Valorization of spent coffee grounds with supercritical fluids

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Spent coffee grounds (SCGs) are a potential sustainable source of high value added compounds. Extractions with pure supercritical CO_2 ($scCO_2$) and $scCO_2$+co-solvents (10% ethanol, 10% *i*-propanol and 5% ethyl lactate) of SCGs were used for valorization of the waste biomass. Conditions for highest yields (30 MPa and 323 K for extractions with co-solvents and 40 MPa and 313 K - for those with pure $scCO_2$) were identified and applied for comparison. The results, in terms of global yield and elemental composition, were compared with those achieved by pure $scCO_2$ and by conventional Soxhlet extraction with *n*-hexane. The highest yield of 12.3%was obtained with $scCO_2$+5% ethyl lactate, yields of (10.1 to 12) % - with the rest of the extractions, and 10.4 %-by the Soxhlet extraction. Quantitative identification of diterpens in the extracts was carried out by H-NMR. Elemental analysis provided useful information for the application of SCGs products, obtained with the tested extraction technologies.

Introduction

The selection of potential feedstock sources of high value added bioproducts with a wide spectrum of applications like biofuels, foods additives, pharmaceutical, cosmetics and other health and well-being related compounds should take into account the abundance and composition of original biomass. The spent coffee grounds (SCGs) are biowastes, obtained in significant amounts after the consumption of non-soluble coffee and from the production of soluble coffee. Coffee is one of the world's most popular beverages and the second largest operated commodity after petroleum [1].The importance of SCGs can be appreciated taking into consideration that coffee production in the world for 2015/2016 was 8.6 million tones according to ICO [2] (9.2million tones, according to USDA [3]).The oil from SCGs consists mainly of triglycerides and small amounts of diglycerides, free fatty acids, together with terpenes, sterols and tocopherols [1],thus representing an important source of raw materials for a variety of industries.

Materials and Methods

The SCGs were obtained from a local coffee shop. The conventional Soxhlet extraction with *n*-hexane was performed for 4 h. The solvent was removed by reduced pressure evaporation and the average yield of coffee oil thus obtained was 10.4 %.

The supercritical extraction (SCE) was carried out in a laboratory apparatus "Applied Separations" with some modifications, namely an addition of a second high pressure pump for the co-solvents used. The pressure of 30 MPa and temperature of 323 K and the solvent to co-solvent ratio were chosen to provide a basis for adequate comparison of the global oil yields obtained.

The ^{1}H-NMR spectra of the crude oil extracts were recorded on a Bruker Avance 400 MHz NMR spectrometer (Bruker Inc., Bremen, Germany), working at 400.13 MHz for 1H-NMR, equipped with a 5 mm PABBO BB-1H probe with 90° proton pulse length of 11.8 µs and an interval time between acquisitions of 30 s, using standard Bruker routines. A CHNO elemental analysis of the samples from the initial, residue and oils obtained from SGC were also performed.

Results and Conclusion

Figure 1 shows the extraction kinetic curves in terms of SCGs oil yield, obtained with $scCO_2$+ different co-solvents, and with pure $scCO_2$ at the optimum conditions of 40 MPa and 313 K. The highest yield was obtained with 5 % ethyl lactate (ELactate). The qualitative and quantitative patterns of the other two extraction curves obtained with isobutanol (IsBut) and ethanol (EtOH) are very similar as final values of the cumulative yields achieved. For the SCE without a co-solvent applied, not only the yield is lower but it also takes longer time to reach the plateau of the extraction.

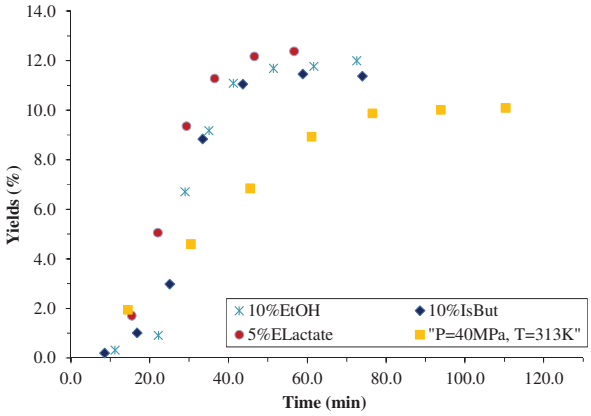

Figure 1. Extraction kinetic curves in terms of SCGs oil yield obtained with scCO2+ different co-solvents. Extractions with the different co-solvents were carried out at 30 MPa and323 K: ✳-10% of ethanol, ♦-10% of isobutanol, ●- 5% Ethyl Lactate. ■-CO_2at P=40 MPa and T=313.

^{1}H-NMR analysis showed that the oils are largely dominated by triacylglycerols (TAGs) with minor amounts of 1,2 diacylglycerols. The main esters are of saturated fatty acids (44.4 - 45.9 %), diunsaturated fatty acids (40.3 -41.5 %) and monounsaturated fatty acids (13.9-15.0 %). Diterpenoids were also quantified in the extracts namely, cafestol (2.23-3.29 %); 16-O-Methyl-Cafestol (2.21-3.61 %) and kahweol (0.97-1.33 %).

Table 1 shows the data for the CHNO elemental analysis of the dry SCGs, before extraction, the SCGs after extraction and the extracts, obtained from the SGC.

The results obtained show elemental compositions similar to those, published by other authors. The higher C and H contents and the lower N and O contents in the extracts are in agreement with the analysis of ^{1}H-NMR where the predominant compounds identified are acylglycerols. All depleted solid matrices contain more nitrogen and less carbon which make them more suitable for certain applications, like composting. The eventual presence of nitrogen in the extracts needs more precise estimation, since nitrogen compounds in fuels should be limited from air pollution point of view, but they might be useful as antioxidants. In any case, Table 1 results show once again that circular production in sustainable biorefineries should separate and use all useful components. In this instance, elemental analysis is a relatively inexpensive tool which in combination with other analytical methods can provide useful information for the development of extraction technologies.

Table 1. Elemental analysis of the SCGs before and after extractions, and the extracted oils, $\%_{mass}$*.

Sample	Carbon	Hydrogen	Nitrogen	Oxygen
Dry Spent Coffee Grounds, before extraction	51.02	7.04	2.10	39.84
Average for the SCG,after the extractions	46.54	6.22	2.28	44.96
Oil from hexane extraction	77.00	11.74	< 0.5	11.26
Oil from SCO_2_40/313 (conditions?)	77.03	12.14	< 0.5	10.83
Oil from SCO_2_30/323_10%Ethanol	76.63	11.49	< 0.5	11.88
Oil from SCO_2_30/323_10%Isobutanol	76.51	11.38	< 0.5	12.11
Oil from SCO_2_30/323_5%Ethyl lactate	76.79	11.52	< 0.5	11.69

*Oxygen is calculated by difference to 100 % (for the extracts – without nitrogen). Less than 0.5 % nitrogen could not be determined quantitatively by the used method. The code used for the SC extractions (e.g., 40/313), shows pressure (MPa)/temperature (K).

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References

[1] A. Murthy, M. Naidu, Resour. Conserv. Recycl., 66 (2012), 45-58.

[2] ICO (International Coffee Organization). "Global coffee production", Available at: http://www.ico.org/monthly_coffee_trade_stats.asp, 2016.

[3] USDA (United States Department of Agriculture) Coffee: World Markets and Trade, Available at:http://apps.fas.usda.gov/psdonline/circulars/coffee.pdf , 2015.