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PROGRAMME

Influence of co-solvents on the supercritical extraction kinetics of spent coffee grounds: experimental and modelling studies

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1. Introduction

Coffee is one of the most widely used beverages. An estimated 3.5 billion cups of coffee are drunk worldwide every day. In EU alone, for the period 2011-2013, 2.5 Mt of coffee were consumed. Taking into consideration that the production of coffee in 2015¹ was approximately 9 Mt and that from each kg of coffee 0.91 kg of solid waste is produced, the importance of a further valorization of this residue becomes obvious. In recent years, the biorefinery concept has been identified as the most promising route for employment of the full potential of a biomass by maximizing its conversion into high value products. Its main bottleneck, however, is how to extract the energy and non- energy compounds from the biomass without damaging one or more of the components, e.g. those which are heat sensitive. Spent coffee grounds (SCGs) contain large amounts of fatty acids, lignin, cellulose, hemicellulose, etc. and can be exploited as an excellent source of value-added energy and non-energy related products (e.g. antioxidants and other functional additives).

2. Results and discussion

Figure 1 shows the extraction kinetic curves in terms of SCGs oil yield, obtained with scCO₂+co-solvents, and with pure scCO₂ at 30 MPa. The highest yield was obtained with the co-solvents, namely with 5 % ethyl lactate (ELactate) at $T = 333.2$ K, while with pure scCO₂ the highest yield at that pressure was attained at $T = 313.2$ K.

The extraction kinetics of SCGs was simulated applying a dynamic model of Sovová and Stateva². The model assumes that the oils are placed on the surface of the solid particles, which allows neglecting internal diffusion. This assumption is well-suited with finely ground substrates where the diffusion path in the particles is short and the extract is easily accessible, resulting in negligible internal mass transfer resistance. The model was planned, validated and executed using gPROMSModel Builder, an equation-oriented modelling and optimization platform for steady-state and dynamic systems. The SCGs oil was represented not by one (or several) of its constituent molecules, but by a hypothetical molecule that takes into full account the actual oil composition. To calculate the solubility of the virtual molecule in the pure scCO₂, and in the scCO₂+co-solvent, the VLE of the systems under consideration was simulated, applying the predictive Soave-Redlich-Kwong (PSRK) cubic EoS. The needed property values of the oil representative virtual molecule were estimated with known group contribution methods but employing non-integer descriptors of

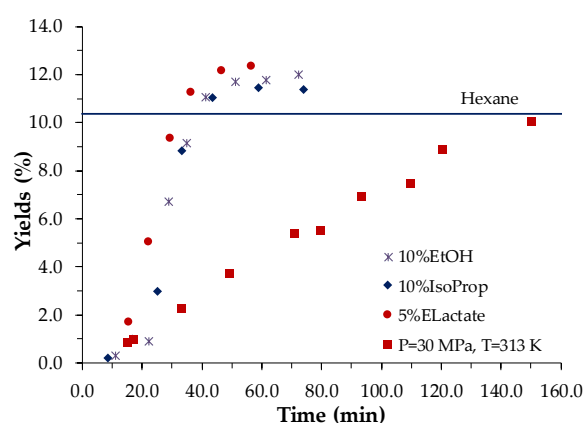


Figure 1. Extraction kinetic curves in terms of SCGs oil yield obtained with scCO₂+different co-solvents. Extractions with the different co-solvents were carried out at 30 MPa and 333.2 K: * -10% of ethanol, ◆ -10% of isopropanol, ● - 5% of Ethyl Lactate. ■ -CO₂ at $P=30$ MPa and $T=313.2$ K

its chemical structure. To the best of our knowledge, there are no studies in the literature, which report representation of an oil by a single hypothetical molecule that takes into consideration all identified triglyceride components.

¹H-NMR analysis showed that the oils obtained from the supercritical fluid extraction and compared with n-hexane, 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, caffeine (0.08-2.07), cafestol (2.23-3.29 %); 16-O-Methyl-Cafestol (2.21-3.61 %) and kahweol (0.97-1.33 %).

Moreover, elemental compositions analysis presents similar results to those, published by other authors. The higher C and H contents and the lower N and O contents in the extracts agree with the analysis of ¹H-NMR where the predominant compounds identified are acylglycerols. The exhausted SCGs contain more nitrogen and less carbon which make them more appropriate for certain applications, like composting. The presence of nitrogen in the extracts decreases their potential as fuels, since nitrogen should be limited from air pollution point of view, but they might be useful as antioxidants.

3. Conclusions

In our work the influence of different co-solvents on the scCO₂ extraction of SCGs in terms of yield and extract compositions and the modelling of the extraction curves is reported for the first time. Quantitative identification of triacylglycerols and diterpenes in the extracts was carried out by ¹H-NMR. Elemental analysis provided useful information for the possible application of SCGs products, obtained with the different co-solvents examined, namely about the total content of nitrogen in the samples and their potential applications.

References

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