

## Modeling and parametric analysis of trans-resveratrol extraction from grape cane waste with pressurized water + ethanol mixture

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### 1. Introduction

Sustainability concerns are driving factors in the food industry by reducing waste after processing the whole feedstock not only into high-value added products but also in energy-rich compounds. Grape cane is a waste of viniculture that contains bioactive compounds like stilbenes (resveratrol and viniferin) that have been extracted by pressurized water systems<sup>1</sup>. Recent studies on modeling and simulation<sup>2</sup> aimed to better understand how the extraction yield is affected by temperature, solvent flow rate and the addition of a co-solvent. Although these studies successfully correlated extraction conditions and particle properties to the yield, there is a lack of studies that investigate those parameters together using the transport phenomena approach. Therefore, this study aims to compare two modeling approaches for the mass transfer between grape cane particles and the pressurized water + ethanol mixture for the extraction of trans-resveratrol (*tR*). A parametric analysis was also performed not only to compare model predictions but also to understand how the dimensionless groups affect the extraction yield of *tR*.

### 2. Materials and Methods

The governing equations for modeling the *tR* extraction are the Navier-Stokes equations in porous media coupled to scalar transport equations for solid and fluid phases<sup>3</sup>. The two resistances model (TRM, eq 1) considers the inner particle diffusion ( $D_p$ ) and convective transport at the boundary layer ( $h_m$ ) in terms of the overall mass transfer coefficient ( $k_f = (R/D_p + 1/h_m)^{-1}$ ):

$$\varepsilon_b \frac{\partial C_f}{\partial t} = \mathbf{u} \cdot \nabla C_f + D_{ax} \nabla^2 C_f + N_{fs} + \varepsilon_b R_f \quad (a), \quad (1 - \varepsilon_b) \frac{\partial C_s}{\partial t} = D \nabla^2 C_s - N_{fs} + (1 - \varepsilon_b) R_s \quad (b) \quad (1)$$

where, subscripts *f* and *s* denote the fluid and solid phases, respectively,  $R$  is the particle radius,  $\varepsilon_b$  is the bed porosity,  $C$  is the dimensionless *tR* concentration, normalized by the initial concentration at the solid phase (grape cane),  $\mathbf{u}$  is the interstitial velocity vector,  $D_{ax}$  is the axial dispersion coefficient,  $N_{fs}$  is the volumetric interphase mass flux ( $k_f a_s (C_s - C_f)$ ) and  $R_i$  is the volumetric *tR* thermal degradation rate at the “*i*” phase. Alternatively, the full particle model (FPM) considers the advective transport over the boundary layer (eq. 2a), in which the interphase mass transfer coefficient at the film layer ( $h_m$ ) and the transient diffusion at the grape cane particles (eq. 2b) are considered.

$$\varepsilon_b \frac{\partial C_f}{\partial t} = \mathbf{u} \cdot \nabla C_f + D_{ax} \nabla^2 C_f + h_m a_s (C_i - C_f) + \varepsilon_b R_f \quad (a), \quad \varepsilon_p \frac{\partial C_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( D r^2 \frac{\partial C_s}{\partial r} \right) + \varepsilon_p R_s \quad (b) \quad (2)$$

where, the subscript *i* denotes the solid-liquid interface,  $r$  is the radial coordinate, and  $\varepsilon_p$  is the particle porosity. Equations 2a and 2b are coupled by the mass balance at the interface ( $-D \partial C_s / \partial r |_{r=R} = h_m (C_i - C_f)$ ).

The set of equations for each model was implemented in the computational fluid dynamic (CFD) software Ansys CFX 19.0. Experimental data of *tR* in-column extraction from grape cane particles using a pressurized water + ethanol mixture<sup>1,2</sup> were used to validate the numerical models. Data reported include fluid and particle properties, *tR* yield (mg/g dw) as a function of time at 5.2 MPa using 7.4% ethanol + water mixture. The inlet boundary condition was defined as a constant flow rate (1 mL min<sup>-1</sup>) and  $C_f = 0$ . At the column outlet, the static pressure was 5.2 MPa whereas Neumann boundary condition was specified for velocity and *tR* concentration. Predicted yields of *tR* from models were calculated from the concentration at the column outlet and compared to experimental data<sup>1</sup> by normalized mean squared error (NMSE). The effect of temperature on the extraction yield was investigated by parametric analysis using dimensionless quantities of Péclet ( $Pe_M = d_p |\mathbf{u}| / D_{ax}$ ) and Biot ( $Bi_M = h_m R / D_p$ ) for mass transfer,  $D_{ax} / D$  ratio, Sherwood ( $Sh = d_p h_m / D_{ax}$ ) and Thiele modulus ( $\phi = (k R^2 / D_p)^{1/2}$ ), where  $d_p$  is the particle diameter ( $2R$ ) and  $k$  is the reaction rate constant.

### 3. Results and discussion

The full particle model presented better agreement to the experimental data (Fig. 1a) when compared to the two resistances model. The NMSE values of 6.36 and 3.33 for TRM and FPM, respectively, are acceptable when errors from experimental measurements are considered<sup>1,3</sup>. Deviation from the models were more evident from 50 to 150 min, where the TRM overestimated the *tR* extraction yield. Although this model is widely used for conjugate mass transfer in porous media<sup>3</sup>, the *tR* concentration profile in the particle was assumed to be in steady state into the inner loop of time stepping during the CFD solution. However, a pressurized fluid system has high extraction rates, so the inner-particle transient diffusion presents a non-linear concentration profile. Thus, since the FPM solved the transient diffusion equation at each time step, non-linearities were considered, and therefore a more accurate prediction of *tR* yield profile was observed.

The temperature increase had an adverse effect in the extraction yield predicted by the FPM, even though the extraction rates increased given by the local slopes between 30 and 100 min (Fig. 1b). Since the model had many variables and properties, the dimensionless quantities (Table 1) were used to better characterize and understand the overall reactive mass transport of *tR*. Péclet number slightly increased with temperature, and values close to one showed that both axial dispersion and advection were important on the *tR* transport along the fluid phase. However, the  $D_{ax}/D$  ratios decreased due to the increase in the inner particle molecular diffusivities ( $D$ ) with temperature<sup>1</sup>. The small increase in Sherwood number corroborated the minor effect of temperature into the advection, whereas the Biot number decreased almost 2-fold from 105 to 140 °C due to the increase in the inner particle *tR* diffusion, which explained the increase in the extraction rate. These rates as well as the *tR* yields were affected by the Thiele modules, in which its increment with temperature suggested that degradation reaction was more sensitive to temperature than the inner particle diffusional transport.

### 4. Conclusions

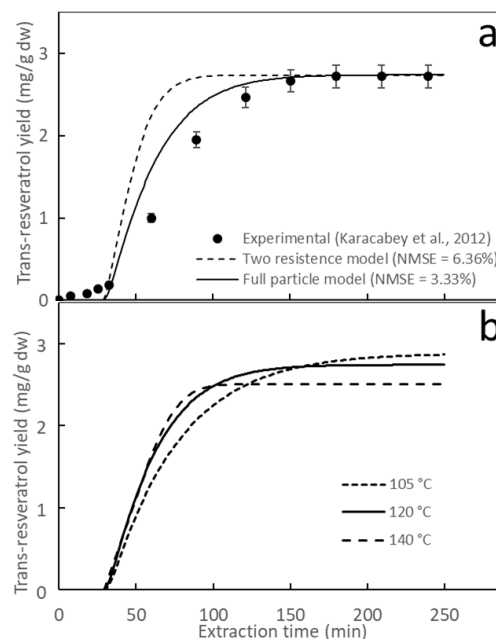
In the present study, two CFD-based models for mass transfer were compared for the extraction of trans-resveratrol (*tR*) from grape cane using a semi-continuous pressurized water + ethanol mixture. Although the two-resistances model predicted the final extraction yield, the full particle model (FPM) was preferred because it considered the inner-particle transient concentration profile. Even though higher temperatures increased the extraction rate, the *tR* degradation rate also increased, resulting in lower yields. A parametric study from the FPM results using dimensionless quantities showed that extraction was controlled not only by the inner particle diffusion rate, but also by the *tR* thermal degradation rate in both phases.

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### References

1. E. Karacabey, G. Mazza, L. Bayındırlı, N. Artık, *Food Bioprocess Technol.* **2012**, *5*, 359–371,
2. S.S. Turgut, A.H. Feyissa, C. Baltacıoğlu, E. Küçüköner, *Chem. Eng. Proc: Proc. Intensification* **2020**, *148*, 107779,
3. J.C. Coimbra, M.A. Martins, L.A. Minim, *Braz. J. Chem. Eng.* **2020**, *37*, 425–438.



**Figure 1.** Extraction yields of trans-resveratrol (*tR*) by (a) full particle and two resistances models and (b) effect of temperature predicted by the FPM.

**Table 1.** Effect of temperature on dimensionless groups on *tR* extraction predicted by the FPM.

| $T$ (°C) | $Pe_M$ | $D_{ax}/D$ | $Sh$ | $Bi_M$ | $\phi$ |
|----------|--------|------------|------|--------|--------|
| 105      | 0.693  | 2200       | 3.22 | 3543   | 0.0413 |
| 120      | 0.695  | 1240       | 3.26 | 2182   | 0.0486 |
| 140      | 0.697  | 839        | 3.30 | 1383   | 0.0490 |