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Extraction kinetics and yield optimization of aronia pomace using supercritical CO_2

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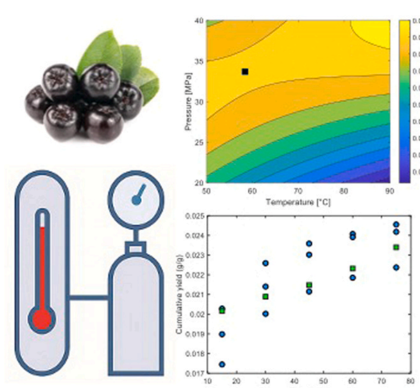
HIGHLIGHTS

- $scCO_2$ with 5 % ethanol yielded 165 mg GAE/100 g, 43 % more phenolics than CO_2 alone.
- A neural network accurately predicted extraction yields across conditions and time.
- Highest yield was 2.7 g extract/100 g pomace at 90 °C, 40 MPa using neat $scCO_2$.
- Crossover point found at 58.4 °C, 33.7 MPa, critical for optimization.

GRAPHICAL ABSTRACT



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ABSTRACT

The increasing interest in *Aronia melanocarpa* berries for their antioxidant properties sets the necessity to define sustainable strategies to valorize the by-products. This study investigates the use of supercritical carbon dioxide ($scCO_2$) extraction, with and without ethanol as a co-solvent, for recovering lipophilic and phenolic compounds from aronia pomace. Extractions were performed at 20, 30, and 40 MPa and temperatures of 50, 70, and 90 °C. A yield of about 2.7 g per 100 g of dried pomace was obtained at 40 MPa and 90 °C. However, the highest total phenolic content of about 165 mg of gallic acid equivalent per 100 g of dried pomace was achieved with 5 % ethanol co-solvent at 50 °C and 30 MPa. The lipid extracts were rich in linoleic acid and the wax portion increased under low-density $scCO_2$ conditions. A feedforward neural network was developed to model extraction kinetics and predict yield as a function of temperature, pressure, and time, demonstrating high predictive accuracy. These findings highlight $scCO_2$ extraction as a viable route for the efficient and selective recovery of valuable bioactives from aronia pomace, contributing to a circular bioeconomy.

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1. Introduction

The genus *Aronia* consists of shrubs native to the eastern United States, and it was introduced to Europe in the 1900. The common name chokeberry derives from observations that birds initially avoid the fruits, typically consuming them only later in the winter when alternative food sources are limited [1]. This is presumed to result from the high tannin content of the berries, which imparts an astringent taste that may also reduce their appeal to humans.

Two species of aronia are commonly recognized: red chokeberry (*Aronia arbutifolia*) and black chokeberry (*Aronia melanocarpa*). In this work, the latter species is considered and hereafter referred to simply as aronia.

Today, various aronia-based products, such as tea [2], powder, capsules, and juices [3], are available to consumers. The global chokeberry market was valued at $356.9 million in 2023 and is projected to exceed $498.7 million by 2033 [4]. This popularity was largely due to its reputation as a functional food due to the high content of components considered beneficial for health and well-being [5]. This provided the momentum for extensive studies in establishing the relationship between the consumption of aronia extracts and different diseases. For example, Asahi et al. [6] provided evidence for using aronia extracts as a safe, cost-effective, and multi-targeted complementary and integrative therapeutic modality in colorectal cancer. Other studies focused on the relation between aronia supplements, arterial function and gut microbiome [7] or the blood glucose level [8] among others.

Together with medical-related studies, other research contributions revolved around aronia berries. In particular, the characterization of the extracts highlighted their richness in phenolic substances such as proanthocyanidins, anthocyanidins and other flavonoids, as well as phenolic acids [9].

From an engineering perspective, it is crucial to establish well-defined processes that ensure the preservation of bioactive compounds in aronia berries extracts or their effective extraction and concentration. These compounds play a significant role in shaping consumer perception of product quality. Therefore, optimizing processing conditions to retain these key constituents is essential for functional efficacy and market competitiveness.

Yuan et al. [10] studied the effect of high-pressure processing as an alternative to thermal processing for aronia puree. The authors concluded that the treatment at 600 MPa for 5 min effectively extends the microbial shelf-life, maintaining the quality and preserving the bioactive antioxidants during 8 weeks of refrigerated storage at 4 °C.

Demircan et al. [11] compared various drying methods and demonstrated that freeze-drying was the most effective in preserving the nutritional and physical properties of aronia berries. This method retained higher levels of bioactive compounds and antioxidant activity while minimizing browning and the formation of undesirable compounds.

This summary underscores aronia berries' growing interest, potential health benefits, and the processing technologies available to preserve their bioactive components. Beyond these aspects, increasing attention is being directed toward the valorization of by-products generated during extraction, particularly through biocascade approaches [12]. Depending on the processing method, the yield of pomace can range from 13 % to 23 % by weight [13], representing a significant volume of residual material. Rather than being relegated to low-value applications such as animal feed or landfill disposal, this by-product presents opportunities for higher-value utilization.

Following this principle, Vagiri and Jensen [13] explored the possibility of using the pomace for the extraction of natural food colour ingredients. The authors proved a valorization pathway for juice production residues by studying the concentration of anthocyanins in the pomace. Andrade et al. [14] optimized a continuous system for the anthocyanins extraction from aronia pomace using a 1.5 % solution of citric acid under pressurized conditions (180 bar and 70 °C) and assisted by ultrasounds. Dulf et al. [15] instead used solid-state fermentation to increase the extractable phenolics and lipids with better nutritional-quality characteristics.

Among all the recovery techniques, supercritical carbon dioxide (scCO_2) extraction has emerged as a green method for valorizing a variety of substrates [16–18]. Wozniak et al. [19] investigated different extraction conditions using relatively high amounts of ethanol as a cosolvent, while Wenzel et al. [20] carried out a similar analysis under comparable conditions. These studies highlight the need for further work to optimize scCO_2 extraction of aronia pomace, not only through experimental trials but also by developing predictive modeling. Modeling not only clarifies the complex mechanisms governing extraction but also enables process optimization, scale-up, and reliable prediction of performance under different operating conditions. Supercritical fluid extraction (SFE) can be mathematically described using general equations that govern solute transport between the solid matrix and the supercritical fluid [21]. These include solute mass balances for both phases and expressions for solute transfer across the interface. However, developing such first-principles models is often challenging because of the coupled nonlinear phenomena involved [22]. To address these challenges, data-driven approaches, as neural network models, have gained interest [23]. Neural networks can learn directly from experimental data, effectively capturing nonlinear extraction dynamics without requiring explicit mechanistic formulations. As a result, they have become powerful tools for predicting extraction yields under diverse operating conditions and for complementing or extending traditional kinetic models [24].

In this work supercritical extraction with neat CO2 and with ethanol was considered and performances compared in terms of yield, lipid profile and total phenolic content. Moreover, a neural network model was developed for the prediction of kinetics in supercritical extraction processes in order to obtain a valid support for process optimization.

2. Materials and methods

2.1. Sample preparation, moisture analysis, and particle size distribution

Aronia pomace was sourced from Elkærholm (Egtved, Denmark). After harvesting, the aronia berries were frozen. Once thawed, the berries were pressed using a hydropress, which separates the fruit juice from the pomace. The pomace was stored at −20 °C until further use. Before extraction, the pomace was defrosted overnight at 4 °C, then dried in a Memmert oven (model 100–800) at 70 °C for 8 h. The drying temperature was selected based on Suslu et al. [25] to preserve the phenolic content. Subsequently, the dried pomace was ground into a fine powder using a knife mill (Retsch Grindomix GM 300) operated at 4000 rpm for 90 s. The resulting powder was stored in sealed Ziploc bags and kept at −20 °C until needed.

The moisture content of the dried pomace was measured in the Shimadzu MOC-120H analyzer. Moisture content was measured using 10 g of sample at a set temperature of 120 °C. The measurement was concluded when the moisture loss over the preceding 30 s fell below 0.10 %. The particle size distribution was measured in a Beckman Coulter LS 13 320 Laser Diffraction Particle Size Analyzer.

The measurements were done in triplicate.

2.2. Soxhlet extraction

Soxhlet extractions were performed in triplicate according to the Official Method of Analysis [26]. The solvents used, ordered from the most polar to the least, are: ethanol (96 % v/v, VWR France), ethyl acetate (99.8 % v/v, VWR Poland), and n-hexane (97 % v/v, VWR Poland). For each extraction, 5 ± 0.005 g of dried aronia pomace and 190 mL of solvents were used. The temperature of the condenser was maintained at 3 °C by using a Büchi circulating cooler, while the heating plate temperature was adjusted according to the solvent used, ranging from 150 to 175 °C. The extractions were carried out for 8 h and the extracts were dried using a rotary evaporator (Büchi R-210).

The extraction yield was evaluated as the ratio between the mass of the dried extract and the mass of the dried sample.

2.3. Supercritical CO_2 extraction

Supercritical fluid extractions were performed using a laboratory-scale setup (Applied Separations Spe-ed™ SFE-2) equipped with a 50 mL stainless steel extraction vessel. Extractions were carried out in semi-batch mode for 75 min. Approximately 33 g of dried aronia pomace was loaded into the extraction vessel. A 15-minute static pressurization step was applied before the dynamic extraction, enabling the system to achieve both thermal and mechanical equilibration. Then, supercritical CO_2 was continuously passed through the reactor, with the flow rate maintained between 3.0 and 3.2 L min^{-1} (measured at 20 °C and atmospheric pressure). Extracts were collected every 15 min corresponding to 5 samples for each run. Each sample was weighed to monitor the extraction yield over time. Extracts for each run were mixed to guarantee sufficient sample quantity for the analyses and stored at −20 °C until further use.

The extractions were conducted under the following conditions: 20, 30, and 40 MPa and 50, 70, and 90 °C. The scCO2 density corresponding to the different operative conditions is reported in Table 1.

The CO_2 density ranged from 533.17 kg/m^3 at 20 MPa and 90 °C to 923.32 kg/m^3 at 40 MPa and 50 °C, representing a variation of approximately 73 %.

The same experimental procedure was applied for the extractions using ethanol (absolute, VWR France) as co-solvent. The modifier was fed to the reactor through a pump (Applied Separations, model 71721). Experiments were conducted at 30 and 40 MPa and 50 °C. The ethanol concentration was fixed at 5 % m/m, as higher concentrations resulted in excessive ethanol entrainment.

All $scCO_2$ extractions were conducted in triplicate.

2.4. Neural network model

A feedforward neural network (NN) was employed to reconstruct the behaviour of the extract yield at different sampling times and operating conditions. The selected inputs to the model included process conditions such as temperature, pressure, and the sampling time. The experimental data obtained at the conditions in Table 1 were divided into training, validation, and test sets to ensure robust model evaluation. Data collected at 70 °C and 40 MPa were used for validation, while data from 50 °C and 30 MPa were used for testing. To identify the optimal network structure, various configurations were evaluated by varying the number of hidden neurons and the activation functions. The optimization of the neural network architecture and training was conducted using the Neural Network Toolbox in MATLAB. The selection of the best model was based on minimizing the mean squared error (MSE) for the validation set.

Considering the number of experimental conditions, a single hidden layer NN was adopted, with the minimum number of hidden neurons required to achieve an accurate description of the system while avoiding overfitting. This approach ensured a balance between model complexity and predictive performance.

Before training, the input data were normalized to a range between −1 and + 1 to ensure consistent scaling and enhance the network's learning efficiency. Similarly, the output data were scaled to fall within the range of −0.95 to + 0.95. This choice is due to the behaviour of the commonly used hyperbolic tangent activation function. Near its extremities (-1 and +1), the derivative of the activation function approaches zero, reducing its sensitivity to changes in input values.

Table 1
Correspondence between $scCO_2$ and operational conditions. Data retrieved from NIST [27].

Pressure [MPa]	Temperature [°C]	Density [kg m^{-3}]
20	50	784.29
	70	659.05
	90	533.17
30	50	870.43
	70	787.97
	90	703.27
40	50	923.32
	70	856.70
	90	789.73

2.5. Total phenolic content

The total phenolic content (TPC) was measured using the Folin-Ciocalteu assay. The assay was performed by mixing 10 μL of an appropriately diluted sample with 100 μL of a 1:10 diluted Folin-Ciocalteu reagent (Sigma-Aldrich) in a 1.5 mL Eppendorf tube, which was then vortexed for 10 s. Subsequently, 80 μL of a 5 % (w/v) sodium carbonate solution was added, and the mixture was vortexed again for 10 s. After a 30-minute incubation period at room temperature, 100 μL of the mixture was transferred to a Greiner Bio-One half-area 96-well plate. The absorbance was then measured at 760 nm using a BioTek Synergy H1 plate reader.

A standard curve was constructed using gallic acid standards in the range of 0–1 mg/mL. The total phenolic content of the samples was expressed as mg of gallic acid equivalents (GAE) in 100 g of dried matter (DM) used for the extraction. All samples were treated in the same manner as the standards.

2.6. FAME determination

For lipid analysis, a secondary extraction was performed. Approximately 0.3 g of the dried sample was placed into an 8 mL glass vial, followed by the addition of 5 mL of hexane (technical grade isomers; Fisher Scientific, Massachusetts, USA). The mixture was vortexed, then shaken for 5 min at 60 rpm (Loopstar, IKA, Germany), and subsequently centrifuged for 5 min at 4000 RCF (Universal 320, Germany). The hexane phase was carefully collected into a round-bottom flask, and the extraction was repeated twice more under the same conditions. All hexane extracts were mixed, evaporated, and the residue weighed.

Approximately 5 mg of the lipid extract was derivatized via acid-catalyzed esterification and analyzed as fatty acid methyl esters (FAMEs) by gas chromatography with flame ionization detection (GC-FID; Shimadzu, Kyoto, Japan), according to the following procedure. A 0.5 μL sample was injected into a GC-FID 2030 using a 1:10 split ratio at 300 °c. It was separated on a 30 m × 0.25 mm × 0.25 μm HP-5MS column (Agilent, Santa Clara, USA). Hydrogen (6.0, Linde, Dublin, Ireland) served as the carrier gas in linear velocity mode at 37 cm/sec. The oven temperature started at 80 °C, then increased at 20 °C/min to 140 °C, where it was held for 15 min. Subsequently, it rose to 230 °C at 3 °C/min, then to 320 °C at 20 °C/min, with a 5-minute hold at the end. The total run time was 46.17 min. Detection was performed at 325 °C using nitrogen as the make-up gas [28] .

2.7. Statistical analysis

ANOVA and post hoc Tukey tests were performed using MATLAB 2024a and cross-validated with Minitab 22. Polynomial models were fitted using a stepwise regression procedure within the General Linear Model (GLM) framework in Minitab 22, with entry and removal significance levels (α) set at 0.10.

3. Results and discussion

The moisture content of the dried pomace used throughout the experimental campaign was 3.29 ± 0.16 %. The pomace's average particle diameter after milling was 795 μm, while the complete distribution is reported in the Supplementary Material (Fig. S1).

3.1. Soxhlet extraction

Soxhlet extraction is commonly used as a reference method to determine the maximum yield of extractable components [29].

The extraction in ethanol resulted in 0.464 ± 0.03 g/g_{DM}. This value is higher than the average yield of 25.9 % reported by Grunovaite et al. [30] and closer to the 35.7 % obtained by Mikami et al. [31], who used a two-step overnight maceration.

However, direct comparison may be misleading due to differences in berry quality and the processing method. Extraction yields with ethyl acetate and n-hexane resulted in 0.171 ± 0.024 g/g_{DM} and 0.063 ± 0.007 g/g_{DM}, respectively. While no reference value was available for ethyl acetate, the yield with n-hexane is consistent with the literature [30].

3.2. Supercritical extraction

Fig. 1 reports the extraction kinetics for the 3 pressures explored and for a temperature of 90 °C expressed as cumulative yield over time. The curves for 50 and 70 °C are reported in the Supplementary Material (Fig. S2, S3).

After approximately 30 min, the amount of extract recovered begins to decrease, which can be attributed to a diffusion-controlled transfer mechanism. Based on this observation, the extraction time was set to 75 min for all trials.

Fig. 2 presents the extraction yields as a function of $scCO_2$ density, grouped according to the 3 temperature levels investigated.

As expected, the yield is influenced by the solvent power expressed by its density and the temperature that enhances the components' solubility. The lowest extraction yields are obtained for the lowest value of the $scCO_2$ density, while the influence of the temperature is visualized in Fig. 3.

The measured values of the yields, expressed as the average of three repetitions with their standard deviations, are provided in the Supplementary Material (Table S1).

Temperature affects solubility through two competing mechanisms: increasing temperature raises the solute vapor pressure, promoting solubility in the supercritical fluid, but simultaneously decreases solvent density. This appears evident at lower extraction pressures (20 MPa) where the solvent density effect dominates, as indicated by a decrease in yield from 50 to 90 °C. At 30 MPa, a crossover point is observed, beyond which vapor pressure becomes the prevailing factor influencing yield, although the differences among values are less pronounced compared to

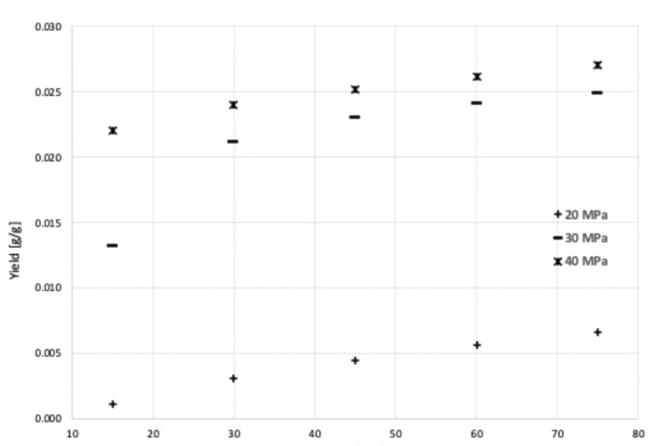

Fig. 1. Extraction kinetics for a temperature of 90 °C.

those at 20 MPa.

The highest yield observed in this study was 0.0269 ± 0.0002 g/g_{DM}, obtained at 40 MPa and 90 °C. This result is comparable to the optimal yield of 0.0295 g/g_{DM} reported by Grunovaite et al. [30] obtained at the same pressure but at the lowest temperature of 40 °C, although their extraction time was 149 min, corresponding to 548 g of CO_2 used, while 414 g were used in the present work.

A preliminary two-way ANOVA was conducted to examine the main effects of pressure and temperature, as well as their interaction, on the extraction yield. The results, summarized in

Table 2, show that both the main effects and the interaction term are statistically significant. This confirms the interpretation from Fig. 3, which indicated a clear interaction between pressure and temperature.

To assess the effect of temperature at each pressure level, separate one-way ANOVA tests were conducted under fixed pressure conditions. Where a statistically significant temperature effect was observed ($p < 0.05$), post-hoc analysis using Tukey's Honestly Significant Difference (HSD) test was applied to determine pairwise differences between temperature levels.

At 20 MPa, the one-way ANOVA revealed a statistically significant effect of temperature on extraction yield ($p < 0.05$). To explore pairwise differences between temperature levels, Tukey's HSD test was performed. Detailed results are provided in Tables S2 and S3 of the Supplementary Material. The results indicated that all temperature levels differed significantly. A positive correlation between temperature and yield was observed, with yield increasing consistently as temperature rose under this pressure condition. This pattern supports the trend shown in Fig. 3.

At 30 MPa (see Table S4 of the Supplementary Material), the ANOVA results showed no statistically significant differences in yield across the tested temperature levels, indicating that temperature had no measurable effect on yield under these conditions. In contrast, at 40 MPa, temperature had a statistically significant effect on extraction yield ($p < 0.05$). Post-hoc analysis using Tukey's HSD test indicated that the yield at 90 °C was significantly higher than those at 50 °C and 70 °C, aligning with the crossover effect observed in Fig. 3. However, no significant difference was detected between the yields at 50 °C and 70 °C. Detailed results are presented in Tables S5 and S6 of the Supplementary Materials.

Based on the ANOVA results, a regression model was developed to further explore the relationship between yield, pressure, and temperature. While mechanistic models can provide physical insight, the present work adopts a polynomial model selected through a stepwise procedure based on a significance threshold of $p < 0.10$. This approach ensures that only statistically significant terms are retained, thereby avoiding overfitting while capturing the effective nonlinearities of the system. In particular, the inclusion of quadratic and interaction terms allows the model to account for higher-order dependence of the yield on temperature and pressure. These contributions are rigorously different from zero, as demonstrated by the stepwise regression and ANOVA (see Tables S7 and S8 of the Supplementary Materials), confirming that they reflect genuine process behaviour rather than noise. As a result, the polynomial model provides a parsimonious yet reliable representation that effectively captures the peculiarities of the process under investigation. A linear polynomial structure was used, and model terms were chosen through a stepwise selection process based on a significance threshold of $p < 0.10$. The final model is reported in Eq. 1 and illustrated in Fig. 4. It accounts for 93.7 % of the variance in the response variable (R^2=0.937), confirming the adequacy of the fitted surface and aligning with the performance of polynomial models previously reported for supercritical fluid extraction in related applications [32,33]. The validity of the model is further supported by residual analysis (see Figure S4 of the Supplementary Materials).

$$Yield = 0.0250 - 7.75 \quad 10^{-4} \quad T + 1.42 \quad 10^{-3} P - 4.1 \quad 10^{-5} P^2 + 2.3 \quad 10^{-5} \quad T \quad P \tag{1}$$

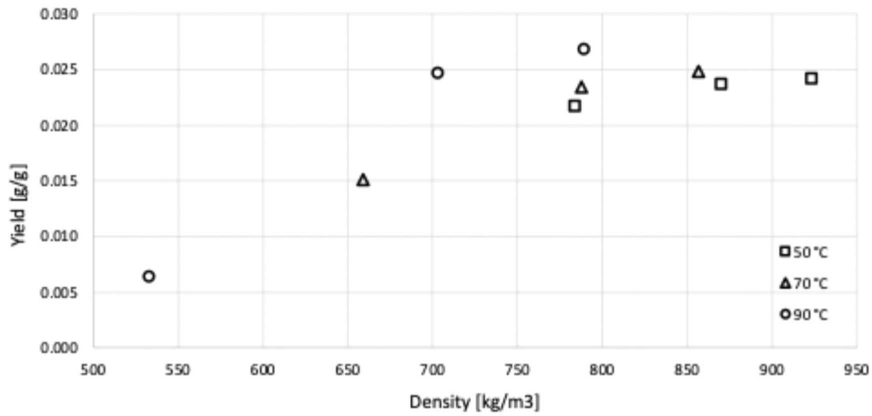

Fig. 2. Extraction yield as a function of $scCO_2$ density.

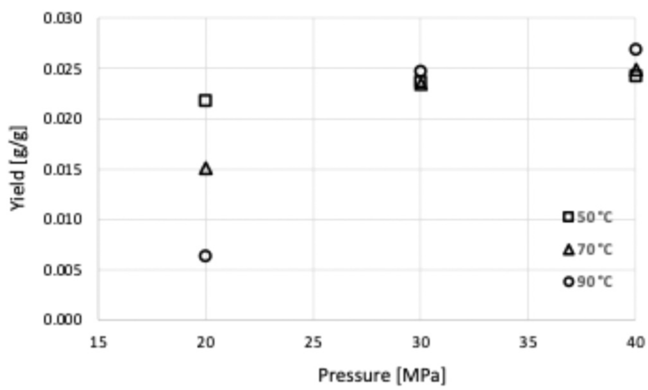

Fig. 3. Extraction yield as a function of the pressure for 3 temperature levels.

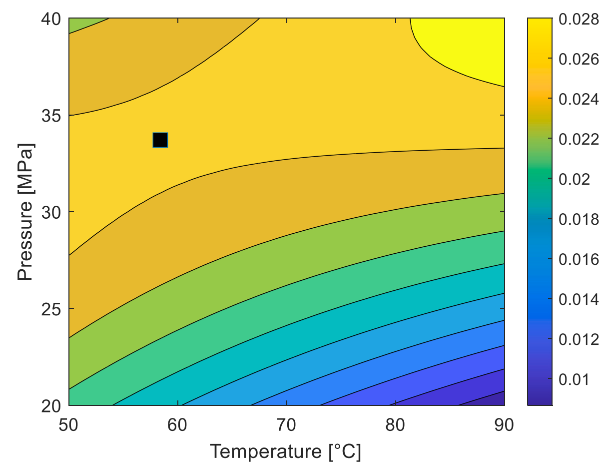

Fig. 4. Response surface contour plot of yield as a function of temperature and pressure. A saddle point (black square) is observed at T = 58 °C and P = 33.7 MPa.

Table 2
2-way ANOVA test summary for yield as a function of temperature and pressure. SS: sum-of-squares, df: degrees of freedom, MS: mean squares, F: F-ratio.

Source	SS	df	MS	F	p-value
Temperature	6.86×10^{-5}	2	3.43×10^{-5}	103	1.42×10^{-10}
Pressure	6.37×10^{-4}	2	3.19×10^{-4}	955	5.38×10^{-19}
Interaction	3.03×10^{-4}	4	7.57×10^{-5}	227	3.91×10^{-15}
Error	6.01×10^{-6}	18	3.34×10^{-7}		
Total	1.01×10^{-3}	26			

As shown in the contour plot of Fig. 4, the yield's dependence on temperature and pressure exhibits a distinct nonlinear behavior. The surface fitted to the experimental data displays a saddle-shaped profile, where the partial derivative of yield with respect to temperature changes sign. The saddle point is located at T = 58 °C and P = 33.7 MPa and identifies the crossover point.

The extraction yields from trials using $scCO_2$–EtOH at 30 MPa and 40 MPa were 0.0273 ± 0.0003 g/g_{DM} and 0.0277 ± 0.0004 g/g_{DM}, respectively, showing no significant difference from each other or the optimal yield achieved with neat $scCO_2$. Nevertheless, this result is lower than the yield of 0.0488 g/g_{DM} reported by Grunovaite et al. [30] for the same ethanol concentration.

3.2.1. *Extraction kinetics*

The NN was trained to predict the extraction yield as a function of process parameters, such as temperature, pressure, and time. The obtained best structure consisted of four hidden neurons and *tansig* activation function in both hidden and output neurons.

Fig. 5 illustrates the results obtained for the test dataset (T = 50 °C and P = 30 MPa). For each point, the three repetitions are reported. As shown, the extraction yields predicted by the neural network model always fall within the range of experimental data variability, demonstrating the model's ability to accurately capture the underlying kinetic behaviour. It is worth noting that the test dataset was not utilized during the training or validation stages, meaning the NN's performance here represents pure prediction. This result highlights the robustness and generalization capability of the NN in modelling the complex extraction processes.

3.3. *Extract characterization*

3.3.1. *Lipid characterization*

The lipid characterization of the extracts is presented in Table 3.

The extracts were dissolved in hexane, and their solubility was assessed. As expected, the hexane solubility of the Soxhlet extracts depends on the polarity of the extraction solvent, ranging from 4 % in the case of ethanol-extracted samples to 90 % for those obtained using hexane.

For $scCO_2$ extraction, the resulting extracts exhibited also over 90 % solubility in hexane, indicating a high content of non-polar components. However, when ethanol was used as a cosolvent, the hexane solubility decreased compared to extracts obtained under the same conditions and neat $scCO_2$. Considering that the average extraction yield using ethanol as cosolvent does not differ significantly from that obtained with pure $scCO_2$, this suggests that the addition of a cosolvent enhances the extraction of more polar compounds, thereby reducing the relative

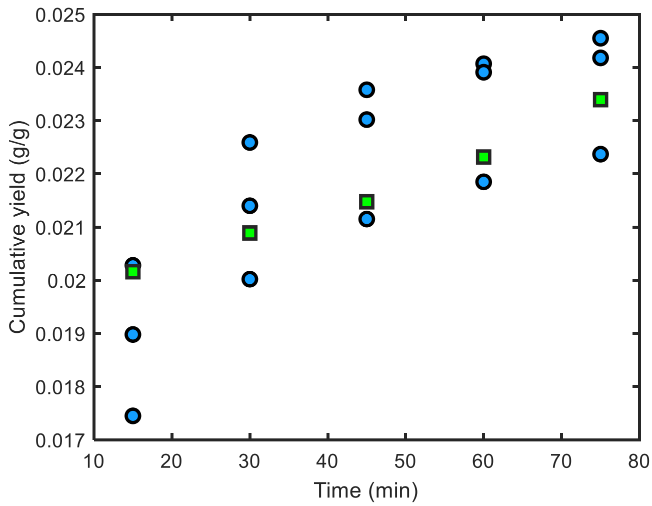

Fig. 5. Comparison between experimental data (blue circle) and calculated yield (green square) for the test dataset.

proportion of non-polar substances in the extract.

The hexane-soluble fraction was subjected to transesterification and subsequently analyzed for its FAME composition. Surprisingly, only about 15 % of this fraction was identified as FAMEs. Among them, linoleic acid methyl ester (C18:2) was predominant, constituting nearly two-thirds of the total FAME content. This high proportion of C18:2 suggests a favorable, health-promoting fatty acid profile [34] . Other FAMEs, such as oleic acid (C18:1), palmitic acid (C16:0), and stearic acid (C18:0), were present in significantly lower concentrations, in descending order of abundance. Overall, the FAME profile exhibited a high unsaturated-to-saturated fatty acid ratio, further highlighting the nutritional quality of the lipid fraction.

Hence, the majority of the hexane-soluble material was not composed of FAMEs. GC–MS analysis revealed the presence of long-chain alkanes, as nonacosane, nonacosan-10-ol, and minor amounts of n-Triacontan. The dominance of nonacosane and its hydroxylated derivative indicates that a significant portion of the extract consists of non-fatty acid constituents, most likely plant-derived waxes [35].

3.3.2. *Effect of the operative conditions on the lipid profile*

In percentage terms, the data show higher wax proportions in the hexane-soluble fraction of extracts obtained at lower pressures. This observation appears counterintuitive, given that the solubility of alkanes in $scCO_2$ is known to increase with pressure [36]. This is due to the dependence of relative compound proportions on the overall extraction yield. At lower pressures, the total extraction yield is low, which results in certain components, such as nonacosane, constituting a comparatively larger fraction of the recovered material. Conversely, at higher pressures the overall yield increases, and these same compounds are diluted within a broader extract matrix. However, this trend could not be extended to the FAME composition.

These findings suggest that reduced pressure may promote the separation of waxes from the triglyceride fraction, a phenomenon particularly evident under the lowest $scCO_2$ density conditions (90 °C, 20 MPa). Among all the extraction trials, the one conducted at the lowest value of $scCO_2$ density is characterized by a high proportion of palmitic acid (C16:0) and stearic acid (C18:0), with only moderate levels of oleic acid (C18:1) and low levels of linoleic acid (C18:2). In order of increasing polarity, the fatty acids follow the sequence: C18:0 < C16:0 < C18:1 < C18:2. This trend suggests that low-density $scCO_2$ conditions preferentially extract more apolar components, while being less effective at recovering the more polar, unsaturated fatty acids.

Overall, higher extraction pressures resulted in lower concentrations of both FAMEs and waxes in the hexane-soluble fraction, suggesting that additional, unidentified components were likely co-extracted under these conditions. In both experiments involving cosolvent addition, the proportion of FAMEs increased, while wax content decreased. This shift can be attributed to the enhanced polarity of the solvent mixture, which promotes the extraction of triglycerides over more apolar waxes. These findings highlight the effectiveness of cosolvent addition as a strategy for selectively modulating extract composition.

3.3.3. *Total phenolic content of extracts*

Among the Soxhlet extracts, ethanol yielded the highest TPC, reaching 495 ± 31 mg GAE per 100 g DM, due to its polarity and affinity for polyphenols. Ethyl acetate and n-hexane extracts showed significantly lower TPCs, 182 ± 11 and 113.0 ± 9.1 mg GAE/100 g DM, respectively, consistent with their lower solvent polarity.

TPC values for the extracts obtained through supercritical fluid extraction are presented in Table 4.

The TPC obtained through supercritical fluid extraction varied significantly depending on temperature, pressure, and the presence of a co-solvent.

When neat $scCO_2$ was used, lower extraction temperatures (50 °C) consistently led to higher TPC values, regardless of the applied pressure. At 50 °C, TPC increased from 107 ± 9 mg GAE/100 g DM at 20 MPa to 115 ± 1 mg GAE/100 g DM at 40 MPa. This trend may be attributed to an increase in solvent density, which improves solubility and mass transfer efficiency.

At higher temperatures (70 °C and 90 °C), TPC values dropped notably. For both temperatures, increasing pressure from 20 to 40 MPa it is still observed an increase of the TPC.

The highest TPCs were observed when ethanol was used as a co-

Table 3
Lipid profile of the extracts.

		$ScCO_2$											Soxhlet		
Temperature [°C]		50	70	90	50	50	70	90	50	50	70	90	Ethanol	Ethylacetate	Hexane
Pressure [MPa]		20	20	20	30	30	30	30	40	40	40	40			
Cosolvent						yes				yes					
Hexane solubility (%)		98	97	96	97	90	98	96	99	90	97	96	4	35	90
FAME	**C16:0 (%)**	1.8	2.4	2.5	1.3	1.6	1.5	1.6	1.3	1.5	1.3	1.4	2.0	2.3	1.5
	C18:2 n−6 (%)	12.0	10.8	7.0	9.2	11.4	10.9	9.5	9.6	10.5	9.0	9.0	11.6	15.5	11.5
	C18:1 n−9 (%)	2.5	2.7	2.0	1.9	2.4	2.2	2.1	1.9	2.2	1.9	1.9	2.8	3.0	2.3
	C18:0 (%)	0.5	0.6	0.7	0.4	0.5	0.5	0.5	0.5	0.5	0.4	0.5	0.6	0.8	0.5
	Sum (%)	16.8	16.4	12.2	12.8	15.9	15.1	13.6	13.3	14.7	12.7	12.7	16.9	21.6	15.8
Wax	**Nonacosane (%)**	9.4	15.0	26.6	5.6	4.5	5.7	6.0	5.9	4.3	5.5	5.3	2.9	2.7	3.7
	Nonacosan−10-ol (%)	6.4	11.7	13.4	4.4	4.4	4.7	5.9	4.7	3.9	4.8	4.2	2.5	2.7	3.0
	Sum (%)	15.8	26.7	40.0	10.0	8.9	10.4	11.9	10.7	8.2	10.3	9.4	5.3	5.4	6.7
Total identified (%)		32.6	43.2	52.2	22.8	24.8	25.5	25.5	24.0	22.9	23.0	22.2	22.3	27.0	22.5

Table 4
TPC of extracts obtained by supercritical fluid extraction.

Temperature [°C]	Pressure [MPa]	TPC mgGAE/100 g DM
50	20	107 ± 9
	30	110 ± 15
	40	115 ± 1
70	20	27 ± 3
	30	822 ± 11
	40	82 ± 1
90	20	26 ± 7
	30	87 ± 5
	40	87 ± 8
50	30 (5 % EtOH)	165 ± 4
50	40 (5 % EtOH)	163 ± 1

solvent (5 % v/v). At 50 °C and 30 MPa, the TPC reached 165 ± 4 mg GAE/100 g DM, and at 40 MPa, 163 ± 1 mg GAE/100 g DM. These values represent a 43 % increase compared to the best result obtained with neat $scCO_2$ (114.8 mg GAE/100 g DM at 50 °C and 40 MPa), confirming the significant enhancement in phenolic recovery when a polar modifier is added.

These findings are also in agreement with those in Table 3, where the extracts obtained with ethanol showed lower solubility in apolar solvents, reflecting their polarity due to the TPC.

4. Conclusions

Aronia berries are gaining increasing attention from consumers due to their high antioxidant capacity, which is among the highest of all berries. If the production is expected to grow, the valorization of the resulting pomace becomes crucial to support a circular economy approach and reduce waste.

In this study, supercritical fluid extraction was investigated under three different pressure and temperature conditions. The crossover point, which defines the operative conditions where the solute vapor pressure becomes more influential than solvent density, was rigorously evaluated. Based on this analysis, a predictive model was developed to estimate the extraction yield as a function of pressure and temperature. The highest extraction yield obtained was 0.0269 ± 0.0002 g per gram of dried pomace at 40 MPa and 90 °C. The addition of 5 percent ethanol as a co-solvent did not result in a significant increase in yield.

However, the total phenolic content of the extracts was significantly higher when ethanol was used, indicating that cosolvent polarity plays an important role in phenolic compound recovery.

It is noteworthy that the maximum TPC of 165 ± 4 mg GAE per 100 g of dried pomace was obtained at 30 MPa and 50 °C, with no significant increase observed when the pressure was raised to 40 MPa. These findings suggest that 30 MPa and 50 °C and 5 % ethanol may represent the optimal conditions for both yield and TPC. However, the solvent evaporation step required under these conditions requires careful consideration in evaluating the overall process economics.

Although the Folin–Ciocalteu assay has limitations and may be affected by the presence of non-phenolic compounds, it still provides a useful indication for preliminary analysis. Additionally, this study contributed a neural network model to predict extraction dynamics and to be used for process optimization and potential industrial scale-up.

Future works should focus on a more comprehensive chemical characterization of the extracts to assess their suitability for different applications. This information will support a valuable economic evaluation and it will help to identify the most promising valorization strategies for this undervalorized feedstock.

CRediT authorship contribution statement

Massimiliano Grosso: Writing – original draft, Methodology, Formal analysis, Data curation. **Ron Hajrizaj:** Writing – review & editing, Methodology, Formal analysis. **Kai Kniepkamp:** Writing – original draft, Methodology, Formal analysis, Data curation. **Stefania Tronci:** Writing – original draft, Methodology, Formal analysis, Data curation. **Lars Duelund:** Writing – review & editing, Methodology, Formal analysis. **Emil Søe Lehmann Carlsen:** Writing – review & editing, Methodology, Formal analysis, Data curation. **Massimiliano Errico:** Writing – original draft, Supervision, Methodology, Funding acquisition, Data curation, Conceptualization, Formal analysis.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Massimiliano Errico reports financial support was provided by University of Southern Denmark. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.supflu.2025.106796.

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