**Review report for CJCE-24-0503**

In this manuscript, authors reported the application of a mathematical model for the supercritical extraction process of essential oil from chamomile flowers. Authors pointed out that the applied model describes the governing mass transfer phenomena in a solid-fluid environment under supercritical conditions using carbon dioxide. They mentioned that the flow of carbon dioxide is assumed to be uniform across any cross-section, although the area available for the fluid phase can vary along the extractor. Furthermore, authors remarked that the physical properties of the solvent are estimated based on the Peng-Robinson equation of state. In addition, they also reported that the model parameters, including the partition factor, internal diffusion coefficient and decaying factor, were determined through maximum likelihood estimation based on experimental data assuming normally distributed errors.

In general, the manuscript is very attractive and interesting, as well as beneficial for applied purposes. I strongly recommend it for publishing in the Canadian Journal of Chemical Engineerings. Meanwhile, the manuscript needs a major and substantial revision before its acceptance. I also invite authors to completely and fully address the comments raised here. The comments are explained below.

1. Please explain and highlight the novelties of this research work with respect to the previously   
   published papers, in the manuscript.   
   ***Thank you for your valuable note! The novelty of the presented behind this work has been elaborated.***

***"This study aims to develop a process model for extracting natural substances from solid materials using supercritical fluids, with a focus on supercritical CO2. The approach involves estimating solvent properties through thermodynamic relationships and determining extraction kinetic parameters via a series of experiments conducted under various conditions. This work presents how a classical first-principle model can be modified to a semi-empirical model with mass transfer. Maximum likelihood estimation is used to solve the parameter estimation problem, after which correlations between parameters and operating conditions are established. By identifying these correlations, the process model can be generalised across a broad range of operating conditions. This generalisation is a key feature of the presented model and a necessary step for future work, which will utilise the dynamics of the supercritical extraction process***."

1. The motivations of conducting this research work are described.  
   ***Thank you for your valuable note! The motivations behind this work have been elaborated as in the text.   
     
   "This study aims to develop a process model for extracting natural substances from solid materials using supercritical fluids, with a focus on supercritical CO2. The approach involves estimating solvent properties through thermodynamic relationships and determining extraction kinetic parameters via a series of experiments conducted under various conditions. This work presents how a classical first-principle model can be modified to a semi-empirical model with mass transfer. Maximum likelihood estimation is used to solve the parameter estimation problem, after which correlations between parameters and operating conditions are established. By identifying these correlations, the process model can be generalised across a broad range of operating conditions. This generalisation is a key feature of the presented model and a necessary step for future work, which will utilise the dynamics of the supercritical extraction process***."
2. English language of manuscript needs a mild revision throughout the manuscript. For example, in page 9, lines 6 and 12, "the desorptiondissolutiondiffusion", must be corrected.   
   ***Thank you for your valuable note! The text has been revised.***
3. The manuscript title is recommended to be improved as "**Mathematical modelling of** **essential oil** supercritical carbon dioxide extraction **from chamomile flowers"**.  
   ***Thank you for your valuable note!  
   The title has been modified according to the comment***
4. The provided highlights must be shortened as well as quantitative reported values.  
   ***Thank you for your valuable note! The highlights have been revised***

* ***A supercritical extraction model with decaying extraction kinetics and Cubic Equation of State is presented***
* ***Model parameters are determined through maximum likelihood estimation based on a set of experimental performed at different operating conditions***
* ***The multiple linear regression is used to find correlations between the estimated parameters and operating conditions***
* ***The close fit between the model predictions and experimental data underscores the model's capability to capture the system dynamics***

1. The last statement of abstract section is ambiguous. In fact, authors did not perform any experiments. Accordingly, please remove it.  
   ***Thank you for your valuable note!  
   The sentence has been removed***
2. The last paragraph of introduction must be rewritten, focusing the importance and necessity of this work.   
   ***Thank you for your valuable note! The necessity of this work has been elaborated on in the text.   
     
   "This study aims to develop a process model for extracting natural substances from solid materials using supercritical fluids, with a focus on supercritical CO2. The approach involves estimating solvent properties through thermodynamic relationships and determining extraction kinetic parameters via a series of experiments conducted under various conditions. This work presents how a classical first-principle model can be modified to a semi-empirical model with mass transfer. Maximum likelihood estimation is used to solve the parameter estimation problem, after which correlations between parameters and operating conditions are established. By identifying these correlations, the process model can be generalised across a broad range of operating conditions. This generalisation is a key feature of the presented model and a necessary step for future work, which will utilise the dynamics of the supercritical extraction process***."
3. As you may know, supercritical fluids such as carbon dioxide (SC-CO2) has many applications in various topics. Authors are requested inserting a proper statement to emphasise the importance of the utilising of SC-CO2 technology to be familiar for readers. For this purpose, write and insert this statement in the introduction section of the main manuscript along with fully cited references in below. "supercritical fluids like supercritical carbon dioxide (SC-CO2) has shown a great ability in various fields including extraction of **essential oil [**

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| [**https://doi.org/10.1016/j.supflu.2016.11.014,**](https://doi.org/10.1016/j.supflu.2016.11.014) | [**https://doi.org/10.1016/j.supflu.2014.07.023,**](https://doi.org/10.1016/j.supflu.2014.07.023) |
| [**https://doi.org/10.1016/j.supflu.2016.04.006,**](https://doi.org/10.1016/j.supflu.2016.04.006,) | [**https://doi.org/10.1016/j.supflu.2011.02.002**](https://doi.org/10.1016/j.supflu.2011.02.002)**,** |
| [**https://doi.org/10.1016/j.supflu.2016.05.015,**](https://doi.org/10.1016/j.supflu.2016.05.015) | [**https://doi.org/10.1016/j.supflu.2017.04.007,**](https://doi.org/10.1016/j.supflu.2017.04.007) |

[**https://doi.org/10.1016/j.jtice.2015.11.003**](https://doi.org/10.1016/j.jtice.2015.11.003)**, ], seed oil [**[**https://doi.org/10.1016/j.supflu.2016.08.019,**](https://doi.org/10.1016/j.supflu.2016.08.019)[**https://doi.org/10.1016/j.supflu.2015.12.004,**](https://doi.org/10.1016/j.supflu.2015.12.004)[**https://doi.org/10.1016/j.supflu.2017.12.026]**](https://doi.org/10.1016/j.supflu.2017.12.026)**, solubility [**[**https://doi.org/10.1002/cben.202200020,**](https://doi.org/10.1002/cben.202200020) **https://doi.org/10.1007/s11814-018-0125-6],**

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| **nanoparticle formation** | **[**[**https://doi.org/10.1016/j.supflu.2017.10.015,**](https://doi.org/10.1016/j.supflu.2017.10.015) |
| [**https://doi.org/10.1016/j.heliyon.2020.e04947,**](https://doi.org/10.1016/j.heliyon.2020.e04947) | [**https://doi.org/10.1016/j.supflu.2021.105163,**](https://doi.org/10.1016/j.supflu.2021.105163) |
| [**https://doi.org/10.1016/j.jcou.2021.101799**](https://doi.org/10.1016/j.jcou.2021.101799)**,** | [**https://doi.org/10.1016/j.supflu.2018.11.007**](https://doi.org/10.1016/j.supflu.2018.11.007) |
| [**https://doi.org/10.1016/j.cherd.2018.12.020**](https://doi.org/10.1016/j.cherd.2018.12.020)**,** | [**https://doi.org/10.1016/j.fluid.2018.11.006**](https://doi.org/10.1016/j.fluid.2018.11.006)**,** |
| [**https://doi.org/10.1016/j.supflu.2018.06.009]**](https://doi.org/10.1016/j.supflu.2018.06.009)**,** | **impregnation** |
| **[**[**https://doi.org/10.1016/j.supflu.2020.104892,**](https://doi.org/10.1016/j.supflu.2020.104892) | [**https://doi.org/10.1016/j.supflu.2022.105674]**](https://doi.org/10.1016/j.supflu.2022.105674)**,** |
| **optimisation and mathematical modeling** | [**[https://doi.org/10.1080/14786419.2017.1361954**](https://doi.org/10.1080/14786419.2017.1361954)**,** |
| [**https://doi.org/10.1016/j.supflu.2017.04.007]**](https://doi.org/10.1016/j.supflu.2017.04.007)**,** | **polymer synthesis** |

**[**[**https://doi.org/10.1016/j.supflu.2022.105679]**](https://doi.org/10.1016/j.supflu.2022.105679)**, etc.**

***Thank you for your valuable note!  
The discussion on the application of CO2 has been elaborated as suggested  
"The supercritical carbon dioxide is commonly used for impregnation as described by Weidner2018, Machado2022 or Fathi2022. Impregnation is defined as modifying the properties of bulk substances by physically or chemically binding/adsorbing impregnates to a bulk material or surface, such as the hydrophobisation of surfaces. The main advantage of using supercritical CO2 is that it desorbs from the surface and evaporates after depressurisation, leaving a solvent-free product. On the other hand, the main disadvantage of using carbon dioxide for impregnation is the low solubility of many drugs of interest.***

***Another application of supercritical CO2 is nanoparticles formation as investigated by Padrela2018, Franco2021, SaadatiArdestani2020 or Sodeifian2022. Supercritical carbon-dioxide-assisted technologies enable the production of different morphologies of different sizes, including nanoparticles and nanocrystals, by modulating operating conditions. Supercritical fluid-based processes have advantages over techniques conventionally employed to produce nanosized particles or crystals, such as reduced use of toxic solvents. Moreover, the CO2 is completely removed from the final product by simple depressurisation.***

***One of the most popular applications of supercritical CO2 is the extraction of essential oils, as described by many researchers, for example, by Sodeifian2017, Reverchon1993 or Sovova1994. Traditional methods, such as distillation and organic solvent extraction, are commonly employed but have drawbacks. Distillation, involves high temperatures that can lead to the thermal degradation of heat-sensitive compounds. This limitation has increased the popularity of alternative techniques, such as supercritical fluid extraction. Supercritical CO2 is appealing due to its distinctive properties: it is inflammable, non-toxic and non-corrosive. Supercritical fluids can exhibit both gas- and liquid-like properties, allowing for adjustable dissolving power through changes in operating conditions."***

1. Literature review on the available models could be completed in the introduction section.  
   ***Thank you for your valuable note!  
   The literature review on the available models has been expanded  
     
   "Goto1996 presented the Shrinking Core (SC) model, which describes a process of irreversible desorption that is followed by diffusion through the pores of a porous solid. When the mass transfer rate of the solute in the non-extracted inner region is significantly slower than in the outer region, where most of the solute has already been extracted, or when the solute concentration exceeds its solubility in the solvent, a distinct boundary may form between the inner and outer regions. As extraction progresses, the core of the inner region shrinks. The model envisions supercritical CO2 extraction as a sharp, inward-moving front, with a completely non-extracted core ahead of the front and a fully extracted shell behind it.***

***Sovova1994 proposed The Broken-and-Intact Cell (BIC) model, which assumes that a portion of the solute, initially stored within plant structures and protected by cell walls, is released during the mechanical breakdown of the material. The solute located in the region of broken cells near the particle surface is directly exposed to the solvent, while the core of the particle contains intact cells with undamaged walls. This model describes three extraction phases: a fast extraction phase for accessible oil, a transient phase, and a slow phase controlled by diffusion. The model has been successfully applied to the extraction of grape oil (Sovova1994b) and caraway oil (Sovova1994a).***

***The Supercritical Fluid Extraction (SFE) process can be be treated similarly to heat transfer, considering solid particles like hot balls cooling down in a uniform environment. Bartle1990 introduced the hot ball diffusion (HBD) model, where spherical particles with uniformly distributed solute diffuse similarly to heat diffusion. Unlike the BIC model, where solute is readily available on the particle surface, the HBD model is suited for systems with small quantities of extractable materials and is not limited by solubility. The model is particularly relevant when internal diffusion controls mass transfer, allowing results from single particles to be extended to the entire bed under uniform conditions. Reverchon1993 have further elaborated on the HBD model and used it to simulate extraction processes for natural materials.***

***Reverchon1996 proposed a model for extraction of essential oils, which are mainly located inside the vegetable cells in organules called vacuoles. Only a small fraction of essential oil might be near the particle surface due to the breaking up of cells during grinding or in epidermal hairs located on the leaf surface. The fraction of oil freely available on the particle surface should not be significant in the case of SFE from leaves. Consequently, the internal mass-transfer resistance should mainly control the SFE of essential oil from leaves. Therefore, the external mass-transfer coefficient was neglected in the development of the model of Reverchon1996. The mass balances were developed in the additional hypotheses that the axial dispersion can be neglected and that the solvent density and flow rate are constant along the bed."***

1. As the authors did not conduct any experimental work by themselves, please remove section 2.4.  
   ***Thank you for your valuable note!  
   The reference to the experimental work was moved to the beginning of the Results section.***
2. Please explain the superiority of the applied model over the similar models in the literature.  
   ***Thank you for your valuable note!  
   The superiority of the model has been elaborated in the text  
     
   "The primary advantage of the proposed model lies in its added flexibility compared to traditional desorption-dissolution-diffusion models found in the literature. While it follows the same assumptions and limitations as these traditional models, it introduces an additional postulate: a decaying internal diffusion coefficient. If there is no actual decay in Di, the presented model can approximate the traditional desorption-dissolution-diffusion models by finding low values of a decaying factor ϒ. In such a case, the exponent approach unity as ϒ goes to zero regardless of . This added flexibility, however, comes at the cost of requiring an extra parameter to be fitted, which could lead to overfitting, especially with limited datasets.***

***The model modification was not derived from theoretical considerations but from analysing assumptions in existing models, such as the BIC model and the Shrinking Core model, and applying corresponding simplifications. As a result, the proposed model should be categorised as semi-empirical. This approach allows for the development of tailored models but may make finding physical interpretations for some parameters challenging.***

***The accuracy of the obtained correlations is heavily influenced by the quality of the dataset and the number of experiments conducted under different operating conditions. A significant limitation is that the dataset was obtained from static experiments (constant operating conditions). Performing a set of experiments under dynamically changing operating conditions would provide more information about the unknown parameters and system dynamics."***

1. Could you report the error between experimental data and model predictions by statistical metrics including AARD%?  
   ***Thank you for your valuable note!  
   Table 2 provides information on modelling errors***
2. In the material section, please insert the name of material.  
   ***Thank you for your valuable note!  
   The material name is mentioned at the beginning of the Method and Material section  
     
   "The supercritical extraction of essential oil from chamomile flowers is described by a first principle model given in Chapter 2.2. The mathematical formulation of the parameter estimation is given in Chapter 2.3. The process model is tested against the experimental dataset Y(t), which was obtained by extracting oil from chamomile flowers. The experiments were conducted by Povh2001 and Rahimi2011, in a semi-batch extractor with a diameter of 3.96 cm and a length of 16.55 cm. Twelve experiments were performed under different operating conditions: 30-40 °C, 100 - 200 bar and 0.12 - 0.24 kg/h. The amount of solid material used for extraction was 75 grams."***
3. The results and discussion section must be strengthening by comparing the similar works and researches such as **[**[**https://doi.org/10.1016/j.supflu.2017.04.007**](https://doi.org/10.1016/j.supflu.2017.04.007)**, https://doi.org/10.1080/14786419.2017.1361954].**   
   ***Thank you for your valuable note!***

* ***The Results section compares the obtained results and the articles of Povh et al. and Rahimi et al., who used the same dataset. As the datasets are the same, the model performance can be directly compared with the model used in this work.***
* [***https://doi.org/10.1016/j.supflu.2017.04.007***](https://doi.org/10.1016/j.supflu.2017.04.007) ***describes the supercritical extraction of E. billardieri at multiple operating conditions. The dataset used in the referred manuscript is different from the dataset used in this work. Moreover, the referred work utilises models with different structures (a first principle model based on the BET theory and an empirical model based on a multiple regression with second-order polynomial). Considering that the presented models and datasets are different from each other, direct comparison becomes not reliable***
* [***https://doi.org/10.1080/14786419.2017.1361954***](https://doi.org/10.1080/14786419.2017.1361954) ***describes the supercritical extraction of oil from Dracocephalum kotschyi Boiss seeds at multiple operating conditions. The dataset used in the referred manuscript is different from the dataset used in this work. Moreover, the referred work utilises models with different structures (an empirical model based on a multiple regression with second-order polynomial). Considering that the presented models and datasets are different from each other, direct comparison becomes not reliable***

1. Explain clearly the limitations of this study?  
   ***Thank you for your valuable note!  
   The model limitations has been elaborated in the text  
     
   "The primary advantage of the proposed model lies in its added flexibility compared to traditional desorption-dissolution-diffusion models found in the literature. While it follows the same assumptions and limitations as these traditional models, it introduces an additional postulate: a decaying internal diffusion coefficient. If there is no actual decay in Di, the presented model can approximate the traditional desorption-dissolution-diffusion models by finding low values of a decaying factor ϒ. In such a case, the exponent approach unity as ϒ goes to zero regardless of . This added flexibility, however, comes at the cost of requiring an extra parameter to be fitted, which could lead to overfitting, especially with limited datasets.***

***The model modification was not derived from theoretical considerations but from analysing assumptions in existing models, such as the BIC model and the Shrinking Core model, and applying corresponding simplifications. As a result, the proposed model should be categorised as semi-empirical. This approach allows for the development of tailored models but may make finding physical interpretations for some parameters challenging.***

***The accuracy of the obtained correlations is heavily influenced by the quality of the dataset and the number of experiments conducted under different operating conditions. A significant limitation is that the dataset was obtained from static experiments (constant operating conditions). Performing a set of experiments under dynamically changing operating conditions would provide more information about the unknown parameters and system dynamics."***

1. Could you correlate the experimental data to two empirical models for solubility determination of components in supercritical carbon dioxide, proposed in these references [[](%5b)[**https://doi.org/10.1016/j.supflu.2019.01.006,**](https://doi.org/10.1016/j.supflu.2019.01.006) [**https://doi.org/10.1016/j.jcou.2024.102687**](https://doi.org/10.1016/j.jcou.2024.102687)**]**?  
   ***Thank you for your valuable note!***

* ***The suggested empirical correlations have been prepared for pure Imatinib Mesylate and Dapagliflozin Propandiol Monohydrate, which do not appear in this work. Considering that suggested correlations can not be used directly in this work.***
* ***The presented model does not utilise solubility directly.***
* ***As discussed in the manuscript, it is assumed that the system did not reach saturation. As a result, the maximum mass of solid dissolved in the solvent or solute concentration in the fluid phase is unknown. If such information is present, the solubility could be used to impose an upper boundary on the state space. As such information is missing, the estimation of solubility might take an arbitrary value, which improves the model fitness but does not necessarily have a physical interpretation.***
* ***Correlating the estimated parameters with solubility models would increase the number of parameters in the empirical correlations for DiR and ϒ. Taking into account the limited dataset that would lead to overfitting.***
* ***To provide an accurate estimation of the solubility, one should analyse the oil composition and perform a set of experiments focused solely on solubility.***

1. Please provide abbreviations and symbol lists.  
   ***Thank you for your valuable note!  
   See the last page of the manuscript***
2. It is recommended removing the last paragraph of conclusion section.  
   ***Thank you for your valuable note!   
   Paragraph removed***
3. Please provide consistency between the abstract and conclusion sections.  
   ***Thank you for your valuable note!  
   The paragraph and concusion section has been revised***
4. The number of references could be increased for this type of research work.  
   ***Thank you for your valuable note!  
   The number of references increased as the result of comments 8, 9***
5. Please set the reference style as per the Journal guidelines.   
   ***Thank you for your valuable note!  
   The citations are superscripted as required***