Subcritical water extraction of phenolic acids from distillery stillage

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INTRODUCTION

Distilleries generate huge amounts of by-products that have a negative impact on the environment, so the management of wastes generated by this sector should be improved. The concept of a circular economy includes the valorization of by-products by the recovery of compounds with valuable functions. Industrial cereal by-products are generated during alcohol production. Thus, phenolic acid recovery from distillery stillage may prove to be an innovative approach to not only reducing the pollution generated in distilleries but also increasing their economic competitiveness of them and the full use of raw materials in the process. Due to the potential health benefits, the importance of bioactive compounds is strongly related to their industrial use in many areas, such as cosmetics, pharmaceuticals, agriculture, etc. To meet the requirement of sustainable development, the recovery of phenolic acids should be carried out using green extraction techniques that minimize the volumes of solvents and avoid the use of toxic ones. One example of such a technique is subcritical water extraction (SWE) which is environmentally friendly because it uses water as a solvent at a temperature above the atmospheric boiling point and the elevated pressure maintains the solvent in its liquid state. However, attention should be paid to the chemical structure of phenolic acids and their interaction with other components during the optimization of extraction.

Based on a literature review, it seems that there is a lack of information on the recovery of high-quality bioactive compounds from distillery stillage employing green extraction procedures. Therefore, this study investigated the effect of SWE conditions on the efficiency of recovery of phenolic acids from distillery stillage.

MATERIALS AND METHODS

This study used distillery stillage from the production of concentrated crude ethyl alcohol from cereals (a company from north-eastern Poland).The characteristics of the stillage is shown in Table 1.

Table 1. Characteristics of distillery stillage

Parameter	Unit	Average concentration (± standard deviation)
COD	mg/L	43600 (±1294)
Total nitrogen	mg/L	4345 (±386)
Ammonium nitrogen	mg/L	8.4 (±2.7)
Total phosphorus	mg/L	280 (±76)
Volatile fatty acids	mg/L	788 (±137)

Extraction of phenolic acids was performed with SWE using a microwave system. 1 g of distillery stillage and 30 mL of water were used for the extraction. The process was carried out for 15, 30, and 60 min at temperatures of 80, 140, and 200°C and the pressure of 4.14 MPa.

After extraction, the samples were centrifuged for 10 min at 10,000 rpm. The supernatants were collected, evaporated to dryness, and then dissolved in 1 mL of methanol and analyzed.The chromatographic separation was performed by Chromatograph (Varian ProStar) equipped with a UV-Vis detector equipped with a Supelcosil C18 column operating at 35°C (Figure 1).

The mobile phase consisted of acetonitrile containing 0.15% formic acid (solvent A) and water containing 0.15% formic acid (solvent B). The separation was performed for 42 min with the following elution gradient ranges: 0–18 min, 1–96% B; 18–35 min, 96–82% B; 35–40 min, 82–75% B.

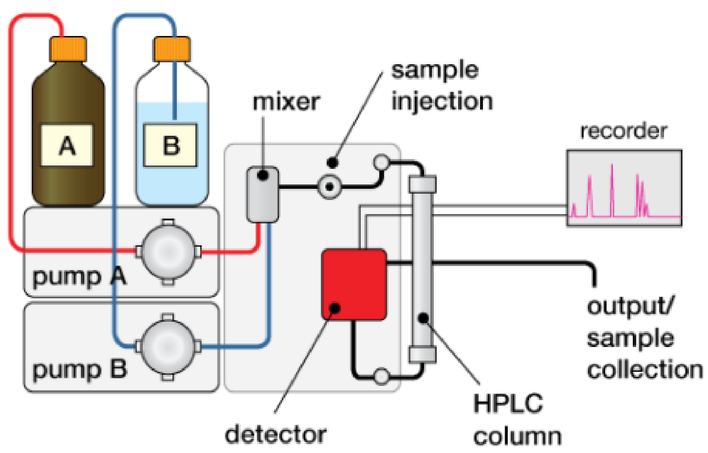

Figure 1. HPLC setup is diagrammed

The detection was performed at the wavelength of 260 nm (p-OH-benzoic, vanillic, syringic acid) and 320 nm (p-coumaric, ferulic, sinapic acid).

RESULTS

Phenolic acids present in the extracts were quantified by HPLC. The influence of the temperature and SWE time on the recovery efficiency was investigated. Figure 2 shows the heatmap which represents the concentrations of individual phenolic acids that were recovered from the stillage with 15-, 30-, and 60-min SWE at 80, 140, and 200°C.

The best conditions were obtained with 30-min SWE at 140°C, which allowed to obtain the total concentration of phenolic acids of 2.88 µg/g DM.

Extending the SWE time from 15 to 30 minutes resulted in obtaining extracts with 1.38 times higher concentrations of phenolic acids. Further extending the SWE time to 60 min gradually decreased the extraction efficiency. Increasing the extraction temperature of SWE from 80 to 140°C increased the yield and recovery by about 20%. However, a further increase in temperature from 140 to 200°C slightly reduced the recovery of phenolic acids by about 13%. The least effective conditions turned out to be 15-min SWE at 80ºC.

In the extracts, ferulic and p-coumaric acids predominated, constituting from 29 to 32% and from 20 to 24% of all detected phenolic acids, respectively, depending on the extraction condition (Figure 2). In turn, p-OH benzoic, vanillic, and sinapic acids accounted for about 8–10%, 13–16%, and 12–14% of the total, respectively. Syringic acid had the smallest share of all phenolic acids in the distillery stillage extracts (about 5–7%).

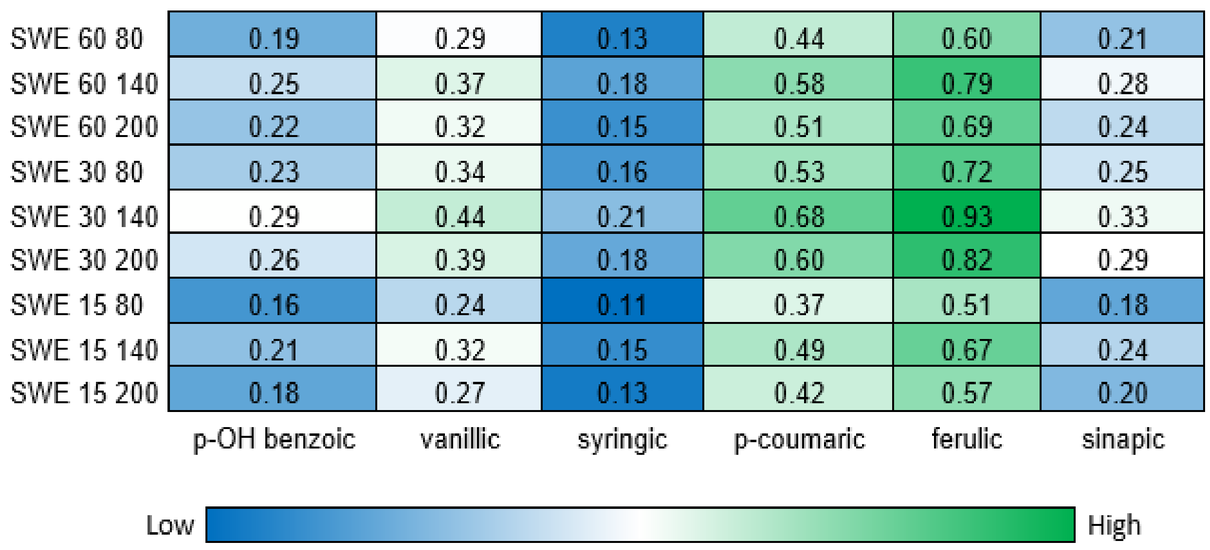

Figure 2. Heatmap of the concentrations of phenolic acids in distillery stillage extracts obtained with SWE. In the abbreviations, the values after SWE represent the extraction time and then extraction temperature. The concentrations of phenolic acids in the table are expressed as microgram per gram dry mass (µg/g DM). The content of individual phenolic acids is represented by a color (green indicates a high content; blue indicates a low content).

CONCLUSIONS

- Distillery stillage is a rich source of bioactive compounds.
- Water under subcritical conditions (temperature of 140°C and pressure of 4.14 MPa) was effective in recovering bioactive compounds from the distillery stillage.
- Elimination of the organic solvent is desirable in the production of organic functional food products and nutraceuticals.
- The extract produced may be labeled as a “natural product”.
- Recovery of phenolic acids from distillery stillage can increase the economic profitability of distilleries and the rate of by-product utilization.

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