

ON MODELLING OF THREE DIMENSIONAL FLOW IN EXTRACTION OF BIOLOGICALLY ACTIVE SUBSTANCES FROM PLANTS

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Abstract. The authors consider the process of extraction from heterogeneous plant material; a novel model offering 3D spatial resolution is proposed and simulation possibilities by applying several modern numerical methods for three dimensional problems are discussed. These types of problems naturally arise when one wishes to mathematically describe the processes of the extraction with solvents such as supercritical carbon dioxide (scCO₂). The results of this process meet the demand of the functional foods, nutraceutical, pharmaceutical and cosmetic industries on bioactive compounds. The models used in typical simulations by the industry offer no spatial resolution of the extraction process, however, when novel designs of extractors are developed, the three dimensional flow of the solvent and its interaction with the plant material should be considered. We propose a coupled system of equations consisting of fluid dynamics equations describing the flow of the solvent and reaction-advection-diffusion equations for the solute, plus equations describing the remaining concentration of solute in the biomass. The exchange of the active material between the solid and fluid is modelled by the Langmuir law. The initial distribution of solute in the plant material is not assumed to be homogeneous, nor are the extraction parameters, i.e. heterogeneous mixture of plant materials can be covered by this model. The equations are discretized by using finite volume techniques and currently implemented in Octave/Matlab environment. As a result, the temporal evolution of the three dimensional distribution of the solute is obtained along with the velocity field of the solvent, allowing detailed studies of the extraction process in a virtual design. The model is modular, allowing integrating tailor-made laws to describe various plant materials. The authors present simulation results and analyse the advantages and disadvantages of the proposed methods and approaches.

Keywords: scCO₂ extraction, virtual design of extractors, PDEs, hydrodynamics.

Introduction

Supercritical carbon dioxide extraction (scCO₂) is a process that has gained popularity in recent years due to its ability to extract valuable compounds from a wide range of materials using CO₂ in its supercritical state. In this state, CO₂ exhibits properties of both a gas and a liquid, making it an effective solvent for extracting compounds from materials such as plant matter, food products, and pharmaceuticals. This method of extraction was first introduced in the late 1970s and was initially used to extract essential oils from plant materials. At that time, more traditional extraction methods, such as those using solvents such as acetone or hexane, were considered to be more risky and potentially harmful to the environment and human health. However, scCO₂ extraction has since become an increasingly popular alternative, as it is considered to be a safer and more environmentally friendly method of extraction.

The use of mathematical modelling techniques to improve the design of industrial extractors for the extraction of biologically active compounds from plants is a crucial aspect of this research. By utilising mathematical models, the research aims to better understand the various physical and chemical processes that take place during the extraction process, such as the flow of solvent through the batch, diffusion of compounds, and thermodynamic equilibria. These models can be used to predict the behaviour of the extraction process under different conditions and to optimise the process parameters to achieve the highest possible yield of biologically active compounds.

Previous works have investigated various aspects of the extraction process including its thermodynamics, mass transfer and mathematical models that can be used for design and optimization of the process. The article [1] presents a model with an analytical solution for the extraction of vegetable oils using supercritical carbon dioxide, which can be used to evaluate extraction parameters by comparing the extraction curves calculated by the model with experimental data. The article [2] discusses the origins and limitations of a simplified mathematical model based on the Broken-and-Intact Cell (BIC) concept, which is used to model supercritical fluid extraction of bioactive compounds from plants and suggests improvements to the model that have been developed since its initial publication. The article [3] provides a comprehensive overview of mathematical modelling techniques applied to the extraction process and offers a detailed examination of the mathematical methods used to describe the various stages of the process. In [4] the mathematical models of the extraction of pennyroyal essential

oils by supercritical CO₂ with or without an axial dispersion are considered and validated by the experimental data. In [5] a detailed description of the finite volume method and its usage in numerical simulation is presented in a thorough manner including the approximation of surface and volume integrals, cell interpolation and treatment of the resulting systems of algebraic equations. In [6; 7] the extraction curves have been compared with the experimental data for particular plant materials. Several stages of the extraction process are considered in [8].

Despite the growing popularity of scCO₂ extraction, current models used in typical simulations by the industry offer no spatial resolution of the extraction process. However, when novel designs of extractors are developed, the three-dimensional flow of the solvent and its interaction with the plant material should be considered.

Lab scale extractors typically operate in a regime that a full batch of biomass is inserted in the extractor at the beginning of the process, and subsequently all parts of the biomass experience very similar history of extraction. However, larger scale extraction processes may need continuous feed of biomass, where the time spent in extractor and hence the content of the active compound to be extracted varies not only in time but in space, requiring more refined mathematical models.

In this article, we address some aspects of mathematical modelling of scCO₂ extraction, including a mathematical model of the process. We propose a coupled system of equations consisting of fluid dynamics equations describing the flow of the solvent and reaction-advection-diffusion equations for the solute, as well as equations describing the remaining concentration of solute in the biomass. The exchange of the active material between the solid and fluid is modelled by the Langmuir law. The initial distribution of solute in the plant material is not necessarily assumed to be homogeneous, nor are the extraction parameters; this means that the model could cover a heterogeneous mixture of plant materials.

The temporal evolution of the three-dimensional distribution of the solute is obtained, along with the velocity field of the solvent, allowing detailed studies of the extraction process in a virtual design. The model is modular, allowing the integration of tailor-made laws to describe various plant materials.

By providing a more detailed understanding of the extraction process, this model has the potential to improve the design of extractors and optimise the extraction process for different types of plant materials. We also provide examples of its applications. This article could be of interest to researchers and practitioners in the field of extraction and might contribute to the further development of scCO₂ extraction technology.

Materials and methods

We develop Matlab/Octave based software to simulate the flow of solvent in the 3D geometry of the extractor around or through the biomass, with desorption of the active compound into the solvent and convective and diffusive transport of the solute with the solvent. The governing equations depend on the extraction regime. In this paper, we consider the case of solvent flowing past fixed densely packed biomass particles, and the exchange of the active compound from the biomass to the solvent occurs on the boundary of the biomass particles, Figures 1 and 2. We note that in the case of the whole extractor geometry densely packed with biomass, the more simple Darcy's equation can be used instead to calculate the solvent velocity field.

We propose a system of partial differential equations consisting of fluid dynamics equations (1)-(2) describing the flow of the solvent and reaction-advection-diffusion equations for the solute (3), plus equations describing the remaining concentration of the active compound in the biomass (4):

$$\frac{\partial v}{\partial t} + \nabla \cdot (v \otimes v) = -\nabla p + \frac{1}{\text{Re}} \Delta v + f, \quad (1)$$

$$\nabla \cdot v = 0, \quad (2)$$

$$\frac{\partial \varphi}{\partial t} + \nabla \cdot (v \varphi) = \alpha \nabla^2 \varphi + R(\varphi), \quad (3)$$

$$\frac{\partial \psi}{\partial t} = -R(\varphi, \psi), \quad (4)$$

where $\varphi(r, t)$ – concentration of the active compound in the solvent;
 $\psi(r, t)$ – concentration of the active compound bounded in the “intact” cells.

The non-homogeneous part f is any external force density one wishes to apply. The equations have been made dimensionless for executing the numerical simulations. The exchange rate is

$$R(\varphi, \psi) = k(\varphi_{eq} - \varphi), \quad (5)$$

$$\varphi_{eq} = \frac{K\psi}{K\psi + 1}, \quad (6)$$

(Langmuir adsorption isotherm; note that other laws can be easily implemented in the structure of our software), with parameters k and K . In simulations presented in this paper we approximate this law with the regime where k is equivalent to one dimensionless unit and K is five times higher. Regarding the Reynolds number in our typical simulations, it belongs to a certain interval in correspondence with [9; 10] and the numerical values are typically between 0.6 and 8.

The only nontrivial boundary conditions are at the inlet:

$$\alpha \frac{\partial \varphi}{\partial n} + v_n \varphi|_{inlet} = 0, \quad (7)$$

provided that the inflowing solvent has $\varphi = 0$. The diffusion coefficient α was taken to be one unit. The remaining boundary conditions are $\varphi_n = 0$ at the walls (lower subscript n at a scalar field stands for a normal derivative, but at a vector field it denotes the normal component), and the appropriate boundary conditions for the velocity and pressure (homogeneous Neumann for pressure at the rigid walls, pressure or velocity conditions at the inflow, Dirichlet pressure at the outlet).

The equations are discretized by using finite volume techniques on a voxel grid and currently implemented in Octave/Matlab environment. In the section below we present some graphical results produced by our code and discuss several features thereof.

Results and discussion

In the following figures we present the geometry of the problem in different points of view as well as the obtained stationary velocity field after solving (1), (2) as well as solutions of (3), (4) for different time steps. For the calculations the dimensions of the geometry have been chosen $30 \times 7.2 \times 0.8$.

We start off with randomly allocating particles. The first will be the two-dimensional projection of the computational domain.

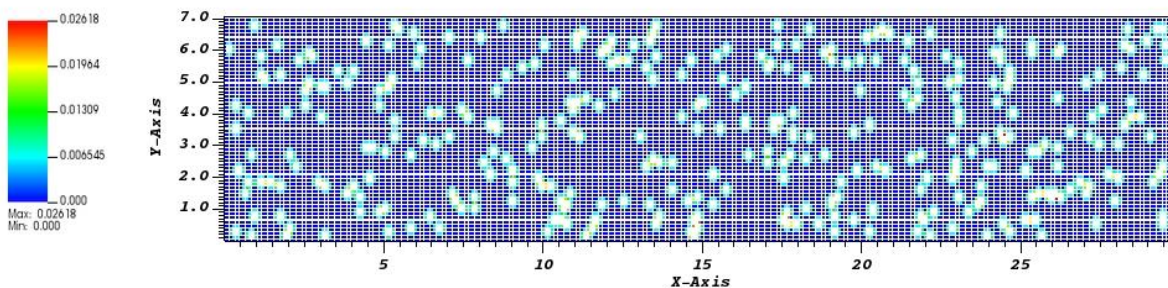


Fig. 1. **Two-dimensional projection of the computational domain; particles (pieces of biomass) allocated randomly**

Moreover, we consider three dimensional resolution in our domain and different types of particle allocation.

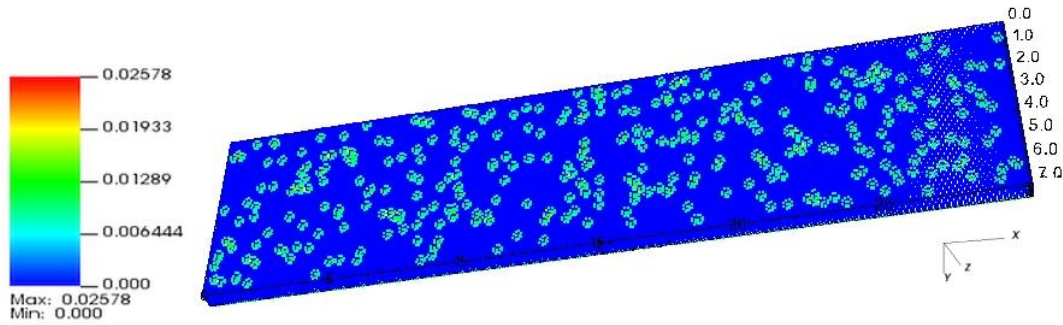


Fig. 2. Three-dimensional setting for the computational domain; particles (pieces of biomass) allocated randomly

By solving (1)-(2) in this domain we obtain a stationary velocity vector field. First setting is the horizontal direction driven field whereas the particles are situated on top of the computational domain and the second one deals with three-dimensional particle allocation with obstacles visible:

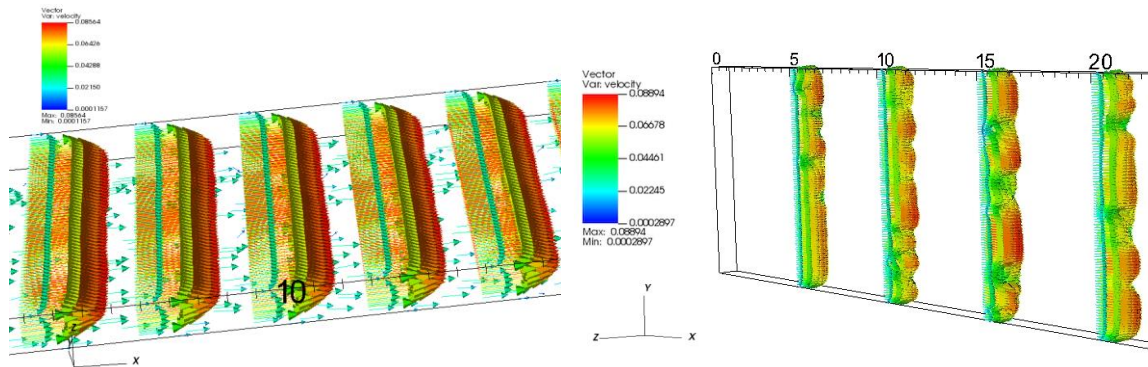


Fig. 3. Zoom shots of three-dimensional setting for the computational domain. Stationary velocity field obtained for surface (left) and submerged (right) particle allocation

In Figures 4-5 for different time moments t , we present the concentration graphs.

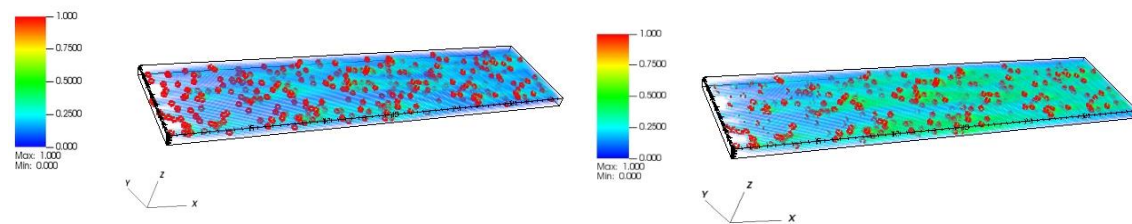


Fig. 4. Initial and sub-terminal states of the extraction process $t = 0$ (left) and $t = 75$ (right)

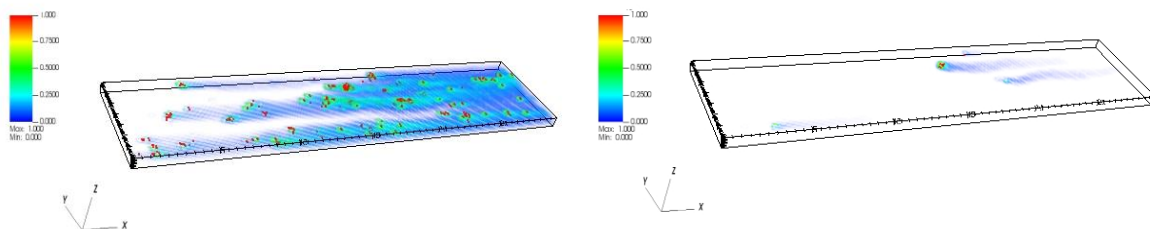


Fig. 5. Sub-terminal and terminal states of the extraction process $t = 150$ (left) and $t = 225$ (right)

For each time moment we have also stored the data to obtain the extraction curve.

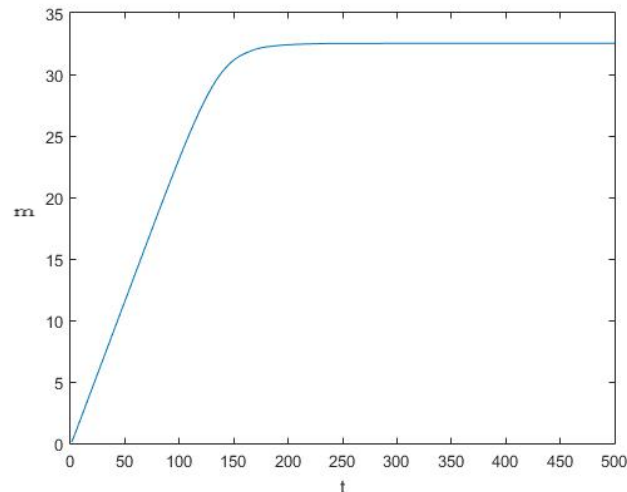


Fig. 6. Extraction curve obtained for simulation up to $t = 500$, where m is extracted mass

Conclusions

1. Snapshots of solution have been obtained in a virtual design computational domain as well as the extraction curve. The solutions depend on the initial conditions, such as initial distribution of the biomass in the extractor, but the extraction curve is less sensitive to initial conditions.
2. The advantage of our research is the 3D resolution with more thorough description of the extraction process. The procedure becomes costly when complex time variable geometries are involved but this could be overcome by introducing more powerful computers.
3. The extraction curves have been compared with the experimental data, similarly as in previous studies, and our numerical results show promising qualitative agreement with the data. In order to achieve quantitative agreement, model parameters can be estimated from experimental data, e.g., the constants in the desorption law can be estimated from the known extraction curve; details to be provided in our follow-up works.

Author contributions

Conceptualization, U.S. and M.M.; methodology, U.S. and M.M.; software, U.S. and M.M.; validation, U.S. and M.M.; formal analysis, U.S. and M.M.; investigation, U.S. and M.M.; data curation, U.S. and M.M.; writing – original draft preparation, U.S. and M.M.; writing – review and editing, U.S. and M.M.; visualization, U.S. and M.M. All authors have read and agreed to the published version of the manuscript.

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