SWE has been used with other types of plant matrix so as such they too can be found in high numbers.

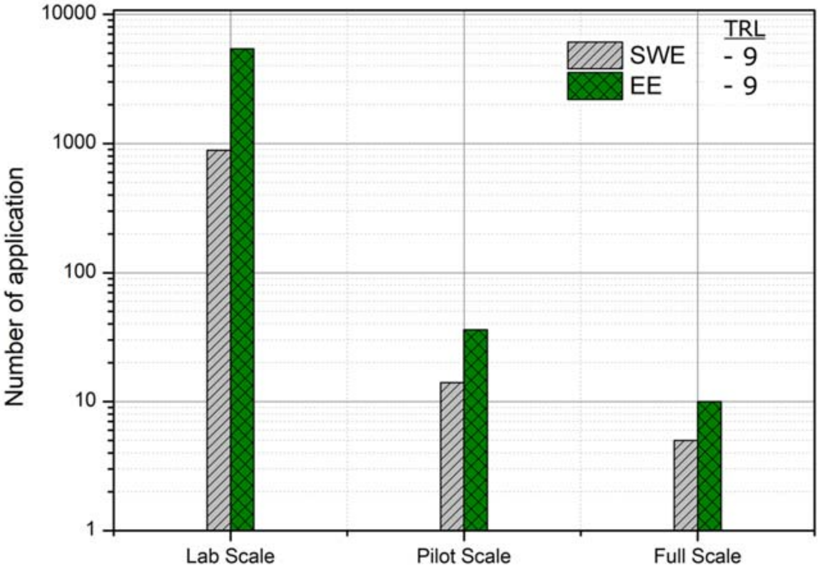

Figure 3: Number of applications and TRLs for subcritical water extraction (SWE) and ethanol extraction (EE)

At the pilot-scale level, the examples found drops down to 10's of examples while at full-scale, these examples are further reduced to less than ten applications. Despite these high numbers, especially at lab scale, the number of full-scale applications is still limited, in the practical sense, probably due to patent issues often encountered in commercial settings. To give an instance, NZ Extracts Ltd uses

SWE under the name 100% Aqua Pure®, Mazza Innovations under the name PhytoClean™ while Laboratoire Phenobio refers to SWE as is. The three-broad applications of SWE are resource recovery from waste, flavour and fragrance, and health and cosmetic ingredients. To this end, from a TRL point of view, the existence of these full-scale applications means both the SWE and EE technologies fall into the TRL range of 7-9.

Both the technologies also have a very high degree of process awareness, as the underlying mass transfer phenomena are well known and documented. From a technical “know-how” point of view, these types of subcritical water-based and ethanol-based extractions and their supporting peripheral equipment such as solvent regeneration are standard unit operations in chemical engineering applications. Hence a final TRL value of TRL9 can be given to both the SWE and EE.

3.3 Economic assessment

Table 4 provides the details on the major equipment and purchasing cost for both processes. The number of heating and cooling units were more in EE than SWE due to the recycle. As a result, the FCI for EE (NZ$5.13 million) was almost on par with FCI for SWE (NZ$5.29 million). The large equipment cost was also due to the extraction vessel capacity of 6.4 m^3. The operating time for EE is 8 h but 1 h for SWE; thus, a larger extraction vessel is necessary to meet the daily throughput demands. The direct and indirect cost items that contributed to the CAPEX estimation are presented in Table 4.

The annual production cost is comprised of variable and fixed cost and general expenses. The fixed cost included labour, supervision, laboratory, maintenance, insurance and taxes, and plant overhead, while variable cost comprised of raw materials, waste treatment, utility services and miscellaneous operating supplies. General expenses were taken as 25% of the direct production cost to cover for R&D, sales expenses, and general overheads. There were notable variations in the individual cost components of COM with the exemption for the COL. The COL was the same in both cases since the same workforce is assumed for SWE and EE, but their per cent contribution to the COM was different (Figure 4). The EE process presented a COM of NZ$4.7 million (NZ$5.57/kg product), which was about 4.6% higher than the NZ$4.49 million COM from SWE (NZ$2.14/kg product) for the same plant capacity, including ethanol recycle. This is mainly due to the cost of ethanol as raw material and additional energy required to remove it from the product. The additional strategy of recovering and recycling ethanol is a cost-saving step with ~81% reduction in raw material cost (CRM).

Table 4: Detailed factorial estimates of total capital investment (reference year: 2020)

S/N	Cost items	Factor	Cost (NZ$)	
			SWE	EE
1	**Total purchase cost of major equipment items**	1	1,349,725.50	1,307,808.10
2	Equipment erection	0.45	1,012,294.10	980,856.10
3	Piping	0.45	607,376.50	588,513.60
4	Instrumentation	0.15	202,458.80	196,171.20
5	Electrical	0.10	134,972.60	130,780.80
6	Buildings, process	0.10	134,972.60	130,780.80
7	Utilities†	0.45	-	-
8	Storages‡	0.20	-	-
9	Site development	0.05	67,486.30	65,390.40
10	Ancillary buildings	0.20	269,945.10	261,561.60
		A. Total physical plant cost (PPC) =	3,779,231.50	3,661,862.60
11	Design and engineering	0.25	944,807.90	915,465.70
12	Contractor's fee	0.05	188,961.60	183,093.10
13	Contingency	0.10	377,923.20	366,186.30
		B. Indirect costs =	1,511,692.70	1,464,745.10
		C. Fixed capital Investment =	5,290,924.20	5,126,607.70
14	Working capital	0.05 of FCI	264,546.21	256,330.39
		D. Total fixed capital investment =	5,555,470.41	5,382,938.09

†provided in COM, ‡provided in PCES

From Figure 4, CRM was the main factor defining the COM in both scenarios; similar influence is recorded in Zabot et al. [11]. It is a common trend for CRM to be a controlling cost factor at the early stages of a project [1]. The COM/kg product was lower for SWE than EE. The input of CWT on the COM was so small that it could not be represented visibly on the charts.

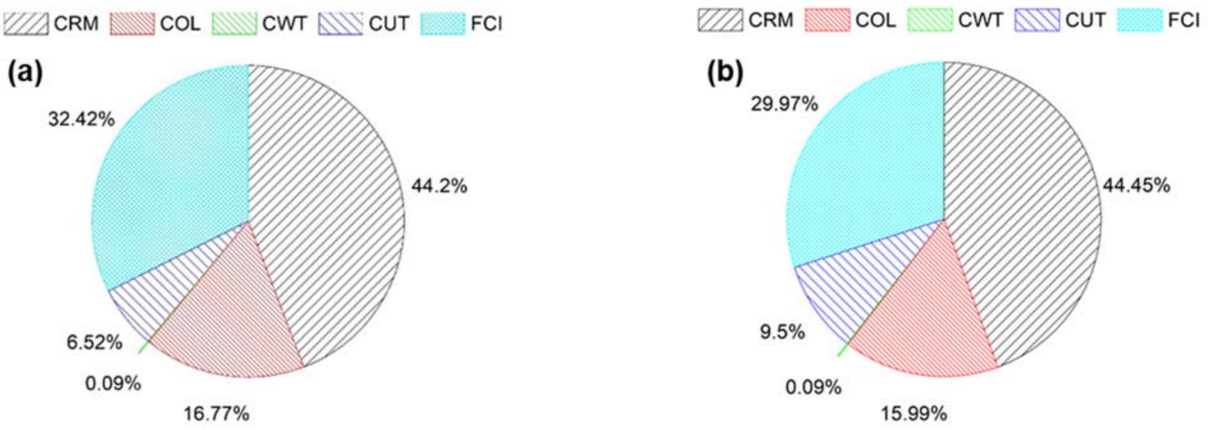

Figure 4: Contribution of individual cost components to the annual production cost for extracts from kānuka leaves using (a) subcritical water extraction (SWE) and (b) ethanol extraction (EE).

The revenues from each extraction process were calculated based on the polyphenol content (gallic acid equivalent) of the extracts at a product sale price estimated at NZ$0.002/mg GA. This information was used in determining the cash flow (Figure 5), which fed the economic indicators used in identifying the more profitable or feasible process. Table 5 shows the results of the profitability indices studied. An operating margin represents the portion of each dollar of revenue that is retained after the annual production cost is considered. It is a function of the CRM and COL and may fluctuate during tough economic times, thus ideal for companies that operate in the same industry [49]. The OpM for SWE was higher than that of EE since COL was the same in both scenarios.

The efficiency of investment in SWE and EE was also evaluated using ROI. This investment tool measures the amount of the return of an investment relative to the cost of investment. The values obtained were higher than 15%, which is the maximum range needed to accept or discard a project [50]. Although it is commonly used, the limitation is that it does not consider the “holding period” of an investment [51]. The annualised ROI is used to counter this limitation by including the number of years of the investment. The annualised ROI for SWE (6%) was still higher than that of EE (4%). Moreover, the payback period for capital investment was shorter for SWE than for EE. The NPV simply represents the surplus that investors can regain from the initial investment. The NPV was positive for both extraction processes, which means that the investment will generate a return higher than the discounted cash flow. As such, these investments can be undertaken. Finally, the IRR also called discounted cash flow rate of return, is the discount rate that would cause the NPV of a project to be \$0 (NPV=0). It assumes that the interim capital cash flows are reinvested at the same rate of return as that of the project that generated them [52]. The values obtained shows that, in addition to the use of non-toxic solvents for extraction, SWE has a competitive chance against EE in terms of economic returns.

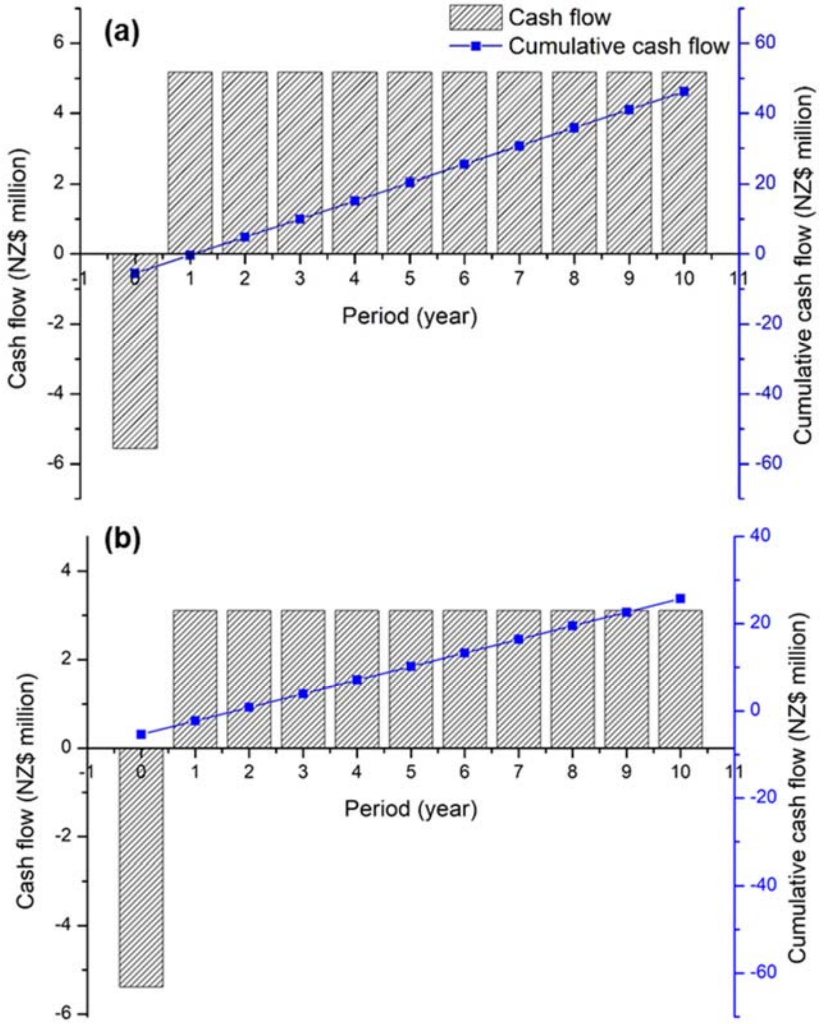

Figure 5: Cash flow of (a) subcritical water extraction (SWE) and (b) ethanol extraction (EE) (reference year: 2020)

Table 5: Profitability indicators of kānuka extract production for the two extraction scenarios, subcritical water extraction (SWE) and ethanol extraction (EE)

	SWE	EE
Unit production cost, NZ$/kg	2.14	5.57
Operating margin, %	59	43
ROI, %	84	48
Payback period, years	1.2	2.1
NPV, NZ$ millions	20.42	10.22
IRR, %	89	50

3.4 Sensitivity analysis

The results of the sensitivity analysis are summarised in Figure 6 and Figure 7. In Figure 6a-b, the annual and unit production cost is shown as having a linear relationship with the cost of kānuka leaves. This trend is expected since the cost of manufacturing is a function of CRM; thus, an increase in raw material cost increases the cost of manufacturing. As the cost price increased, the contribution of CRM to the annual production cost became more prominent and finally overtook shares of FCI as the most dominant cost component, at a cost price of NZ$40 per kg dry leaves. The opposite effect was observed in Figure 6c for NPV. The increasing cost of kānuka leaves had a negative impact on the NPV. NPV is dependent on the cash flow (positive and negative) from the production process. So as raw material cost (negative cash flow) increased, annual cash flow decreased, leading to a decreasing NPV. The effect of the product price on NPV is shown in Figure 6d. In order to make profit, the minimum product selling prices for ethanol and subcritical water extracts should cut-off at NZ$0.002 and NZ$0.0015, respectively. Lastly, the variation in SWE vessel capacity ranging from 100 – 2000 L was analysed. A change in plant size led to a corresponding change in equipment size, raw material and utility required per hour. A decrease in plant size caused a corresponding decrease in FCI (Figure 7). However, the per cent contribution of FCI to production cost increased (Figure 7) due to the decrease in key variable costs such as raw material cost (CRM) and utility cost, as a result of this vessel capacity reduction.

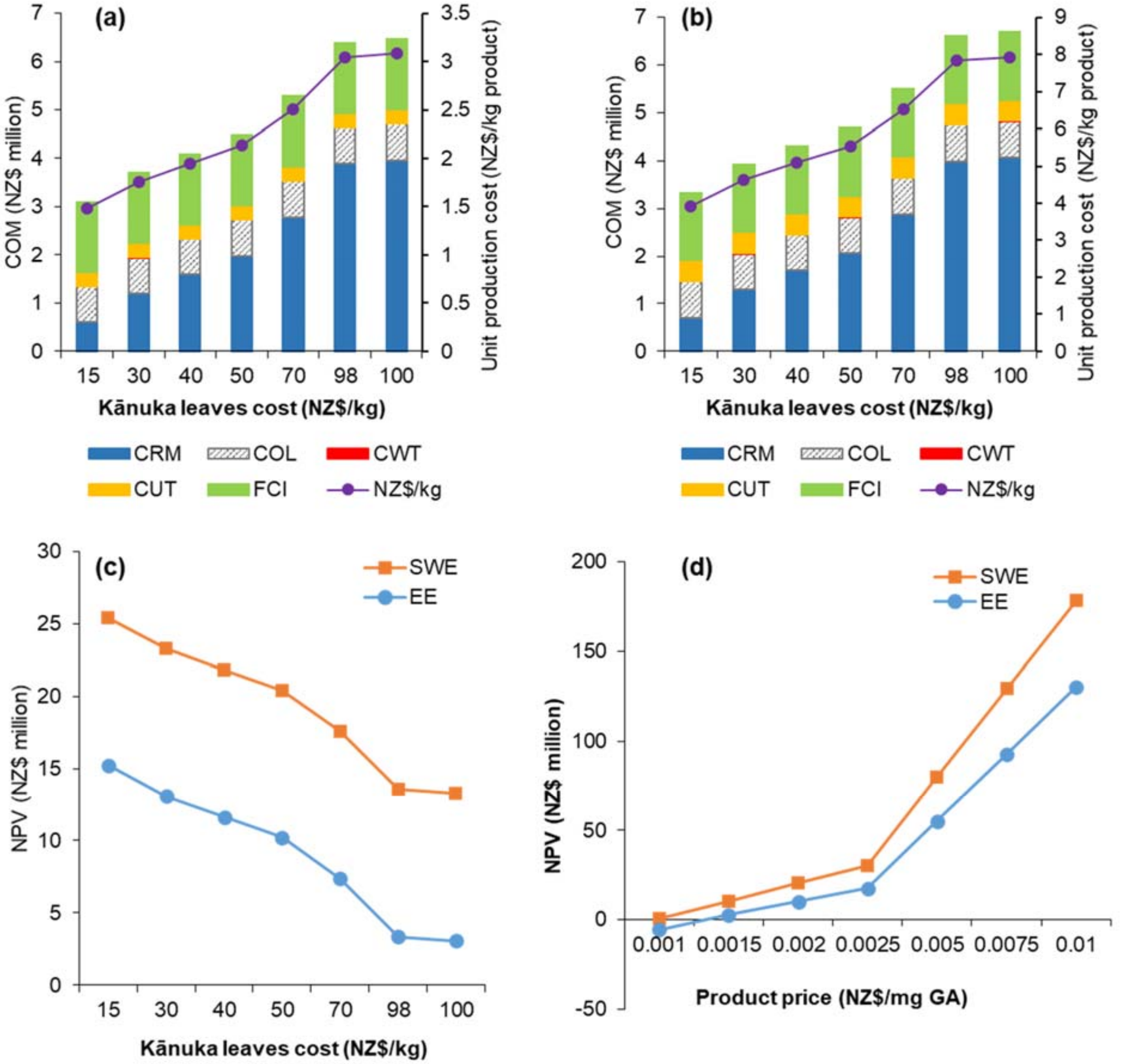

Figure 6: Cost of manufacturing as a function of the cost of kānuka leaves for (a) subcritical water extraction (SWE), (b) ethanol extraction (EE); and the impact of variation in (c) kānuka leaves cost and (d) product sale prices on NPV for SWE and EE.

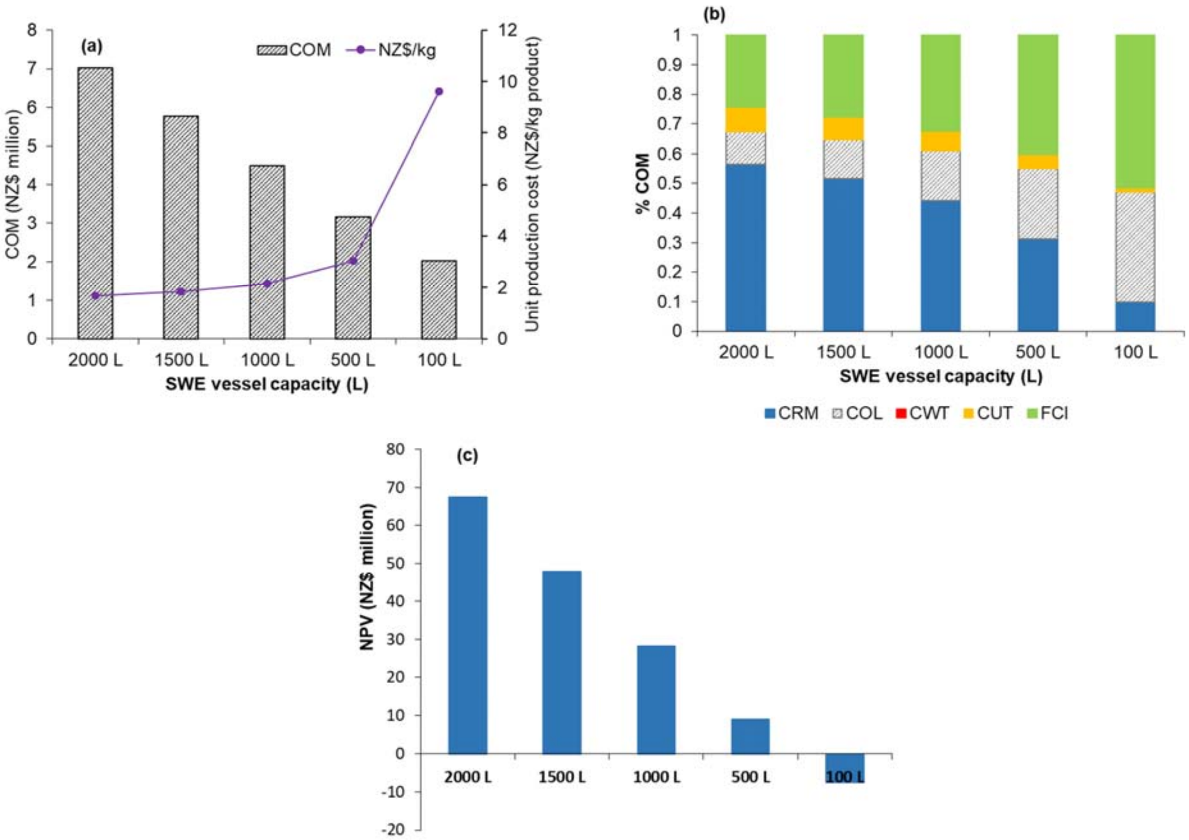

Figure 7: Effect of using different vessel capacities on (a) cost of manufacturing, (b) contribution of each component to COM, and (c) NPV for kānuka extract production using subcritical water extraction (SWE).

3.5 Environmental impact analysis

Eight impact categories were individually weighted and summed to give the total impact per kilogram of products (Figure 8). To assess both processes independent of their production rates, the results were presented as PEI generated within the process and that leaving/emitted by the system per kilogram of product. The generated PEI for both extraction processes were in the negative, indicating no influence of the processes on the environment. From figure 9, EE had a higher total PEI leaving the system than SWE. One reason is the contribution of the PCOP category, which is evaluated relative to organic solvent, in this case, ethanol, with concerns related to volatility [53]. Values for global atmospheric impact were all below zero for both extraction scenarios. Overall, the HTPE was the most influential impact of the total PEI leaving the system, for both kānuka leaves extraction scenarios, mainly due to the presence of gallic acid (polyphenol marker). Gallic acid, if not appropriately handled, has probable harmful effects as seen in suppliers' safety data sheets [30, 54]. With the inclusion of energy consumption to the analysis, the global atmospheric impacts factors, especially AP, became the more significant for total PEI generated and emitted for both scenarios, but more so for SWE. From our results, HTPE was the major contributor to the PEI leaving the system for both processes. Regardless, these values were all very small (<1) to be considered as having a severe environmental impact.

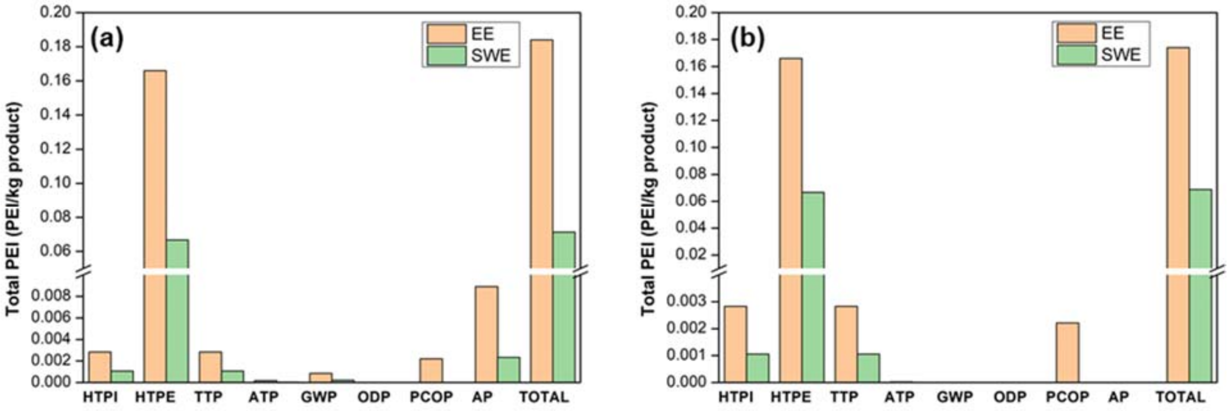

Figure 8: Potential Environmental Impacts of the two extraction scenarios per kilogram product (a) with and (b) without energy consumption

The carbon footprint due to the energy requirement per kilogram kānuka extract was higher for EE (0.50 kg CO_2-eq/kg kānuka extract) than for SWE (0.13 kg CO_2-eq/kg kānuka extract). The trend is like results in figure 8 and is associated with the solvent removal stage in EE. Additional relevant aspects to consider from the environmental standpoint are the impact of trace components on the final product and the generation and handling of solid residues. For the former, the EE technique is a major culprit; thus, a basis for developing and proposing SWE.

4 Conclusions

As evident from the studies, this is the first research assessing the technical readiness, economic feasibility, and environmental impact of using subcritical water extraction (SWE) in producing bioactive kānuka leaves extracts. A baseline throughput of 32 MT/year of kānuka leaves was employed in developing the TEA model. Our TEA results show the competitive advantage of using SWE over EE despite that industrial application is comparatively lower. Both extraction techniques are highly ranked TRL-based technologies as they have reached commercial stage. The comparative study demonstrated that the COM of the kānuka leaves extracts using SWE was 4% lower than EE while the NPV was 20% higher, for the same feedstock rate. These numbers are possible because of the duration of EE, which made the number of batches eight times less than in SWE. This long processing time is prevalent in EE processes. The product and feedstock price had a significant impact on the profitability of the process based on the results of the sensitivity analysis. It is quite apparent that SWE provides a better process option of the two since it has the highest rate of production and profits and the lowest PEI. It is important to note that sustainable availability of feedstock is crucial to the implementation of this process. The methodology used in this study can also be extended to value-recovery from other plant matrices using different extraction technologies.

Acknowledgment

The authors wish to acknowledge the insights given by Mr Mike Turner of New Zealand Extracts on bioactive product costing.

Declaration of competing interest

The authors declare no conflict of interest in the publication of this study.

Funding: This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

References

[1] S.O. Essien, B. Young, S. Baroutian, Recent advances in subcritical water and supercritical carbon dioxide extraction of bioactive compounds from plant materials, Trends Food Sci. Tech., 97 (2020) 156-169. https://doi.org/10.1016/j.tifs.2020.01.014.

[2] S.J. Bloor, Antiviral Phloroglucinols From New Zealand Kunzea Species, J. Nat. Prod., 55 (1992) 43-47.

[3] I. Braithwaite, A. Hunt, J. Riley, J. Fingleton, J. Kocks, A. Corin, C. Helm, D. Sheahan, C. Tofield, B. Montgomery, M. Holliday, M. Weatherall, R. Beasley, 2015. Randomised controlled trial of topical kānuka honey for the treatment of rosacea, BMJ Open, 5,e007651. https://doi.org/10.1136/bmjopen-2015-007651.

[4] S. Gannabathula, M.a. Skinner, D. Rosendale, J.M. Greenwood, A.N. Mutukumira, G. Steinhorn, J. Stephens, G.W. Krissansen, R.C. Schlothauer, Arabinogalactan proteins contribute to the immunostimulatory properties of New Zealand honeys, Immunopharmacol. Immunotoxicol., 34 (2012) 598-607. https://doi.org/10.3109/08923973.2011.641974.

[5] S.O. Essien, S. Baroutian, K. Dell, B. Young, Value-added potential of New Zealand mānuka and kānuka products: A review, Ind. Crop. Prod., 130 (2019) 198-207. https://doi.org/10.1016/j.indcrop.2018.12.083.

[6] S.O. Essien, B. Young, S. Baroutian, 2020. Subcritical water extraction for selective recovery of phenolic bioactives from kānuka leaves, J Supercrit. Fluid, 158,104721. https://doi.org/10.1016/j.supflu.2019.104721.

[7] Vegconomist, Plant Extracts Market: Global Scenario and Market Highlights, https://vegconomist.com/studies-and-numbers/plant-extracts-market-global-scenario-market-highlights/, 2019 (accessed 28 April 2020).

[8] R. Todd, S. Baroutian, A techno-economic comparison of subcritical water, supercritical CO 2 and organic solvent extraction of bioactives from grape marc, J Clean. Prod., 158 (2017) 349-358. https://doi.org/10.1016/j.jclepro.2017.05.043.

[9] A. Asiedu, S. Ben, E. Resurreccion, S. Kumar, Techno-economic analysis of protein concentrate produced by flash hydrolysis of microalgae, Environ. Prog. Sustain. Energy, 37 (2018) 881-890. https://doi.org/10.1002/ep.12722.

[10] R. Vardanega, P.I.N. Carvalho, D.T. Santos, M.A.A. Meireles, Obtaining prebiotic carbohydrates and beta-ecdysone from Brazilian ginseng by subcritical water extraction, Innov. Food Sci. Emerg. Technol., 42 (2017) 73-82. https://doi.org/10.1016/j.ifset.2017.05.007.

[11] G.L. Zabot, M.N. Moraes, P.I.N. Carvalho, M.A.A. Meireles, New proposal for extracting rosemary compounds: Process intensification and economic evaluation, Ind. Crop. Prod., 77 (2015) 758-771. https://doi.org/10.1016/j.indcrop.2015.09.053.

[12] P.F. Martins, M.M.R. de Melo, C.M. Silva, Techno-economic optimization of the subcritical fluid extraction of oil from Moringa oleifera seeds and subsequent production of a purified sterols fraction, J Supercrit. Fluid, 107 (2016) 682-689. https://doi.org/10.1016/j.supflu.2015.07.031.

[13] J. Wang, Z. Cui, Y. Li, L. Cao, Z. Lu, 2020. Techno-economic analysis and environmental impact assessment of citric acid production through different recovery methods, J Clean. Prod., 249,119315. https://doi.org/10.1016/j.jclepro.2019.119315.

[14] K. Duba, L. Fiori, Supercritical CO2 extraction of grape seeds oil: scale-up and economic analysis, Int. J. Food Sci. Technol., 54 (2019) 1306-1312. https://doi.org/10.1111/ijfs.14104.

[15] C.G. Pereira, M.A.A. Meireles, Supercritical Fluid Extraction of Bioactive Compounds: Fundamentals, Applications and Economic Perspectives, Food Bioprocess. Tech., 3 (2010) 340-372. https://doi.org/10.1007/s11947-009-0263-2.

[16] M. Ravber, Ž. Knez, M. Škerget, Isolation of phenolic compounds from larch wood waste using pressurized hot water: extraction, analysis and economic evaluation, Cellulose, 22 (2015) 3359-3375. https://doi.org/10.1007/s10570-015-0719-7.

[17] J.Q. Albarelli, D.T. Santos, M.J. Cocero, M.A.A. Meireles, Perspectives on the integration of a supercritical fluid extraction plant to a sugarcane biorefinery: thermo-economical evaluation of CO2 recycle systems, Food Sci. Tech., 38 (2017) 13-18. https://doi.org/10.1590/1678-457x.33516.

[18] G.M. Wilson, Vapor-Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing, J. Am. Chem. Soc., 86 (1964) 127-130. https://doi.org/10.1021/ja01056a002.

[19] K.G. Joback, R.C. Reid, Estimation of pure-component properties from group-contributions, Chem. Eng. Commun., 57 (1987) 233-243. https://doi.org/10.1080/00986448708960487.

[20] F. Mosca, G.I. Hidalgo, J. Villasante, M.P. Almajano, 2018. Continuous or Batch Solid-Liquid Extraction of Antioxidant Compounds from Seeds of Sterculia apetala Plant and Kinetic Release Study, Molecules, 23,1759. https://doi.org/10.3390/molecules23071759.

[21] K. Tochigi, H. Inoue, K. Kojima, Determination of azeotropes in binary systems at reduced pressures, Fluid Phase Equilib., 22 (1985) 343-352. https://doi.org/10.1016/0378-3812(85)87030-8.

[22] V.H. Álvarez, S. Mattedi, M. Iglesias, R. Gonzalez-Olmos, J.M. Resa, Phase equilibria of binary mixtures containing methyl acetate, water, methanol or ethanol at 101.3 kPa, Phys. Chem. Liq., 49 (2011) 52-71. https://doi.org/10.1080/00319100903012403.

[23] R.J. Wooley, V. Putsche, Development of an ASPEN PLUS physical property database for biofuels components, National Renewable Energy Laboratory, Colorado, 1996.

[24] Cheméo, Chemical Properties of Benzoic acid, 3,4,5-trihydroxy- (CAS 149-91-7), https://www.chemeo.com/cid/30-592-1/Benzoic%20acid%2C%203%2C4%2C5-trihydroxy-#ref-joback, 2016 (accessed 8 April 2020).

[25] T.O. Dabir, V.G. Gaikar, S. Jayaraman, S. Mukherjee, Thermodynamic modeling studies of aqueous solubility of caffeine, gallic acid and their cocrystal in the temperature range of 303 K–363 K, Fluid Phase Equilib., 456 (2018) 65-76. https://doi.org/10.1016/j.fluid.2017.09.021.

[26] A. Daneshfar, H.S. Ghaziaskar, N. Homayoun, Solubility of Gallic Acid in Methanol, Ethanol, Water, and Ethyl Acetate, J. Chem. Eng. Data, 53 (2008) 776-778. https://doi.org/10.1021/je700633w.

[27] J. Dykyj, J. Svoboda, R.C. Wilhoit, M. Frenkel, K.R. Hall, Organic Compounds, C1 to C57. Part 1, in: K.R. Hall (Ed.) Vapor Pressure and Antoine Constants for Oxygen Containing Organic Compounds, Springer-Verlag Berlin Heidelberg, 2000, pp. 14-111.

[28] National Center for Biotechnology Information, PubChem Database. Gallic acid, CID=370. https://pubchem.ncbi.nlm.nih.gov/compound/Gallic-acid, 2020 (accessed 8 April 2020)

[29] National Center for Biotechnology Information, PubChem Database. Cellulose, CID=16211032. https://pubchem.ncbi.nlm.nih.gov/compound/CELLULOSE, 2020 (accessed 8 April 2020)

[30] Chemwatch, Gallic acid. 2018 (accessed 8 April 2020)

[31] S.M. Vilas-Boas, P. Brandão, M.A.R. Martins, L.P. Silva, T.B. Schreiner, L. Fernandes, O. Ferreira, S.P. Pinho, Solubility and solid phase studies of isomeric phenolic acids in pure solvents, J. Mol. Liq., 272 (2018) 1048-1057. https://doi.org/10.1016/j.molliq.2018.10.108.

[32] NASA, Technology Readiness Level, https://www.nasa.gov/directorates/heo/scan/engineering/technology/txt_accordion1.html, 2012 (accessed 22 May 2020).

[33] B. Li, I.A. Udugama, S.S. Mansouri, W. Yu, S. Baroutian, K.V. Gernaey, B.R. Young, An exploration of barriers for commercializing phosphorus recovery technologies, J Clean. Prod., 229 (2019) 1342-1354. https://doi.org/10.1016/j.jclepro.2019.05.042.

[34] G. Náthia-Neves, R. Vardanega, M.A.A. Meireles, Extraction of natural blue colorant from Genipa americana L. using green technologies: Techno-economic evaluation, Food Bioprod. Process., 114 (2019) 132-143. https://doi.org/10.1016/j.fbp.2018.12.004.

[35] Matches, Matches' Process Equipment Cost Estimates. https://www.matche.com/equipcost/EquipmentIndex.html, 2014 (accessed 14 April 2020)

[36] Chemical Engineering, The Chemical Engineering Plant Cost Index, https://www.chemengonline.com/pci, 2019 (accessed 14 April 2020).

[37] R.K. Sinnott, 6 - Costing and Project Evaluation, in: Coulson and Richardson's Chemical Engineering Volume 6 - Chemical Engineering Design (4th Edition), Elsevier, 2005, pp. 243-279.

[38] Ministry of Business Innovation and Employment, Energy Prices, 2020. https://www.mbie.govt.nz/building-and-energy/energy-and-natural-resources/energy-statistics-and-modelling/energy-statistics/energy-prices/.

[39] Lab Alley, Food Grade Ethanol, https://www.laballey.com/products/buy-pure-food-grade-ethanol-undenatured-acs-usp-grade-55-gallon-drum-poly-700, 2020 (accessed 16 April 2020).

[40] Watercare, Non-domestic water and wastewater charges and IGC, https://www.watercare.co.nz/CMSPages/GetAzureFile.aspx?path=~\watercarepublicweb\media\watercare-media-library\fees-charges\non_domestic_charges.pdf&hash=018ea5c71d0912f5e7f2e2a7f695bf2ec3827c86de6dbbf9a4fd162676aa0ee5, 2020 (accessed 15 April 2020).

[41] J. Cristobal, C. Caldeira, S. Corrado, S. Sala, Techno-economic and profitability analysis of food waste biorefineries at European level, Bioresour. Technol., 259 (2018) 244-252. https://doi.org/10.1016/j.biortech.2018.03.016.

[42] D. Dursun, A. Koulouris, A.C. Dalgıç, Process Simulation and Techno Economic Analysis of Astaxanthin Production from Agro-Industrial Wastes, Waste Biomass Volari., 11 (2018) 943-954. https://doi.org/10.1007/s12649-018-0439-y.

[43] G.L. Zabot, I.P. Bitencourte, M.V. Tres, M.A.A. Meireles, Process intensification for producing powdered extracts rich in bioactive compounds: An economic approach, J Supercrit. Fluid, 119 (2017) 261-273. https://doi.org/10.1016/j.supflu.2016.10.003.

[44] H. Cabezas, J.C. Bare, S.K. Mallick, Pollution prevention with chemical process simulators: the generalized waste reduction (WAR) algorithm—full version, Comput. Chem. Eng., 23 (1999) 623-634. https://doi.org/10.1016/S0098-1354(98)00298-1.

[45] D. Young, R. Scharp, H. Cabezas, The waste reduction (WAR) algorithm: environmental impacts, energy consumption, and engineering economics, Waste Manage. (Oxford), 20 (2000) 605-615. https://doi.org/10.1016/S0956-053X(00)00047-7.

[46] IPCC, 2006 IPCC Guidelines for National Greenhouse Gas Inventories, Prepared by the National Greenhouse Gas Inventories Programme, in: Eggleston H.S., Buendia L., Miwa K., Ngara T., T. K. (Eds.), IGES, Japan, 2006.

[47] L.V. Daza Serna, C.E. Orrego Alzate, C.A. Cardona Alzate, Supercritical fluids as a green technology for the pretreatment of lignocellulosic biomass, Bioresour. Technol., 199 (2016) 113-120. https://doi.org/10.1016/j.biortech.2015.09.078.

[48] J. Moncada, J.A. Tamayo, C.A. Cardona, Techno-economic and environmental assessment of essential oil extraction from Oregano (*Origanum vulgare*) and Rosemary (*Rosmarinus officinalis*) in Colombia, J Clean. Prod., 112 (2016) 172-181. https://doi.org/10.1016/j.jclepro.2015.09.067.

[49] W. Kenton, M. James, Operating Margin Definition, https://www.investopedia.com/terms/o/operatingmargin.asp, 2020 (accessed 12 May 2020).

[50] R. Vardanega, P.I.N. Carvalho, J.Q. Albarelli, D.T. Santos, M.A.A. Meireles, Techno-economic evaluation of obtaining Brazilian ginseng extracts in potential production scenarios, Food Bioprod. Process., 101 (2017) 45-55. https://doi.org/10.1016/j.fbp.2016.10.010.

[51] J. Chen, J. Mansa, Return on Investment (ROI), https://www.investopedia.com/terms/r/returnoninvestment.asp, 2020 (accessed 16 May 2020).

[52] CFO, Internal Rate of Return: A Cautionary Tale https://www.cfo.com/strategy/2004/10/internal-rate-of-return-a-cautionary-tale/, 2004 (accessed 23 April 2020).

[53] S. Meramo-Hurtado, C. Alarcón-Suesca, Á.D. González-Delgado, 2020. Exergetic sensibility analysis and environmental evaluation of chitosan production from shrimp exoskeleton in Colombia, J Clean. Prod., 248,119285. https://doi.org/10.1016/j.jclepro.2019.119285.

[54] Cayman chemical, Safety Data Sheet - Gallic acid, https://www.caymanchem.com/msdss/11846m.pdf, 2019 (accessed 13 May 2020).

APPENDIX A

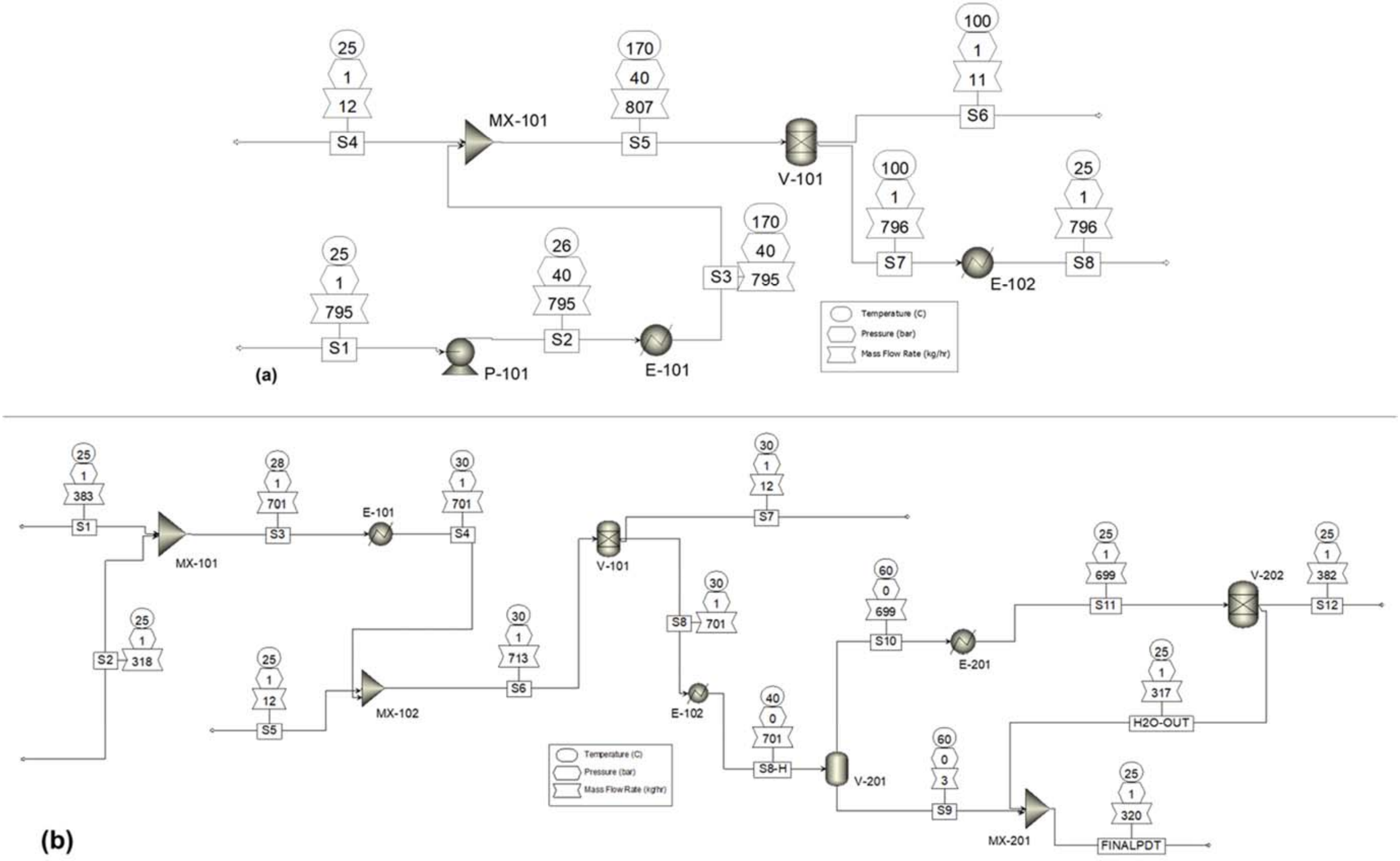

Figure A.1: Flowsheet of (a) subcritical water extraction and (b) ethanol extraction developed in the Aspen Plus® software

603