

Concentration of phenolic compounds from apple pomace extracts by nanofiltration at lab and pilot scale with a techno-economic assessment

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1 **Concentration of phenolic compounds from apple pomace extracts by nanofiltration at**  
2 **lab and pilot scale with a techno-economic assessment**

3

4

5 **Abstract**

6

7 Apple pomace can be used as resource for the extraction of phenolic compounds with anti-  
8 oxidant properties. Pressing of apple in juice and pomace at lab scale in open air (aerobic)  
9 and under N<sub>2</sub> atmosphere (anaerobic) showed a recovery of phenolic compounds of 85% in  
10 juice and pomace after anaerobic pressing, compared to 43% after aerobic pressing,  
11 indicating loss of phenolic compounds by oxidation and the advantage of anaerobic over  
12 aerobic pressing. After a membrane screening and concentration test at lab scale, the  
13 commercial nanofiltration membrane NFX was selected to concentrate phenolic compounds  
14 in an ethanol:water extract of apple pomace. At pilot scale, the concentration of ten  
15 selected phenolic compounds and quinic acid increased from 59.5 mg L<sup>-1</sup> in the  
16 ethanol:water extract to 1256.1 mg L<sup>-1</sup> in the final retentate, i.e. by a factor 21.1. The  
17 volume of the crude extract was reduced by a factor of 28.5 during the filtration, indicating  
18 some loss of phenolic compounds during pilot testing due to membrane fouling or oxidation  
19 of polyphenols. The pilot concentration test using a spiral-wound membrane module  
20 showed good flux and concentration of phenolic compounds, indicating the technical  
21 feasibility of membrane technology for efficient concentration of polyphenols in an  
22 ethanol:water extraction solvent. Unfortunately, the extraction and concentration process  
23 was not economically feasible under the assumptions made.

24

25 **Practical Applications**

26

27 The valorization of food waste for the production of high-added value products is an  
28 increasingly hot topic. Phytochemicals are present in relatively low concentration in the fruit  
29 matrix and concentration in the extraction solvent is necessary to develop an industrially  
30 relevant process. In this study, membrane filtration was selected for concentration due to its  
31 low energy consumption and mild processing conditions compared to other technologies.  
32 Membrane screening and testing at lab and pilot scale with techno-economic assessment can

33 be used by food and nutraceutical industries to evaluate membrane technology for  
34 concentration of phytochemicals extracted from agroindustrial by-products.

35

### 36 **Keywords**

37 Phenolic compounds, apple pomace, nanofiltration, pilot scale, techno-economic assessment

38

39

### 40 **Introduction**

41

42 Food processing by-products are often used as feed or bioenergy source. In general, they  
43 still contain useful major compounds like carbohydrates, proteins and fats, and minor  
44 compounds like polyphenols, carotenoids or terpenes. These compounds are high-added  
45 value valorisation products from food waste. The use of food waste as renewable resource  
46 for the production of chemicals, materials and fuels is getting more and more attention (Lin  
47 *et al.* 2013; Garcia-Gonzalez *et al.* 2015).

48 Apple pomace is a left-over residue (25-30% of the total processed apple) after pressing of  
49 apple to juice. Worldwide, 3 to 4.2 million tonnes of apple pomace are generated per year  
50 (Lin *et al.* 2013). Apple pomace is used for several applications like feed or as substrate for  
51 biotechnological applications like production of enzymes, single cell protein, ethanol and  
52 organic acids (Schieber *et al.* 2003; Bushan *et al.* 2008; Vendruscolo *et al.* 2008; Wijngaard  
53 and Brunton 2010). On an industrial scale, apple pomace is used for the production of  
54 pectin. Extraction of phytochemicals from waste products, such as apple pomace, has  
55 received much interest in recent years due to the use of natural and low cost sources of  
56 phytochemicals for incorporation into foods or beverages (Schieber *et al.* 2003; Wijngaard  
57 and Brunton 2010; Harbourne *et al.* 2013). Apple pomace contains many polyphenols  
58 including chlorogenic acid, catechins, procyanidins and quercetin glycosides (Harbourne *et al.*  
59 *et al.* 2013). Polyphenols are secondary plant metabolites with anti-oxidant properties.  
60 Phenolic compounds can be easily oxidized by exposure to air during the pressing of apple  
61 in the juice industry and are lost in a process called enzymatic browning (Van der Sluis *et al.*  
62 *et al.* 2002). Enzymatic browning is the oxidation of polyphenols by polyphenol oxidase,  
63 resulting in a brown colour. It has two disadvantages: production of a brown colour which is  
64 not attractive for consumers and the decrease in concentration of phenolic compounds in the  
65 apple juice (Van der Sluis *et al.* 2002; De Paepe *et al.* 2015a) with decrease in value.

66 Antioxidants work effectively as disease preventing species and a consensus exists that a  
67 diet rich in fruit and vegetables is beneficial for health in preventing coronary heart disease  
68 and some forms of cancer (Matés 2013).

69 Phytochemicals make up less than 10% of the plant matrix (Harjo *et al.* 2004), therefore  
70 they need to be extracted to prepare phytochemical rich foods and beverages (Sarmiento *et*  
71 *al.* 2008; Harbourne *et al.* 2013). Organic solvents are often used for extraction of  
72 phytochemicals. Polyphenols can be extracted with conventional solvents like water,  
73 methanol, ethanol, ethyl acetate and acetone or a mixture of these solvents (Sarmiento *et al.*  
74 2008). Hasbay Adil *et al.* (2007) used subcritical CO<sub>2</sub> and ethanol for extraction of  
75 polyphenols from apple pomace. After optimization with response surface methodology,  
76 Wijngaard and Brunton (2010) used 56% ethanol or 65% acetone as food grade solvents for  
77 extraction of polyphenols from apple pomace. Since the concentration of polyphenols in  
78 fruit and vegetables is relatively low, the polyphenols in the extraction solvent need to be  
79 concentrated to obtain a feasible process at industrial scale. Membrane separation  
80 technology offers several advantages like low energy consumption and mild operating  
81 conditions for separation of thermolabile compounds (Sarmiento *et al.* 2008), compared to  
82 more traditional separation methods like distillation or adsorption. Nawaz *et al.* (2006) used  
83 ultrafiltration membranes to concentrate polyphenols from grape seeds, while Sarmiento *et*  
84 *al.* (2008) used polymeric membranes for concentration of polyphenols from cocoa seeds.  
85 Saleh *et al.* (2006) used nanofiltration membranes with molecular weight cut-off of 250 and  
86 1000 Da to recover phenolic compounds from apple juice for nutraceutical use.

87 In this study, the optimized solvent extraction of Wijngaard and Brunton (2010), i.e. ethanol  
88 56% or acetone 65%, was used to recover phenolic compounds from apple pomace, and  
89 nanofiltration membranes were subsequently used to concentrate polyphenols in the  
90 extraction solvent at both lab and pilot scale. Furthermore, a techno-economic assessment  
91 (TEA) was made to study the economic feasibility of the extraction and separation process  
92 and to determine the most important process parameters. The TEA exists of four different,  
93 integrated steps: (1) market analysis, (2) process flow diagram and mass and energy  
94 balance, (3) economic analysis, and (4) uncertainty analysis (Van Dael *et al.* 2015). Taking  
95 into account the uncertainty of the data, the last step is crucial in order to provide food waste  
96 processors a proper insight in the techno-economic performance of the process. To our  
97 knowledge, this is the first report of the concentration of phenolic compounds from apple  
98 pomace extracts by nanofiltration at pilot scale with a TEA in scientific literature.

99

100

## 101 **Materials and methods**

102

### 103 *Plant material*

104

105 The apple cultivar used for the pressing on lab and pilot scale was ‘Golden Delicious’  
106 obtained from a local distributor in Belgium. The fresh apples were stored at 4 °C until use.

107

### 108 *Mechanical pressing of apples at lab scale*

109

110 One kg of apples with peels and seeds, but without stalks was cut in eight pieces and  
111 mechanically pressed using a screw press into two fractions: apple juice and apple pomace.  
112 For the aerobic experiments, the apples were cut and pressed in open air. For the anaerobic  
113 experiments, the apples were cut and pressed in an anaerobic glove box filled with N<sub>2</sub> to  
114 prevent oxidation of the phenolic compounds.

115

### 116 *Mechanical pressing of apple at pilot scale*

117

118 The pressing of the apples at pilot scale was performed at the Food Pilot of the Institute for  
119 Agriculture, Fisheries and Food Research (ILVO) in Melle, Belgium. First, the apples with  
120 peels, seeds and stalks (200 kg) were cut with a grinding system (Multicut 1500, Bruckner  
121 Liquid Food Tech – VacuIQ, Germany) under N<sub>2</sub> atmosphere to prevent oxidation of  
122 polyphenols in the apple juice and pomace, and then pumped to the spiral-filter press  
123 (VacuIQ 1000-300, VacuIQ, Germany) as described by De Paepe *et al.* (2015a). During  
124 the stabile phase of the pressing (after 30 minutes of pressing), the juice and the pomace  
125 were collected during one minute to calculate the juice yield as described by De Paepe *et al.*  
126 (2015a). The apple pomace was sampled immediately after leaving the press to prevent  
127 oxidation of the polyphenols and vacuum packed in plastic bags (subsamples of 2 kg). The  
128 apple pomace and apple juice were immediately frozen at -25 °C and stored at -18 °C until  
129 extraction. An overview of the process parameters of the grinding system and the spiral-  
130 filter press is shown in Table 1. The juice yield was very high (83.3%), indicating a

131 production of 83.3 kg apple juice (and 16.7 kg apple pomace) starting from 100 kg fresh  
132 apple (if no losses during pressing are taken into account).

133

#### 134 *Analytical extraction of phenolic compounds*

135

136 The analytical extraction of phenolic compounds from apple, apple pomace and apple juice  
137 was performed on freeze-dried samples. The samples were immediately frozen in liquid  
138 nitrogen to avoid enzymatic browning and transferred into a freeze dryer with heated  
139 shelves at 25 °C (GAM-MA 1-16 LSC Martin Christ, Germany). After the freeze-drying  
140 process, the samples were grounded in a commercial blender (DP705 La Moulinette,  
141 Belgium) and stored under N<sub>2</sub> atmosphere in an amber-coloured flask at -18 °C.

142 The phenolic compounds were further extracted from the freeze-dried samples according to  
143 the detailed protocol of De Paepe *et al.* (2013).

144

#### 145 *Extraction of apple pomace at lab scale*

146

147 The polyphenols in the apple pomace were extracted in erlenmeyer flasks with the method  
148 described by Wijngaard and Brunton (2010). The apple pomace was freeze-dried (as  
149 described above) prior to extraction for the membrane screening tests or extracted fresh for  
150 the lab concentration tests. Extraction conditions for ethanol 56% were an extraction  
151 temperature of 80 °C and 31 min extraction time. Extraction with acetone 65% was  
152 performed at 25 °C during 60 min. The solid to liquid ratio was 10 g dry weight (DW) apple  
153 pomace L<sup>-1</sup> solvent. After extraction, the samples were centrifuged for 10 min at 931 g  
154 (Beckman Coulter Allegra X-15R, USA) and 10 mL of the supernatant was filtered through  
155 0.22 µm PVDF syringe filters (Pall Gelman Laboratory, UK). The solvents used were  
156 analytical grade and purchased from VWR (Belgium). The extracts were stored under N<sub>2</sub>  
157 atmosphere at -18 °C.

158

#### 159 *Extraction of apple pomace at pilot scale*

160

161 The extraction of the phenolic compounds from the apple pomace at pilot scale was  
162 performed at the chemical pilot plant of Agfa-Gevaert NV in Westerlo, Belgium. The pilot  
163 plant was chosen for explosion safety due to the extraction with ethanol:water at 80 °C.

164 Prior to extraction, the frozen apple pomace was defrosted overnight at 4 °C. The extraction  
165 was performed in a 1000 L chemical reactor of glass enamel. The reactor was filled with  
166 252 kg ethanol and 198 kg distilled water and heated under N<sub>2</sub> atmosphere up to 75 °C. The  
167 apple pomace (26.8 kg) was added to the reactor and extracted (under N<sub>2</sub> atmosphere) at 80  
168 °C during 31 minutes under continuous stirring at 120 rpm with a three-blade impeller.  
169 After extraction, the reactor was cooled to 25 °C during 75 minutes. The solid to liquid ratio  
170 was 12 g DW apple pomace L<sup>-1</sup> solvent.

171 The extraction solvent was separated from the apple pomace by filtration using a bag filter  
172 with pore size 100 µm, followed by a candle filtration (Roki PEH pore size 2 µm, ROKI  
173 Techno, Japan) at a pressure of 0.3 bar. The filtration was performed under N<sub>2</sub> atmosphere.  
174 The candle filtration was performed with one candle filter for every 30 L of extraction  
175 solvent. The filtrate (380 kg) was stored in two 200 L steel drums, flushed with N<sub>2</sub>, and  
176 stored at 4 °C.

177

#### 178 *Analysis of phenolic compounds*

179

180 Identification and quantification of the selected phenolic compounds were performed via an  
181 Ultra High Performance Liquid Chromatography-Mass Spectroscopy (UHPLC-MS)  
182 method, as described in detail by De Paepe *et al.* (2013). An analytical standard was used  
183 for the calibration of each individual phenolic compound.

184

#### 185 *Membrane screening*

186

187 The membrane screening was carried out on a high pressure bench-top cross-flow filtration  
188 unit equipped with a temperature controlled feed vessel (1000 mL), a circulation pump and  
189 a membrane test cell. The transmembrane pressure was generated by N<sub>2</sub> gas. A circular, flat  
190 test cell (Amafilter, the Netherlands) with an active surface area of 0.0044 m<sup>2</sup> was used. The  
191 membrane coupons were sealed with Kalrez<sup>®</sup> o-rings. MEFIAS software was used for  
192 process monitoring. An overview of the used commercial nanofiltration membranes with  
193 nominal molecular weight cut-off (MWCO) is shown in Table 2. Two types of  
194 nanofiltration membranes were selected, i.e. standard polyamide-based membranes for  
195 water filtration, and organic solvent nanofiltration (OSN) membranes (Vandezande *et al.*  
196 2008; Marchetti *et al.* 2014).

197 The feed solutions (450 mL) were an ethanol:water and an acetone:water extract from apple  
198 pomace, prepared by the extraction method at lab scale. The membrane screening was  
199 carried out in batch mode at a flow rate of 800 L h<sup>-1</sup>, corresponding with a cross-flow  
200 velocity of approx. 1.7 m s<sup>-1</sup>, a temperature of 22 ± 1 °C and a trans-membrane pressure of  
201 20 or 30 ± 1 bar. The initial feed after circulation was sampled, as well as the permeate and  
202 retentate at steady-state conditions. All samples were stored under N<sub>2</sub> atmosphere at -18°C  
203 until analysis.

204

#### 205 *Concentration test at lab scale*

206

207 Two laboratory stainless cross-flow filtration units with capacity of 1000-4000 mL (CF1)  
208 and 300-1000 mL (CF2) were used. The feed solution (3500 mL) was an ethanol:water  
209 extract from apple pomace, prepared by the extraction method at lab scale. The  
210 ethanol:water extract was first concentrated on CF1 until approx. 1000 mL and was further  
211 concentrated on CF2 until approx. 300 mL. The transmembrane pressure was generated by  
212 N<sub>2</sub> gas. A rectangular test cell (PS Prozesstechnik GmbH, Switzerland) with active  
213 membrane surface area of 0.01 m<sup>2</sup> was used for both CF1 and CF2. The commercial flat  
214 polyamide-based membrane NFX (Table 2) was used without specific pretreatment. The  
215 membrane coupons were sealed with Kalrez<sup>®</sup> o-rings. MEFIAS software was used for  
216 process monitoring of permeate flux. The concentration test was carried out at a flow rate of  
217 800 L h<sup>-1</sup> (cross-flow velocity of approx. 1.8 m s<sup>-1</sup>), a temperature of 20 ± 1 °C and a trans-  
218 membrane pressure of 20 ± 1 bar. The initial feed after circulation was sampled, as well as  
219 the permeate and retentate at regular time points during concentration at increasing volume  
220 concentration factor (VCF). All samples were stored under N<sub>2</sub> atmosphere at -18°C until  
221 analysis.

222

#### 223 *Concentration test at pilot scale*

224

225 The concentration of the phenolic compounds from the ethanol:water extract was performed  
226 with a mobile, semi-automatic, cross-flow solvent pilot unit (ATEX design) with a feed tank  
227 of 400 L. The concentration test at pilot scale was also conducted with the commercial  
228 membrane NFX (Table 2), this time using a 3838 spiral-wound module (3.8 inch diameter,  
229 38 inch length, 31 mil feed spacer) with active surface area of 8.92 m<sup>2</sup> (Synder Filtration,



230 USA). The feed volume at pilot scale was 409 L and batch concentration was performed  
231 during 8 days, until minimal feed volume (60 L). The membrane module was operated at a  
232 feed flow of 6500 Lh<sup>-1</sup>, corresponding with a cross-flow velocity of approx. 2 m s<sup>-1</sup>. Further  
233 concentration of the final retentate of the pilot scale test was performed at lab scale using  
234 test unit CF1 and a rectangular cell (0.01 m<sup>2</sup>) with a flat NFX membrane, as described  
235 above. The feed volume (4.8 L) for the lab scale test, following pilot scale, was further  
236 concentrated during 9 days. The pilot test and further concentration at lab scale were  
237 conducted at 20 ± 1 °C and 20 ± 0.25 bar. Samples were taken and stored as described at lab  
238 scale.

239

#### 240 *Membrane flux and retention*

241

242 The membrane flux  $J$  (kg m<sup>-2</sup> h<sup>-1</sup>) was determined by weighing the permeate samples and  
243 calculated according to

$$244 \quad J = m/At$$

245 with  $m$  the weight of the permeate per unit membrane area  $A$  and time  $t$ . The density of the  
246 solvents was used to convert the flux in L m<sup>-2</sup> h<sup>-1</sup>.

247 The retention of component  $i$  ( $R_i$ ) was calculated according to

$$248 \quad R_i = (1 - C_{p_i}/C_{r_i}) \times 100\%$$

249 with  $C_{p_i}$  and  $C_{r_i}$  the concentrations of component  $i$  in the permeate and in the retentate,  
250 respectively.

251

#### 252 *Techno-economic assessment (TEA)*

253

254 For the TEA, an economic lifetime of ten years and a weighted average cost of capital  
255 (WACC) of 5.41% was assumed. Based on Eurostat data, a labour cost of 39 euro h<sup>-1</sup> (cost  
256 for Belgium in 2015, [http://ec.europa.eu/eurostat/statistics-  
257 explained/index.php/Hourly\\_labour\\_costs](http://ec.europa.eu/eurostat/statistics-explained/index.php/Hourly_labour_costs), accessed on July 14, 2016) and an electricity  
258 price of 93 euro MWh<sup>-1</sup> (price for industrial consumers in Belgium with a consumption of  
259 20.000-70.000 MWh year<sup>-1</sup>, year 2015 semester 2, all taxes included,  
260 <http://ec.europa.eu/eurostat/web/energy/data/database>, accessed on July 14, 2016) was  
261 chosen. The maintenance costs for the total process were estimated at 2.5% of the  
262 investment costs. A water price of 3.7 euro m<sup>-3</sup> (average price for a company in Flanders,

263 Belgium in 2012 with a consumption of 1000 m<sup>3</sup> year<sup>-1</sup>,  
264 [https://www.vmm.be/publicaties/vergelijking-van-de-kostprijs-van-water-afvalwater-](https://www.vmm.be/publicaties/vergelijking-van-de-kostprijs-van-water-afvalwater-hemelwater-voor-de-gebruikers-in-verschillende-europese-landen)  
265 [hemelwater-voor-de-gebruikers-in-verschillende-europese-landen](https://www.vmm.be/publicaties/vergelijking-van-de-kostprijs-van-water-afvalwater-hemelwater-voor-de-gebruikers-in-verschillende-europese-landen), accessed on July 14,  
266 2016) and an ethanol price of 0.55 euro L<sup>-1</sup> (price of January, 2016,  
267 <http://www.platts.com/price-assessments/agriculture/ethanol>, accessed on July 14, 2016)  
268 was assumed. The selling price of polyphenols amounts to 28 euro kg<sup>-1</sup>, based on our market  
269 analysis.

270

271

## 272 **Results and Discussion**

273

### 274 *Fractionation of phenolic compounds between apple pomace and juice*

275

276 De Paepe *et al.* (2015a) selected ten marker phenolic components for apple fruits:  
277 chlorogenic acid, isoquercitrin, hyperin, rutin, avicularin, quercitrin, phlorizin, catechin,  
278 epicatechin and procyanidin B2 (Table 3). Quinic acid is a cyclic polyol and not a  
279 polyphenol since it does not contain an aromatic ring. It was included in this study since it is  
280 an important secondary metabolite in apple fruits with similar structure.

281 An overview of the concentration of these ten selected phenolic components and quinic acid  
282 in apple fruits is shown in Table 4. In total, the apple fruits contained 3.8 mg g<sup>-1</sup> dry weight  
283 (DW) phenolic compounds (without quinic acid). This total concentration is higher  
284 compared to De Paepe *et al.* (2015b), who analysed phenolic compounds in 47 apple  
285 cultivars. The flesh (without peel) of the same apple cultivar contained 1.4 mg g<sup>-1</sup> DW,  
286 while in our study also the peel of the apple was included in the sample, explaining the  
287 higher concentration of phenolic compounds.

288 The apples were pressed in apple juice and apple pomace under aerobic and anaerobic  
289 conditions. The recovery of phenolic compounds compared to the phenolic concentration in  
290 the total apple was 85% in juice and pomace after anaerobic pressing, compared to only  
291 43% after aerobic pressing, indicating the advantage of anaerobic pressing over aerobic  
292 pressing. Some loss of apple (5-6%) was observed in the press, leading to a decrease in  
293 recovery. Furthermore, in intact plant cells, polyphenols and polyphenol oxidase are  
294 physically separated in distinct compartments (Renard *et al.* 2001): the polyphenols are  
295 present in the vacuoles and the polyphenol oxidase in the chloroplasts (Vela *et al.* 2003).

296 When cells are ruptured by pressing, the polyphenols come into contact with the polyphenol  
297 oxidase with subsequent loss of phenolic compounds by oxidation. Oxidation of  
298 polyphenols in apple juice and pomace should be avoided, for example by vacuum-  
299 deaeration, gas sparging or ascorbic acid addition as often used in the juice industry (Garcia-  
300 Torres *et al.* 2009).

301

### 302 *Extraction of polyphenols*

303

304 The total concentration of the ten marker phenolic compounds was 3.0 mg g<sup>-1</sup> DW for  
305 ethanol:water, compared to about 3.4 mg g<sup>-1</sup> DW for acetone:water (Table 5). This indicates  
306 that acetone:water is a slightly better extraction solvent for polyphenols from apple pomace,  
307 compared to ethanol:water. These data are in comparison with Wijngaard and Brunton  
308 (2010).

309

### 310 *Membrane screening*

311

312 A set of selected membranes was screened for an ethanol:water and an acetone:water  
313 extract. The time-average permeate fluxes at steady-state conditions of the tested  
314 membranes are summarized in Table 6.

315 In general, the selected phenolic compounds and quinic acid are removed well from the  
316 ethanol:water and acetone:water extracts (data not shown), with retentions well over 90%,  
317 in many cases over 95%. In general, the difference in retentions among the tested  
318 membranes is very small. Several studies reported comparable polyphenol retentions of 93  
319 to 100% for comparable commercial polymeric nanofiltration membranes (Sarmiento *et al.*  
320 2008; Tylkowski *et al.* 2010; Cissé *et al.* 2011) . The permeate flux of the membranes tested  
321 on the ethanol:water extract ranges by a factor two, i.e. 12 L m<sup>-2</sup> h<sup>-1</sup> for DuraMem200 to 23  
322 L m<sup>-2</sup> h<sup>-1</sup> for NF90, both at 20 bar. As comparison for the NF90 membrane, Machado *et al.*  
323 (2013) reported a lower average permeate flux of 7 L m<sup>-2</sup> h<sup>-1</sup> for an ethanol 95% extract of  
324 pequi, but also at a lower pressure of 8 bar. For the acetone:water extract, the fluxes of  
325 NF030306 and NanoPro AS3012 are about one order of magnitude lower than those of  
326 DuraMem200 and DuraMem300. The DuraMem200 membrane displays an increased flux  
327 at increased operating pressure, which was also observed by others (Cissé *et al.* 2011; Couto  
328 *et al.* 2011; Acosta *et al.* 2017) for other nanofiltration membranes. A membrane with high

329 retention (more than 95%) of phenolic compounds and high permeate flux is essential to  
330 obtain a yield-optimized concentration process. Among the tested membranes, NF90 and  
331 NFX perform best for the ethanol:water extract, while DuraMem200 (30 bar) is the most  
332 suitable membrane for the acetone:water extract. NF270, a similar nanofiltration membrane  
333 as NF90 and NFX with MWCO of 150-300 Da, showed the highest potential for  
334 concentration of polyphenolic compounds from blackberry juice (Acosta *et al.* 2017).  
335 Machado *et al.* (2013) used the NF90 membrane for the concentration of polyphenols from  
336 an alcoholic and aqueous extract of pequi, a typical Brazilian fruit. Wijngaard and Brunton  
337 (2010) concluded that both ethanol:water and acetone:water are suitable to replace methanol  
338 for a food grade and more environmentally friendly extraction of polyphenols from apple  
339 pomace. In this study, the ethanol:water extraction method was selected over acetone:water  
340 to produce a polyphenol rich extract from apple pomace for further concentration tests after  
341 personal communication with several food companies. This selection is in accordance with  
342 Machado *et al.* (2013), who used ethanol for polyphenol extraction due to its GRAS  
343 (generally-recognized-as-safe) status. Furthermore, the acetone:water extracts need  
344 significantly more expensive organic solvent nanofiltration membranes, compared to  
345 cheaper regular membranes for water filtration for the ethanol:water extracts. The NFX  
346 membrane was selected over the NF90 membrane after communication with membrane  
347 suppliers Synder Filtration and Dow Filmtec on the (potential) suitability of their spiral-  
348 wound modules (membranes, glues, spacers) for solutions with an ethanol content as high as  
349 56%.

#### 350 *Concentration test at lab scale*

351

352 A longer term batch concentration test at lab scale was conducted with the NFX membrane  
353 to further investigate the feasibility of nanofiltration to concentrate phenolic compounds  
354 from an ethanol:water extract of apple pomace. For the ethanol:water extract, the total  
355 volume concentration factor (VCF), i.e. the volumetric ratio of the initial feed to the final  
356 retentate, was 32.4. Fig. 1 shows the evolution of the permeate flux of the membrane as  
357 function of the VCF. As expected, fluxes decrease with increasing VCF, which can be  
358 explained by increasing solute concentrations in the boundary layer at the feed side of the  
359 membrane. For the ethanol:water extract, the flux decreased from 24.9 to 3.6 L m<sup>-2</sup> h<sup>-1</sup> at  
360 final VCF. The feed/retentate concentrations of the ten selected phenolic compounds and  
361 quinic acid are plotted as function of increasing VCF in Fig. 2 for the ethanol:water extract.

362 The differences in retention behaviour of individual polyphenol compounds appear to point  
363 to differences in concentration, functionality and affinity with the membrane surface, and  
364 interactions with macromolecules co-extracted with the polyphenols. A systematic study  
365 using model mixtures with increasing complexity would allow to gain more insight into the  
366 phenomena underpinning the differences observed. This is however beyond the scope of the  
367 present study. The results show an increase of the total phenolic concentration (sum of ten  
368 selected phenolic compounds and quinic acid) from 38.7 mg L<sup>-1</sup> in the feed to 718.8 mg L<sup>-1</sup>  
369 in the final retentate, i.e. by a factor of 18.6 for the ethanol:water extract, compared to a  
370 total VCF of 32.4. Both factors are not equal and this can be explained by losses of phenolic  
371 compounds upon sampling, oxidation or fouling of the membranes. Membrane fouling  
372 during apple juice clarification may be caused by pectins, tannins, proteins, starch,  
373 hemicellulose and cellulose (Mondor *et al.* 2000).

374 For the ethanol:water extract, the average retention of the phenolic compounds was 98-99%,  
375 except for quinic acid (96%), catechin (83%) and epicatechin (93%), due to their relatively  
376 low molecular weight (192 Da for quinic acid and 290 Da for catechin and epicatechin). The  
377 other phenolic compounds have a higher MW in the range 354-611 Da. These observations  
378 can be explained by the nominal MWCO of the NFX membrane of 150-300 Da, which is  
379 defined as the molecular weight of the solute that is retained for 90% by the membrane  
380 (Mustafa *et al.* 2014). Machado *et al.* (2013) showed a 97% retention of total polyphenols  
381 from an aqueous extract of pequi, compared to only 15% retention from a 95% ethanol  
382 extract using a similar NF90 membrane. The large difference in retention between aqueous  
383 and ethanol extract was explained by the hydrophilic nature of the NF90 membrane and this  
384 can be affected by hydration/solvation of the pore wall. The effective pore size could be the  
385 smallest in water and the largest in ethanol. In our study, 56% ethanol was used and not  
386 95% ethanol, explaining the good retention by the hydrophilic NFX membrane.

387

#### 388 *Pilot concentration test*

389

390 The initial feed (409 L) was concentrated on the pilot unit until 60 L, corresponding to a  
391 VCF of 6.9, in about 8 days. Afterwards, a subsample (4.82 L) of the obtained concentrate  
392 was further concentrated on the lab scale unit CF1 until 1.16 L, corresponding to a VCF of  
393 4.2 (about 9 days of operation). Hence, a total VCF of 28.5 was reached.

394 Fig. 3 shows the evolution of the permeate flux of the membrane as function of the VCF. As  
395 expected, fluxes decrease with increasing VCF, which can be ascribed to increasing solute  
396 concentrations at the feed side of the membrane and membrane fouling, as described for the  
397 lab concentration tests. During the pilot test, the flux decreased from 6.8 initially to 0.4 L m<sup>-2</sup>  
398 h<sup>-1</sup> at VCF 6.9. Cissé *et al.* (2011) showed a decrease in flux over time from 40 to about 5 L  
399 m<sup>-2</sup> h<sup>-1</sup> at a VCF of about 6 for a similar flat-sheet nanofiltration membrane for an aqueous  
400 roselle extract at semi-industrial scale. At the start of the lab test with the retentate of the  
401 pilot test, the flux increased again to 10.3 L m<sup>-2</sup> h<sup>-1</sup> and gradually decreased to 0.4 L m<sup>-2</sup> h<sup>-1</sup>  
402 at the maximal VCF of 28.5. The initial flux at lab scale (10.3 L m<sup>-2</sup> h<sup>-1</sup>) was significantly  
403 higher compared to the start flux at pilot scale (6.8 L.m<sup>-2</sup>.h<sup>-1</sup>) and this can be explained by  
404 the use of a new NFX membrane for the lab test and the difference in module design (spiral  
405 wound module vs. flat sheet membrane) and feed flow.

406 The evolution of concentrations of the ten selected phenolic compounds and quinic acid are  
407 shown as function of increasing VCF in Fig. 4. The phenolic compounds were progressively  
408 concentrated by the NFX membrane in both pilot and further lab scale testing. The  
409 concentration of the ten selected phenolic compounds and quinic acid increased from  
410 59.5 mg L<sup>-1</sup> in the ethanol:water extract (feed) to 1256.1 mg L<sup>-1</sup> in the final retentate, hence  
411 the polyphenols were concentrated by a factor 21.1. This increase in concentration is  
412 somewhat lower than the total VCF reached (28.5), pointing to some losses across the  
413 membrane to the permeate side (e.g. oxidation) and fouling on the membrane surface, but  
414 losses during sampling and draining of the test units may have occurred as well. This  
415 observation was not in accordance with Cissé *et al.* (2011), who showed a VCF of about 6  
416 and the concentration of roselle extract from 4 to 25 g total soluble solids per 100 g,  
417 multiplying by 6 the anthocyanin concentration.

418 The average retention of the phenolic compounds was 97-98%, except for quinic acid  
419 (92%), catechin (78%) and epicatechin (87%). These observations are similar to the lab  
420 concentration tests and are expected given the MWCO of the NFX membrane of 150-300  
421 Da.

422 In conclusion, phenolic compounds were efficiently concentrated from a hydro-alcoholic  
423 crude extract at pilot scale using a commercial membrane module, indicating the technical  
424 feasibility of nanofiltration for mild concentration of phenolic compounds.

425

426 *Techno-economic assessment*

427

428 The results of the pilot concentration test are directly integrated in the economic model to  
429 have good insight into the economic feasibility of the process. For the analyses we assumed  
430 a total input of ca. 5,000 ton apple pomace per year, resulting in ca. 3,800 kg of polyphenol.  
431 The total yearly energy use in the process amounted to approximately 3,400 MWh. This  
432 energy use resulted mainly from the extraction step. The total investment cost for the  
433 process amounts to 150,000 euro. The operational costs of 760,000 euro are higher than the  
434 yearly revenues of 105,000 euro. From this analysis it can be concluded that the resulting  
435 net present value (NPV) amounts to minus 5 million euro. This means the process is, under  
436 the assumptions made, not economically feasible. The total cost per kg polyphenol extracted  
437 is 203 euro under the assumptions made. Taking into account that the current market price  
438 for polyphenol is only 28 euro per kg, the costs for extracting polyphenols should be  
439 reduced drastically. Therefore, using an uncertainty analysis, we identified the most  
440 important parameters that determined the economic feasibility. If we only take into account  
441 the economic parameters, the ethanol use and electricity price are most important. These  
442 determine respectively 54% and 40% of the variance in the NPV. The price of phenolic  
443 compounds and the wage rate also influence the NPV, however, to a much smaller amount,  
444 i.e. 4% and 2% respectively. In a second analysis we took into account both technical and  
445 economic parameters. From this second analysis it is concluded that mainly the recycling  
446 rate of the ethanol has a large impact on the variation into the NPV. In future research these  
447 results should be taken into account. An optimization in the energy use has to be  
448 investigated. A decrease in the electricity price itself is only possible if the installation is  
449 exploited by a company with a high energy use. Possibly, another extraction solvent with a  
450 similar extraction yield and a lower price can be an option for improvement.

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452

## 453 **Conclusions**

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455 On lab scale, phytochemicals are often extracted with the use of organic solvents. In recent  
456 years, a trend towards the use of environmentally friendly extraction solvents and the use of  
457 food by-products as resource for extraction is emerging. This study showed at lab and pilot  
458 scale the extraction of phenolic compounds from apple pomace, an industrial by-product  
459 from the fruit juice industry, with ethanol:water (56%) as extraction solvent. However,

460 phytochemicals like polyphenols are present in relatively low concentration in the fruit  
461 matrix and concentration in the extraction solvent is necessary to develop an industrially  
462 relevant process. In this study, nanofiltration was selected for concentration due to its low  
463 energy consumption and mild processing conditions compared to other technologies. This  
464 study showed the technical feasibility of extraction and membrane based concentration of  
465 polyphenols from apple pomace at lab and pilot scale. Unfortunately, the extraction and  
466 concentration process was not economically feasible under the assumptions made. The  
467 electricity price and ethanol use had the highest influence on the economic feasibility of the  
468 full process under investigation.

469 These results suggest that research about polyphenol extraction from fruit by-products and  
470 membrane concentration processing should be continued to make the process economically  
471 feasible. An important point of attention for new research is the correlation of a detailed  
472 polyphenol analysis as performed in this study, with a total polyphenol analysis for example  
473 by the Folin-Ciocalteu colorimetric method, and with the antioxidant capacity since there is  
474 no consensus in literature on a positive correlation between total phenolics and anti-oxidant  
475 activity. In this way, the effect of nanofiltration on anti-oxidant activity of apple extract at  
476 lab and pilot scale can be studied.

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## 478 **References**

479

480 Acosta, O., Vaillant, F., Pérez, A.M., Dornier, M. (2017). Concentration of polyphenolic  
481 compounds in blackberry (*Rubus Adenotrichos* Schltdl.) juice by nanofiltration. J. Food  
482 Process Eng. 40, e12343.

483

484 Bushan, S., Kalia, K., Sharma, M., Singh, B., Ahuja, P.S. (2008). Processing of apple  
485 pomace for bioactive molecules. Crit. Rev. Biotechnol. 28, 285-296.

486

487 Cissé, M., Vaillant, F., Pallet, D., Dornier, M. (2011). Selecting ultrafiltration and  
488 nanofiltration membranes to concentrate anthocyanins from roselle extract (*Hibiscus*  
489 *sabdariffa* L.). Food Res. Int. 44, 2607-2614.

490



491 Couto, D.S., Dornier, M., Pallet, D., Reynes, M., Dijoux, D., Freitas, S.P., Cabral, L.M.C.  
492 (2011) Evaluation of nanofiltration membranes for the retention of anthocyanins of açai  
493 (*Euterpe oleracea Mart.*) juice. *Desalin. Water Treat.* 27, 108-113.  
494  
495 De Paepe, D., Servaes, K., Noten, B., Diels, L., De Loose, M., Van Droogenbroeck, B.,  
496 Voorspoels, S. (2013). An improved mass spectrometric method for identification and  
497 quantification of phenolic compounds in apple fruits. *Food Chem.* 136, 368-375.  
498  
499 De Paepe, D., Coudijzer, K., Noten, B., Valkenburg, D., Servaes, K., De Loose, M., Diels,  
500 L., Voorspoels, S., Van Droogenbroeck, B. (2015a). A comparative study between spiral-  
501 filter press and belt press implemented in a cloudy apple juice production process. *Food*  
502 *Chem.* 173, 986-996.  
503  
504 De Paepe, D., Valkenburg, D., Noten, B., Servaes, K., Diels, L., De Loose, M., Van  
505 Droogenbroeck, B., Voorspoels, S. (2015b). Variability of the phenolic profiles in the fruits  
506 from old, recent and new apple cultivars cultivated in Belgium. *Metabolomics* 11, 739-752.  
507  
508 Dubreuil, M.F.S., Vandezande, P., Van Hecke, W.H.S., Porto-Carrero, W.J., Dotremont,  
509 C.T.E. (2013). Study on ageing/fouling phenomena and the effect of upstream nanofiltration  
510 on *in-situ* product recovery of n-butanol through poly[1-(trimethylsilyl)-1-propyne]  
511 pervaporation membranes. *J. Membr. Sci.* 447, 134-143.  
512  
513 Garcia-Gonzalez, L., Bijttebier, S., Voorspoels, S., Uyttebroek, M., Elst, K., Dejonghe, W.,  
514 Satyawali, Y., Pant, D., Vanbroekhoven, K., De Wever, H. (2015). Cascaded valorization of  
515 food waste using bioconversions as core processes. In: Ravishankar, R.V. (ed) *Advances in*  
516 *food biotechnology*. Wiley, New York, pp. 427-441.  
517  
518 Garcia-Torres, R., Ponagandla, N.R., Rouseff, R.L., Goodrich-Schneider, R.M., Reyes-De-  
519 Corcuera, J.I. (2009). Effects of dissolved oxygen in fruit juices and methods of removal.  
520 *Compr. Rev. Food Sci. Food Saf.* 8, 409-423.  
521  
522 Harbourne, N., Marete, E., Jacquier, J.C., O’Riordan, D. (2013). Conventional extraction  
523 techniques for phytochemicals. In: Tiwari, B.K., Brunton, N.P., Brennan, C.S. (eds)

524 Handbook of Plant Food Phytochemicals: sources, stability and extraction, Wiley,  
525 Chichester, pp. 399-411.  
526

527 Harjo, B., Wibowo, C., Ng, K.M. (2004). Development of natural product manufacturing  
528 processes: Phytochemicals. Chem. Eng. Res. Des. 82, 1010-1028.  
529

530 Hasbay Adil, I., Çetin, H.I., Yener, M.E., Bayindirli, A. (2007). Subcritical (carbon dioxide  
531 + ethanol) extraction of polyphenols from apple and peach pomaces, and determination of  
532 the antioxidant activities of the extracts. J. Supercrit. Fluids 43, 55-63.  
533

534 Lin, C.S.K., Pfaltzgraff, L.A., Herrero-Davila, L., Mubofu, E.B., Abderrahim, S., Clark,  
535 J.H., Koutinas, A.A., Kopsahelis, N., Stamatelatos, K., Dickson, F., Thankappan, S.,  
536 Mohamed, Z., Brocklesby, R., Luque, R. (2013). Food waste as a valuable resource for the  
537 production of chemicals, materials and fuels: current situation and global perspective.  
538 Energy Environ. Sci. 6, 426-464.  
539

540 Machado, M.T.C., Mello, B.C.B.S., Hubinger, M.D. (2013). Study of alcoholic and aqueous  
541 extraction of pequi (*Caryocar brasiliense* Camb.) natural antioxidants and extracts  
542 concentration by nanofiltration. J. Food Eng. 117, 450-457.  
543

544 Marchetti, P., Jimenez-Solomon, M.F., Székely, G., Livingston, A.G. (2014). Molecular  
545 separation with organic solvent nanofiltration: a critical review. Chem. Rev. 114, 10735-  
546 10806.  
547

548 Matés, J.M. (2013) Pharmacology of phytochemicals. In: Tiwari, B.K., Brunton, N.P.,  
549 Brennan, C.S. (eds) Handbook of plant food phytochemicals: sources, stability and  
550 extraction, Wiley, Chichester, pp. 68-104.  
551

552 Mondor, M., Girard, B., Moresoli, C. (2000). Modeling flux behavior for membrane  
553 filtration of apple juice. Food Res. Int. 33, 539-548.  
554

555 Mustafa, G., Wyns, K., Vandezande, P., Buekenhoudt, A., Meynen, V. (2014) Novel  
556 grafting method efficiently decreases irreversible fouling of ceramic nanofiltration  
557 membranes. *J. Membr. Sci.* 470, 369-377.

558

559 Nawaz, H., Shi, J., Mittal, G.S., Kakuda, Y. (2006). Extraction of polyphenols from grape  
560 seeds and concentration by ultrafiltration. *Sep. Purif. Technol.* 48, 176-181.

561

562 Renard, C.M.G.C., Baron, A., Guyot, S., Drilleau, J.-F. (2001). Interactions between apple  
563 cell walls and native apple polyphenols: quantification and some consequences. *Int. J. Biol.*  
564 *Macromol.* 29, 115-125.

565

566 Saleh, Z.S., Stanley, R., Wibisono, R. (2006). Separation and concentration of health  
567 compounds by membrane filtration. *Int. J. Food Eng.* 2, Iss 3, Art 4.

568

569 Sarmiento, L.A.V., Machado, R.A.F., Petrus, J.C.C., Tamanini, T.R., Bolzan, A. (2008).  
570 Extraction of polyphenols from cocoa seeds and concentration through polymeric  
571 membranes. *J. Supercrit. Fluids* 45, 64-69.

572

573 Schieber, A., Hilt, P., Streker, P., Endreß, H.-U., Rentschler, C., Carle, R. (2003). A new  
574 process for the combined recovery of pectin and phenolic compounds from apple pomace.  
575 *Innov. Food Sci. Emerg. Technol.* 4, 99-107.

576

577 Tylkowski, B., Trusheva, B., Bankova, V., Giamberini, M., Peev, G., Nikolova, A. (2010).  
578 Extraction of biologically active compounds from propolis and concentration of extract by  
579 nanofiltration. *J. Membr. Sci.* 348, 124-130.

580

581 Van Dael, M., Kuppens, T., Lizin, S., Van Passel, S. (2015). Techno-economic assessment  
582 methodology for ultrasonic production of biofuels. In: Fang, Z., Smith, R.L. Jr., Qi, X. (eds)  
583 *Production of biofuels and chemicals with ultrasound*, Springer, Dordrecht, pp. 317-345.

584

585 Van der Sluis, A.A., Dekker, M., Skrede, G., Jongen, W.M. (2002). Activity and  
586 concentration of polyphenolic antioxidants in apple juice. 1. Effect of existing production  
587 methods. *J. Agric. Food Chem.* 50, 7211-7219.

588

589 Vandezande, P., Gevers, L.E.M., Vankelecom, I.F.J. (2008). Solvent resistant nanofiltration:  
590 separating on a molecular level. *Chem. Soc. Rev.* 37, 365-405.

591

592 Vela, G., León, D.M., García, H.S. (2003). Polyphenoloxidase activity during ripening and  
593 chilling stress in 'Manila' mangoes. *J. Horticult. Sci. Biotechnol.* 78, 104-107.

594

595 Vendruscolo, F., Albuquerque, P.M., Streit, F., Esposito, E., Ninow, J.L. (2008). Apple  
596 pomace: a versatile substrate for biotechnological applications. *Crit. Rev. Biotechnol.* 28, 1-  
597 12.

598

599 Wijngaard, H.H., Brunton, N. (2010). The optimisation of solid-liquid extraction of  
600 antioxidants from apple pomace by response surface methodology. *J. Food Eng.* 96, 134-  
601 140.

602

603 Wijngaard, H.H., Trifunovic, O., Bongers, P. (2013). Novel extraction techniques for  
604 phytochemicals. In: Tiwari, B.K., Brunton, N.P., Brennan, C.S. (eds) *Handbook of plant*  
605 *food phytochemicals: sources, stability and extraction*, Wiley, Chichester, pp. 412-433.

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617 TABLE 1.

618 PROCESS PARAMETERS OF GRINDING SYSTEM (MULTICUT) AND SPIRAL-

619 FILTER PRESS

Parameter	Unit	Value
Rotation speed screw Multicut	rpm	11.2
Rotation speed knives Multicut	rpm	1440
Number of teeth on knives	-	5
Inclination of spiral	degrees	38-25
Number of canals in spiral	-	4
Frequency of spiral	%	100
Frequency of feed pump	%	12
Frequency of vacuum pump	%	100
Pore size filter	µm	100
Absolute N <sub>2</sub> pressure in Multicut	bar	1.6
Absolute pressure in extraction cell	bar	0.15
Absolute pressure bottom of spiral	bar	1.1
Yield juice	% (w/w)	83.3
Throughput (mass flow apple)	kg h <sup>-1</sup>	446

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639 TABLE 2.

640 OVERVIEW OF USED MEMBRANES

Membrane	Manufacturer	Filtration application	MWCO (Da) <sup>a</sup>
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DuraMem200	Evonik (Germany)	organic solvent (e.g. acetone)	200
Desal-5 DK	GE Osmonics (USA)	water	150-350
NFX	Synder Filtration (USA)	water	150-300
NF90	Dow Filmtec (USA)	water	n.a. <sup>b</sup>
DuraMem300	Evonik (Germany)	organic solvent (e.g. acetone)	300
NF030306	SolSep (the Netherlands)	organic solvent (e.g. acetone)	n.a.
NanoPro AS3012	AMS Technologies (Israel)	organic solvent (e.g. acetone)	180

641 <sup>a</sup> MWCO: molecular weight cut-off

642 <sup>b</sup> n.a.: not available

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665 TABLE 3.

666 NOMENCLATURE AND MOLECULAR WEIGHT (MW) OF TEN SELECTED

667 PHENOLIC MARKER COMPOUNDS AND QUINIC ACID IN APPLE FRUITS

Phenolic class	Name	Common name	MW (g mol <sup>-1</sup> )
Cyclitols	Quinic acid	Quinic acid	192
Hydroxycinnamic acids	<i>Trans</i> -3-caffeoylquinic acid	Chlorogenic acid	354
Flavonols	Quercetin-3- <i>O</i> -glucoside	Isoquercitrin	464
	Quercetin-3- <i>O</i> -galactoside	Hyperin	464
	Quercetin-3- <i>O</i> -rutinoside	Rutin	611
	Quercetin-3- <i>O</i> -arabinoside	Avicularin	434
	Quercetin-3- <i>O</i> -rhamnoside	Quercitrin	448
Dihydrochalcones	Phloretin-2'- <i>O</i> -glucoside	Phlorizin	436
Flavanols	(+)-Catechin	Catechin	290
	(-)-Epicatechin	Epicatechin	290
Procyanidins	(-)-Epicatechin-(4 $\beta$ $\rightarrow$ 8)-(-)-epicatechin	Procyanidin B2	579

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689 TABLE 4.

690 AVERAGE CONCENTRATION OF PHENOLIC COMPOUNDS IN APPLE AND  
 691 AVERAGE FRACTIONATION IN JUICE AND POMACE AFTER AEROBIC AND  
 692 ANAEROBIC PRESSING ( $\pm$  STANDARD DEVIATION FOR N = 2)

Phenolic compound	Concentration		Fractionation (%)		
	$\mu\text{g g}^{-1}$ DW		Aerobic pressing		Anaerobic pressing
	Apple	Juice	Pomace	Juice	Pomace
Quinic acid	1285 $\pm$ 7	48.6 $\pm$ 1.6	17.7 $\pm$ 1.7	65.2 $\pm$ 0.7	32.6 $\pm$ 1.7
Chlorogenic acid	1390 $\pm$ 0	38.5 $\pm$ 2.2	2.8 $\pm$ 0.1	61.2 $\pm$ 0.6	22.5 $\pm$ 4.5
Isoquercitrin	39 $\pm$ 1	8.3 $\pm$ 0.6	27.3 $\pm$ 2.0	11.9 $\pm$ 0.7	39.8 $\pm$ 1.4
Hyperin	217 $\pm$ 15	4.3 $\pm$ 0.3	29.5 $\pm$ 2.2	5.2 $\pm$ 0.4	42.6 $\pm$ 7.7
Rutin	10 $\pm$ 0	5.0 $\pm$ 0.2	22.4 $\pm$ 1.2	7.1 $\pm$ 0.2	32.6 $\pm$ 3.0
Avicularin	213 $\pm$ 14	6.8 $\pm$ 0.5	38.3 $\pm$ 3.0	10.0 $\pm$ 0.7	59.0 $\pm$ 11.3
Quercitrin	169 $\pm$ 8	9.2 $\pm$ 0.5	41.5 $\pm$ 2.0	18.7 $\pm$ 0.9	64.8 $\pm$ 11.2
				51.3 $\pm$	
Phlorizin	261 $\pm$ 69	27.5 $\pm$ 7.3	21.8 $\pm$ 5.8	13.6	76.1 $\pm$ 21.2
Catechin	25 $\pm$ 1	47.1 $\pm$ 1.4	4.2 $\pm$ 0.2	84.8 $\pm$ 2.4	29.8 $\pm$ 1.2
Epicatechin	471 $\pm$ 13	43.0 $\pm$ 3.3	7.3 $\pm$ 0.2	75.0 $\pm$ 2.1	35.3 $\pm$ 4.3
Procyanidin B2	1020 $\pm$ 14	37.4 $\pm$ 1.8	4.2 $\pm$ 0.1	57.9 $\pm$ 0.8	20.4 $\pm$ 3.6
Total without quinic acid	3813 $\pm$ 75	32.7 $\pm$ 1.2	10.6 $\pm$ 0.2	52.9 $\pm$ 1.1	32.5 $\pm$ 2.3
Total with quinic acid	5098 $\pm$ 75	36.7 $\pm$ 1.0	12.4 $\pm$ 0.5	56.0 $\pm$ 0.9	32.5 $\pm$ 1.8

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TABLE 5.



707 AVERAGE CONCENTRATION OF PHENOLIC COMPOUNDS IN EXTRACTS FOR  
 708 SCREENING TESTS ( $\pm$  STANDARD DEVIATION FOR N = 5)

Concentration ( $\mu\text{g g}^{-1}$ DW) Phenolic compound	Screening tests	
	Ethanol:water	Acetone:water
Quinic acid	498 $\pm$ 17	542 $\pm$ 51
Cathechin	18 $\pm$ 0	19 $\pm$ 1
Epicatechin	431 $\pm$ 34	474 $\pm$ 38
Chlorogenic acid	363 $\pm$ 12	421 $\pm$ 19
Avicularin	400 $\pm$ 21	448 $\pm$ 41
Phlorizin	566 $\pm$ 34	605 $\pm$ 96
Quercitrin	360 $\pm$ 16	414 $\pm$ 33
Hyperin	250 $\pm$ 9	291 $\pm$ 22
Isoquercitrin	46 $\pm$ 3	51 $\pm$ 3
Procyanidin B2	561 $\pm$ 30	687 $\pm$ 72
Rutin	11 $\pm$ 0	13 $\pm$ 1
Total without quinic acid	3007 $\pm$ 64	3423 $\pm$ 133
Total with quinic acid	3505 $\pm$ 66	3965 $\pm$ 142

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723 TABLE 6.  
 724 MEMBRANE SCREENING TEST: TIME-AVERAGE PERMEATE FLUX OF  
 725 SCREENED MEMBRANES AT STEADY-STATE CONDITIONS FOR THE  
 726 ETHANOL:WATER AND ACETONE:WATER EXTRACTS

Membrane	Pressure (bar)	Permeate flux (L m <sup>-2</sup> h <sup>-1</sup> )	
		Ethanol:water	Acetone:water
DuraMem200	20	11.9	17.0
DuraMem200	30	15.2	19.5
Desal-5 DK	20	13.6	n.d.
NFX	20	13.5	n.d.
NF90	20	22.7	n.d.
DuraMem300	20	n.d. <sup>a</sup>	16.0
NF030306	20	n.d.	1.1
NanoPro AS3012	20	n.d.	1.3

727 <sup>a</sup>n.d.: not determined

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753