



**HAL**  
open science

# Modelling the transfer and degradation kinetics of aroma compounds from liquid media into coffee beans during simulated wet processing conditions

F. Hadj Salem, N. Achir, N. Sieczkowski, R. Boulanger, A. Collignan

► **To cite this version:**

F. Hadj Salem, N. Achir, N. Sieczkowski, R. Boulanger, A. Collignan. Modelling the transfer and degradation kinetics of aroma compounds from liquid media into coffee beans during simulated wet processing conditions. *Journal of Food Engineering*, 2022, pp.111303. 10.1016/j.jfoodeng.2022.111303 . hal-03892186

**HAL Id: hal-03892186**

<https://institut-agro-montpellier.hal.science/hal-03892186v1>

Submitted on 8 Jan 2025

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

1 **Title page**

2 **Modelling the transfer and degradation kinetics of aroma**  
3 **compounds from liquid media into coffee beans during simulated**  
4 **wet processing conditions**

5  
6 **F. Hadj Salem<sup>1,2,3</sup>, N. Achir<sup>2</sup>, N. Sieczkowski<sup>3</sup>, R. Boulanger<sup>1,2</sup>, A. Collignan<sup>2</sup>,**

7 <sup>1</sup> CIRAD, UMR Qualisud, F-34398 Montpellier, France.

8 <sup>2</sup> Qualisud, Univ Montpellier, CIRAD, Institut Agro, Univ d'Avignon, Univ de La Réunion,  
9 Montpellier, France.

10 <sup>3</sup> Lallemand, SAS, 19 rue des Briquetiers, 31700 Blagnac, France.

11  
12 **Corresponding author**

13 Corresponding author: Fatma HADJ SALEM

14 Mailing address: CIRAD- International Cooperation in Agricultural Research for Development

15 B-16, 73 Rue Jean François Breton, 34398 Montpellier, France

16 Tel.: +33 6 13 26 20 66

17 E-mail : fatma.hadj\_salem@cirad.fr

18

19

20

21 **Abstract**

22 Models of increasing complexity were developed to identify and represent mechanisms  
23 affecting the evolution of the concentration of 3 aroma compounds (2-phenylethanol,  
24 isoamyl acetate and butanal) usually produced by yeasts and transferred to coffee beans  
25 during the fermentation. Model parameters were identified from simulated wet treatment  
26 performed with four media (M1: dehulled beans, M2: demucilaginated beans, M3: depulped  
27 beans, M4: depulped beans with yeast), at 25 °C using labeled aroma compounds. The  
28 transfer of 2-phenylethanol was well described by a model including evolving resistance  
29 over time ( $R^2=0.98$ ) while the accumulation of isoamyl acetate and butanal was better  
30 described by a model including two first order reactions in parallel ( $r^2= 0.87-0.66$  and  $r^2=$   
31  $0.80-0.67$ , respectively). The model development contributed to understand several  
32 mechanisms involved during fermentation such as the evolutive parchment resistance and  
33 the complex degradation reactions that take place simultaneously and have a significant  
34 impact on the compounds transfer.

35 **Key words:** fermentation; mass transfer; coffee; model; aroma compounds.

36

37

38

39

40

## 41        **1. Introduction**

42        Coffee aroma is a key attribute that defines the quality of the final coffee product (Otero et  
43        al., 2018) and it is significantly related to the chemical composition of beans (Pereira et al.,  
44        2019). This chemical content depends on several factors such as agricultural variables,  
45        coffee variety and postharvest process conditions (Hameed et al., 2018). Several studies  
46        have highlighted that postharvest processing, in particular wet processing, could have a  
47        direct impact on the quality and value of the final product (D. P. de C. Neto et al., 2018;  
48        Pereira et al., 2017).

49        Wet processing requires several complex steps: depulping, fermenting and drying. First,  
50        the skin and pulp of the coffee cherries are removed mechanically leaving a viscous  
51        mucilage adhering to the parchment (Avallone et al., 2001). This step could initiate the  
52        germination-related metabolism in the coffee beans. Selmar et al. (2006) measured the  
53        expression of the germination-specific enzyme isocitrate lyase and they reported that the  
54        germination-related metabolism recorded the highest activity throughout the post-harvest  
55        process during the first 2 days of the coffee wet-process which could significantly affect the  
56        beans' chemical composition (Knopp et al., 2006). Then the depulped beans are fermented  
57        to degrade the mucilage layer by microorganisms that produce extracellular enzymes such  
58        as protease, pectinase and cellulase (Elhalis et al., 2021). The removal of this highly  
59        hydrated tissue, rich in pectic substances, is essential to facilitate the drying of the beans to  
60        avoid the growth of undesirable fungi and spoilage bacteria (D. P. D. C. Neto et al., 2020).  
61        During this step, the metabolism of yeast can lead to the hydrolysis of mucilage  
62        macromolecules and the generation of important metabolites such as flavor compounds  
63        like esters, alcohols, aldehydes, ketones, and terpenoids (Hameed et al., 2018; Lee et al.,

64 2015; Martinez et al., 2019). Some of these metabolites can diffuse into coffee beans by  
65 crossing the parchment layer and therefore contribute to the aroma profile of coffee such as  
66 2-phenylethanol, isoamyl acetate and butanal (Hadj Salem et al., 2020; Pereira et al., 2019).  
67 Parchment, a fibrous layer with a similar structure to wood (Ramírez-Martínez et al., 2013),  
68 is a natural means of protecting coffee seeds from digesting enzymes in the gut of  
69 frugivorous animals, keeps the coffee seed available to germination-related metabolism  
70 after harvesting (De Castro & Marraccini, 2006; Selmar et al., 2006) and acts like a transfer  
71 resistance layer (Hadj Salem et al., 2020). Finally, the beans are sundried to 10-12%  
72 moisture content to facilitate storage and transport (Pereira et al., 2019). In fact, several  
73 studies were performed to modulate the coffee aroma profile using yeast starter cultures  
74 (Bressani et al., 2018; Lee et al., 2017; Martinez et al., 2019; Pereira et al., 2015). However,  
75 the direct link between the microbial activities during fermentation and coffee quality is not  
76 yet established as long as the mechanisms of diffusion/reactions involved are not yet well  
77 known (Pereira et al., 2019). Having a good knowledge of these mechanisms and control of  
78 the fermentation parameters will allow the coffee producers to improve the quality of the  
79 final product, to produce specialty coffee and even to predict its aromatic profile through a  
80 mathematical model.

81 This work aims at building a dynamic model in order to better understand the evolution of  
82 the concentration of three aroma compounds in coffee beans during fermentation and to  
83 identify the mechanisms involved in this wet processing step which have a direct impact on  
84 the transfer of metabolites. The implementation of this model follows a progressive  
85 approach and uses data from the monitoring of transfer kinetics of labeled molecules  
86 obtained in our previous study (Hadj Salem et al., 2020).

<b>Nomenclature</b>	<b>88</b>
Abbreviations	89
DFORP	Double First Order Reaction in Parallel
FOR	First Order Reaction
MTER	Mass Transfer with Evolving Resistance
MTR	Mass Transfer with parchment Resistance
SMT	Simple Mass Transfer
Variables	
C	Concentration [Kg/m <sup>3</sup> ]
df	Degree of freedom
g	Fraction of the initial concentration
K	Mass transfer coefficient [h <sup>-1</sup> ]
k	Rate constant [h <sup>-1</sup> ]
n	Number of beans
p	Adjusted parameter
R	Mass transfer resistance [h <sup>-1</sup> ]
t	Time [h]
V	Volume [m <sup>3</sup> ]
Subscripts and superscripts	
0	Initial (at t=0)
1	First parameter
2	Second parameter
C	Coffee
d	Degradation
e	External
W	Water

## 90 **2. Materials and methods**

### 91 **2.1. Experimental setup**

92 Transfer kinetic data used to build the model were obtained from our previous study (Hadj  
93 Salem et al., 2020), in which the transfer kinetics of three volatile molecules labeled with a  
94 stable isotope (butyraldehyde, 2-phenylethanol and isoamyl acetate) were monitored  
95 during simulated fermentations over five timings (0, 6, 12, 24 and 48 hours). To investigate  
96 transfer kinetic parameters, a progressive experimental approach was followed by carrying  
97 out four study media of increasing complexity: Medium M1, being the simplest, contained  
98 coffee beans without parchment; Medium M2 contained coffee beans with parchment;  
99 Medium M3 contained depulped coffee beans composed of beans with parchment and  
100 mucilage and medium M4 contained coffee beans with parchment and mucilage, inoculated  
101 with a yeast selected for coffee fermentation LSCC1 (Lallemand SAS, France). All trials were  
102 conducted at 25 °C, at an agitation speed of 120 rpm and in triplicate.

#### 103 **2.1.1. Plant material and labeled compounds**

104 The additional experimental tests were performed with the same raw material and the  
105 same molecules used to study the transfer kinetics in our previous study (Hadj Salem et al.,  
106 2020). Following the same pre-treatment protocol, the depulped coffee, purchased from the  
107 Tarrazu cooperative (Tarrazu, Costa Rica), was disinfected using chlorinated solution  
108 before handling to avoid any microbiological reactions. The labeled molecules, including an  
109 aldehyde butyraldehyde ( $\text{CH}_3\text{CH}_2\text{CD}_2\text{CHO}$ ), an alcohol 2-phenylethanol ( $\text{C}_6\text{D}_5\text{CH}_2\text{CH}_2\text{OH}$ )  
110 and an ester isoamyl acetate ( $((\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{OCOCD}_3)$ ), were purchased from CDN-  
111 isotopes (Quebec, Canada).

112

### 113        **2.1.2. Experimental approach to study reaction kinetics in coffee beans**

114        The degradation kinetics of the labeled molecules in the coffee bean was studied in two  
115        steps. First, a transfer of the labeled molecules into the coffee beans was carried out by  
116        submerging depulped coffee cherries in distilled water (10g of coffee beans/10 ml)  
117        containing 40 µg/ml of the molecules studied. The transfer was carried out three times (3, 9  
118        and 27 hours) to obtain three different initial concentrations. The coffee beans were then  
119        washed to stop the transfer reaction and placed under vacuum in a hermetic bag. In the  
120        second stage, the hermetic bags containing the coffee beans were placed in an oven at 25 °C  
121        to study the degradation kinetics of the previously transferred molecules over five periods  
122        of time (0, 3, 6, 9 and 15 hours). At the end of the reaction, the coffee bean samples were  
123        ground and analyzed by SPME-GC-MS using the same method previously described in Hadj  
124        Salem et al. (2020). All the tests were independent and performed in triplicate.

### 125        **2.2. Mathematical model**

126        A simplified schematic representation of the studied system is shown in Fig.1, illustrating  
127        the possible mechanisms involved in the evolution of molecule concentration in the coffee  
128        bean during fermentation. The simulated fermentation tests were performed in a finite  
129        closed system with a known initial external concentration of labeled molecules,  $C_{e0}$ , in the  
130        liquid phase. In this system, mass transfer passed from the liquid phase (solution with a  
131        concentration  $C_e(t)$ ) to the solid phase (coffee bean) through the resistance of the  
132        parchment and mucilage layers. In the coffee bean, the transferred molecules could undergo  
133        a degradation reaction. Hence, the concentration of the labeled molecules,  $C(t)$ , contained in  
134        the coffee beans during fermentation could be the result of the transfer and reaction  
135        mechanisms.



136 The predictive model of the evolution of the concentration of volatile molecules in coffee  
137 beans during simulated fermentation was developed using a progressive approach. The  
138 mathematical model (presented in the following sections) was implemented in Matlab  
139 R2020b (The Mathworks Inc., Natick, MA). The parameters were identified by nonlinear  
140 least-squares regression analysis, with Optimization Toolbox in Matlab and experimental  
141 data reported in table 1. Statistical parameters such as the sum of squared errors (SSE),  
142 root mean squared error (RMSE) and coefficient of determination ( $r^2$ ) were calculated by  
143 Matlab to determine goodness-of-fit of the model. An F-test was performed to see which  
144 model is statistically better by verifying the H0 hypothesis, which states that the simpler  
145 model fits better. F-critical values were obtained using F-table with p-value = 0.05. F-  
146 statistic was estimated using the degrees of freedom (df) and the sum of squared errors  
147 (SSE) of the compared models, with the following equation:

$$F = \frac{\frac{SSE1 - SSE2}{df1 - df2}}{\frac{SSE2}{df2}}$$

148  
149 The first model (1) is the one with the fewer parameters, the simpler model.

### 150 **2.2.1. Simple Mass Transfer model (SMT)**

151 The hypothesis adopted to build the mass transfer model are: (1) the coffee bean is  
152 considered a homogeneous solid body; (2) the distributions of the marked molecules are  
153 assumed as homogeneous in the liquid fraction and in the solid phase after transfer,  
154 considering a rapid and non-limiting diffusion within the bean; (3) volume of the  
155 compartments is kept constant; (4) the mass transfer is governed only by the concentration  
156 gradient between the two compartments. The concentration of labeled volatiles transferred  
157 into the coffee bean can be calculated from the following ODE (Eq. (1)):

158 
$$\frac{dC}{dt} = K * (C_e(t) - C(t)) \quad (1)$$

159 Where  $t$  is the time,  $C_e$  is the external concentration of labeled volatiles and  $K$  is the effective  
160 global mass transfer coefficient including several mechanisms such as convective transfer  
161 at the interface.

162 In the first modeling step, it is considered that there is no loss of the total mass of the  
163 molecules in the system, neither by leakage nor by reaction, so this total mass will be  
164 distributed between the liquid and solid phases:

165 
$$m_e(t) = m_{e0} - m(t)$$

166 (2)

167 By converting this mass balance into an equivalent volume concentration, we obtain an  
168 affine equation of the variation of the concentration outside (Eq. (3)).

169 
$$C_e(t) = -V * C(t) + C_{e0}$$

170 (3)

171 With  $C_e$ , expressed as a function of the variation of the concentration inside  $C$  and having a  
172 slope  $V$  equal to the ratio of the volume of the solid phase,  $V_c$ , divided by the volume of the  
173 liquid phase  $V_w$  (Eq.4)):

174 
$$V = \frac{V_c}{V_w}$$

175 (4)

176 By replacing the expression of the external concentration,  $C_e$ , in Eq. (1) by Eq. (3), we obtain  
177 the ODE (Eq. (5)):

178  $\frac{dC}{dt} = K * (C_{e0} - C(t) * (V + 1))$

179 (5)

180 With the initial conditions:

181  $C(0) = 0; C_e(0) = C_{e0}; \text{ at } t = 0$

182 The limit conditions are reached when the transfer flux of the molecules becomes equal to  
183 zero and the concentration in the solid phase reaches the equilibrium concentration  $C_{eq}$ :

184  $\frac{dc}{dt} = 0 \text{ when } C_{eq} = \frac{C_{e0}}{(V+1)}$

185 which leads to the following analytical solution:

186  $C(t) = C_{e0} * \frac{(1 - e^{-K*t*(V+1)})}{(V+1)}$

187 (6)

### 188 **2.2.2. Mass Transfer model with parchment Resistance (MTR)**

189 It is assumed that the parchment plays the role of resistance in the transfer of molecules  
190 into the coffee bean. It is expressed in the model with a resistance term R that is added in  
191 series to the effective global transfer coefficient:

192  $C(t) = C_{e0} * \frac{(1 - e^{-\left(\frac{1}{\left(\frac{1}{K}\right)+R}\right)*t*(V+1)})}{V+1}$

193 (7)

194 **2.2.3. Mass Transfer model with parchment Resistance and First Order Reaction**  
195 **(MTR-FOR)**

196 The degradation reaction of transferred labeled compounds is assumed to occur  
197 instantaneously in coffee beans and the concentration of the volatiles, C, in the coffee bean  
198 becomes equal to the concentration of the transferred volatiles, undergoing a degradation  
199 proportional to the rate constant  $k_d$ . As a first approach, the reaction model is described by  
200 the simple first order differential equation (FOR).

201 A general model, which predicts the evolution of the concentration of a volatile molecule in  
202 the coffee bean during fermentation, is constructed by coupling the models proposed above.  
203 This model (Eq. (8)) considers that the transfer of molecules is governed by a concentration  
204 gradient between the liquid phase (solution) and the solid phase (coffee bean) subject to  
205 the resistance of the parchment, R, and that the transferred concentration undergoes an  
206 instantaneous degradation reaction.

$$207 \quad C(t) = C_{e0} * \frac{1 - e^{-\left(\frac{1}{\left(\frac{1}{R}\right) + R\right) * t * (V+1)}}}{V+1} * e^{-k_d * t} \quad (8)$$

208 **3. Results and discussion**

209 **3.1. Experimental data of transfer and degradation kinetics**

210 The results of the transfer kinetics of labeled molecules in coffee beans during simulated  
211 fermentations, shown in Fig 2.a, were exported from our previous work Hadj Salem et al.,  
212 (2020). As previously described, the transfer of 2-phenylethanol was continuous showing a  
213 first exponential regime followed by a deceleration phase when approaching the

214 equilibrium concentration, which is equal to 41.5% of the initial concentration in the  
215 solution. The transfer kinetic of this higher alcohol was monotonous and affected by  
216 parchment resistance revealed by the data obtained on the M2 medium. The transfer of  
217 isoamyl acetate and butanal was different and showed a transition through a maximum  
218 followed by a loss of the molecules in the coffee bean. To explain the nature of this loss,  
219 previously described as a degradation reaction, tests were conducted to monitor the  
220 evolution of these labeled molecules in the coffee bean after their transfer. The results of  
221 the degradation kinetics are reported in Fig 2.b. As expected, the amount of 2-  
222 phenylethanol transferred remained relatively stable in the coffee bean after 15h, which  
223 agrees with what was observed in the transfer kinetics.

224 In the absence of degradation, the equilibrium concentration could be reached, and the  
225 mass balance could be achieved, which indicates that the experimental device was  
226 completely hermetic. This observation confirms that isoamyl acetate and butanal showed  
227 significant degradation due to the reaction.

228 Trials to monitor degradation kinetics were conducted to understand the mechanisms  
229 occurring in the coffee bean after the transfer of the molecules. The degradation kinetics of  
230 these two molecules, isoamyl acetate and butanal, showed two regimes regardless of the  
231 initial concentration. A first regime marked by a high degradation rate was observed from  
232 the beginning up to 6h of reaction, followed by a second regime with a much slower  
233 degradation rate at 15h, to reach less than 20% and 40% of remaining isoamyl acetate and  
234 butanal, respectively, in coffee beans. Because of the low temperature, reactions are more  
235 likely to be activated by enzymes. Selmar et al. (2006) reported the existence of enzymatic  
236 activity associated with the germination-related metabolism. This metabolism could be

237 activated after pulping and contact between the bean and water (Selmar et al., 2006).  
238 Therefore, it can be assumed that these molecules transferred to the coffee bean undergo  
239 enzymatic degradation. These degradation kinetic monitoring trials were conducted to  
240 understand the mechanisms occurring in the coffee bean after the transfer of the molecules.

### 241 **3.2. Simple Mass Transfer model (SMT)**

242 As described above (section 3), a progressive approach was taken to develop a predictive  
243 model of the evolution of volatile concentration in coffee beans during simulated  
244 fermentation and to understand the mechanisms involved in aroma transfer. A first model  
245 based on a simple mass transfer governed by a concentration gradient (SMT), described by  
246 Eq. (6), was fitted to the transfer kinetics of 2-phenylethanol in the coffee beans of M1  
247 media (contained coffee beans without parchment) to estimate the global mass transfer  
248 coefficient  $K$  by using experimental data reported in table 1. This data set was chosen  
249 because the previous experiments showed that 2-phenylethanol did not significantly react,  
250 contrary to isoamyl acetate and butanal, and its accumulation in the bean is only driven by  
251 mass transfer.

252 The model fit is shown in Fig. 3.a and the adjusted parameters are reported in table 2.

253 The model used reproduced reality relatively accurately with  $r^2$  of 0.89. It could be noticed  
254 that the model slightly underestimated the transfer from 6h to 18h, then it also slightly  
255 overestimated the transfer from 18h to 48h (Fig. 3.a). This slight discrepancy between the  
256 model and the experimental data could be explained by one of the simplifying hypotheses  
257 where the coffee bean is considered as a homogeneous solid body. However, Ramírez-  
258 Martínez et al., (2013) reported a heterogeneous structure of the coffee bean observed by a

259 rupture of the tissue in the upper part of the endosperm (bean) and called it “natural  
260 discontinuity”, which could lead to more complex transfer mechanisms due to an  
261 inhomogeneous distribution of the concentration of volatile molecules in the coffee bean.

### 262 **3.3. Mass transfer with parchment resistance**

263 The parchment was considered as an additional resistance to the transfer of molecules into  
264 the coffee bean, in particular for the transfer of 2-phenylethanol (Hadj Salem et al., 2020;  
265 Ramírez-Martínez et al., 2013). This resistance  $R$  was added in series to the mass transfer  
266 coefficient  $K$  as described in Eq. (7) which represents the mass transfer model with  
267 parchment resistance (MTR). The MTR model was fitted to the transfer kinetics of 2-  
268 phenylethanol in coffee beans of M2 media (contained coffee beans with parchment). The  
269 model fit is shown in Fig. 3.b and the adjusted parameters are reported in table 2.

270 The MTR model significantly underestimated the transfer from the beginning up to 24  
271 hours, then it overestimated the transfer until the end. This model did not reproduce the  
272 reality correctly due to its significant discrepancy with the experimental observations ( $r^2 =$   
273 0.80). This discrepancy could be explained by the assumption of considering the parchment  
274 has a fixed resistance structure. Indeed, Siddharth & Karthiayani, (2014) studied the  
275 evolution of the parchment’s physical properties during fermentation, and they reported a  
276 decrease in parchment porosity with the increase in the fermentation duration. This  
277 porosity decrease could be explained by the expansion of the mucilage volume during  
278 fermentation that could obstruct the parchment pore space (Siddharth & Karthiayani,  
279 2014) and induce an evolving parchment resistance. Despite the mechanical removal of the  
280 mucilage layer, some of the mucilage cells remained adhered to the parchment. Based on

281 the data reported by these researchers, it is proposed to use an exponential evolution of the  
282 global mass transfer coefficient  $K$  during fermentation as described in Eq. (9):

$$283 \quad K = (K_1 * e^{p*t}) + K_2 \quad (9)$$

284 The parameters of Eq (9) were estimated by fitting this equation to the transfer kinetics of  
285 2-phenylethanol in coffee beans in medium M2 and reported in table 2. The initial mass  
286 transfer coefficient  $K_1$  was estimated from the first hours of transfer and the final mass  
287 transfer coefficient  $K_2$  was estimated from the last hours of transfer,  $p$  is the exponential  
288 parameter of the transition between the two mass transfer coefficients. The Mass Transfer  
289 model with Evolving Resistance (MTER) was constructed by replacing eq (9) in eq (6). The  
290 model fit is shown in Fig. 3.b and the adjusted parameters are reported in table 2. The  
291 MTER model, with  $r^2$  of 0.98, correctly reproduced the experimental observations of the  
292 transfer kinetics of 2-phenylethanol in coffee beans during fermentation with the M2  
293 medium. An F-test was conducted in order to better compare the two models MTR and  
294 MTER. The MTR is considered as the simpler model with less parameters. The F-statistic  
295 and F-critic values, 69.48 and 9.26 respectively, were determined and reported in table 2.  
296 The F-statistic calculated from data is greater than the critical value of the F-distribution.  
297 This induces a rejection of the  $H_0$  hypothesis and confirm that the MTER model is statically  
298 better than the MTR model.

299 Accordingly, the observed discrepancy between the SMT model and experimental data  
300 obtained with M1 media, described above, could be explained by the evolving structure of  
301 coffee beans during the fermentation.



302 Through this model, it can be deduced that the transfer rate of 2-phenylethanol in coffee  
303 bean could be governed by the concentration gradient and the evolving structure of coffee  
304 bean and the parchment during fermentation. These mechanisms are linked to the duration  
305 of fermentation where a significant decrease in the transfer rate of 2-phenylethanol could  
306 be observed after 15 hours of fermentation due to the obstruction of the parchment pores.  
307 Therefore, to ensure a significant transfer of this molecule, which confers a floral note to the  
308 aromatic profile (Pereira et al., 2019), it may be recommended to use yeasts capable of  
309 producing a large quantity of this molecule from the first hours of fermentation with an  
310 addition of liquefying enzymes to quickly dissolve the mucilage, or alternatively, to proceed  
311 with a second fermentation of the coffee bean without the parchment.

#### 312 **3.4. Mass transfer coupled with the degradation reaction**

313 Isoamyl acetate and butanal underwent an instantaneous degradation reaction in the coffee  
314 bean after transfer (Fig. 2). A simple mass transfer model coupled to a first order  
315 degradation reaction SMT-FOR, described by Eq. (8), was fitted to the transfer kinetics of  
316 isoamyl acetate and butanal obtained with the M1 media. Model fits are shown in Fig. 4 and  
317 the adjusted parameters are reported in table 3. As expected from the trend of Fig 2b, the  
318 SMT-FOR did not correctly reproduce the experimental data with  $r^2$  of 0.31 and 0.26,  
319 respectively for isoamyl acetate and butanal. It is possible that the molecules underwent  
320 several reactions occurring simultaneously in the coffee beans and could be described by  
321 Double First Order Reaction in Parallel DFORP. The DFORP has been reported by several  
322 researchers (Briones & Sarmah, 2019) to describe degradation reactions that occur at the  
323 same time and especially when enzymes are involved; the model equation is given by Eq.  
324 (10):

325  $C(t) = C_0 * (g * e^{-k_{d1}*t} + (1 - g) * e^{-k_{d2}*t})$

326 (10)

327 The constant  $g$  refers to the fraction of the initial concentration  $C_0$  of molecule in the coffee  
328 bean which enters the first reaction with the rate constant  $k_{d1}$ . Therefore, the  $(1-g)$   
329 corresponds to the fraction undergoing the second reaction with the rate constant  $k_{d2}$ . This  
330 model was coupled with the model of mass transfer SMT-DFORP given by the Eq. (11):

331  $C(t) = C_{e0} * \left( \frac{1 - e^{-K*t*(V+1)}}{(V+1)} \right) * (g * e^{-k_{d1}*t} + (1 - g) * e^{-k_{d2}*t})$

332 (11)

333 The SMT-DFORP model fitted well with the transfer kinetics of isoamyl acetate and butanal  
334 obtained with M1 media that are shown in Fig. 4 and the adjusted parameters are reported  
335 in table 3. The model correctly reproduced the experimental observations of the transfer  
336 kinetics of isoamyl acetate with  $r^2$  of 0.95 and the transfer kinetics of butanal less correctly  
337 with  $r^2$  of 0.76 by significantly underestimating the concentrations of this aldehyde towards  
338 the end of fermentation. This significant discrepancy was not observed for isoamyl acetate;  
339 hence it could be postulated that butanal could be subject to another transfer mechanism in  
340 the coffee bean and/or to another type of reaction.

341 The MTER model coupled with the DFORP was adjusted to the experimental transfer  
342 kinetics of isoamyl acetate and butanal obtained with M2 media. The MTER-DFORP model  
343 fits are shown in Fig. 4 and the adjusted parameters are reported in table 3. A significant  
344 difference was observed between the two models SMT-DFORP and MTER-DFORP fitted  
345 with the transfer kinetics of isoamyl acetate and butanal obtained with M2 media (Fig. 4).

346 The two models SMT-DFORP and MTER-DFORP were compared using an F-test to  
347 determine statistically the best fitting model taking into account their degrees of freedom.  
348 The SMT-DFORP is considered as the simpler model with less parameters. The F-statistic  
349 and F-critic values, reported in table 3, were determined for isoamyl acetate fits, 0.505 and  
350 199.5 respectively, and for butanal fits with 0.554 and 199.5 respectively. The F-statistic  
351 values calculated from data for both molecules are lower than the critical value of the F-  
352 distribution. Interpreting this results, the H0 hypothesis cannot be rejected and confirm  
353 that the SMT-DFORP model is statically better than the MTER-DFORP.

354 Indeed, the MTER-DFORP model significantly underestimated the transfer of these two  
355 molecules into the coffee beans and did not reproduced reality like the SMT-DFORP model  
356 did.

357 Thus, the parchment and the decrease in its porosity during fermentation did not  
358 significantly affect the transfer of this ester and aldehyde. This fact is in line with the  
359 experimental observations (Fig. 2). Only 2-phenylethanol was held back by this physical  
360 resistance which could be related to its conformation, structure and chemical properties.  
361 This fibrous layer acts as a molecule filter with a resistance that increases with the duration  
362 of fermentation. Isoamyl acetate, which confers a fruity note to the coffee (Lee et al., 2015;  
363 Sunarharum et al., 2014), and butanal, which confers a green note (Evangelista et al., 2014;  
364 Pereira et al., 2019), are not retained by the parchment. Their maximum concentration in  
365 the coffee bean is only reached between 15 and 20 hours for the ester and at only 6 hours of  
366 fermentation for the aldehyde, and then decreases due to the complex degradation  
367 reactions that could be linked to the germination metabolisms. To avoid this degradation  
368 and to be able to increase the content of these aromatic molecules in the coffee bean, it is

369 suggested that the germination metabolism be modulated, either by heat treatment or by  
370 chemical treatment, before bringing the beans into contact with water.

### 371 3.5. General model

372 During fermentation, it has been shown that certain molecules could interact with the yeast,  
373 and this interaction was described as an adhesion of these molecules to the yeast wall cells  
374 (Chalier et al., 2007; Comuzzo et al., 2011). Hadj Salem et al., (2020) reported that the  
375 addition of yeast to the fermentation medium induced the adsorption of butanal on the cell  
376 walls, which strongly reduced the availability of this aldehyde for transfer to the coffee  
377 beans. However, this adsorption phenomenon was not observed for 2-phenylethanol and  
378 isoamyl acetate (Comuzzo et al., 2011). This interaction phenomenon was implemented in  
379 the model as a term equivalent to the percentage of  $C_{e0}$  available for transfer,  $L$  (%), which  
380 was identified from experimental trials reported in Hadj Salem et al. (2020), where butanal  
381 availability was estimated with and without yeast in the medium. A general form of the  
382 model MTER-DFORP is given by Eq. (12):

$$383 \quad C(t) = L * C_{e0} * \left( \frac{1 - e^{-(K_1 * e^{p*t} + K_2) * t * (V+1)}}}{V+1} \right) * (g * e^{-k_{d1} * t} + (1 - g) * e^{-k_{d2} * t})$$

384 (12)

385 Fig. 5 illustrates the results obtained when the MTER-DFORP model was used to simulate  
386 the evolution of the concentration of volatiles (2-phenylethanol, isoamyl acetate and  
387 butanal) in coffee bean during simulated fermentation of M3 media (containing depulped  
388 coffee beans) and M4 media (containing depulped coffee beans inoculated with yeasts). The  
389 parameters of the model, estimated from the fits on M1 and M2, are summarized in table 4.

390 The model accurately predicted the transfer kinetics of 2-phenylethanol into coffee beans  
391 during simulated fermentation of M3 and M4 media, with  $r^2$  of 0.98 and 0.97, respectively.  
392 However, it was less accurate in predicting the transfer kinetics of isoamyl acetate and  
393 butanal especially on M4 media. This could be due to the existence of other phenomena  
394 linked to the fermentative activity of the yeast, which play a role in the transfer of these  
395 molecules.

396 By comparing the estimated parameters for each molecule, a different and specific behavior  
397 of each molecule could be observed. 2-phenylethanol appears to be an interesting molecule  
398 with a transfer coefficient 3 to 10 times higher than that of butanal and isoamyl acetate,  
399 respectively. Despite a transfer coefficient 3 times higher than isoamyl acetate, butanal  
400 undergoes several reactions in the coffee bean inducing a higher loss than isoamyl acetate.  
401 Therefore, it will be more interesting to favor the transfer of this ester than that of aldehyde  
402 in the selection of ester producing starters.

### 403 **Conclusion**

404 The model developed here constitutes a first step towards a dynamic view of development  
405 of the aroma profile of coffee beans during fermentation. This dynamic model allows for the  
406 first time, to predict the evolution of three volatile concentrations, 2-phenylethanol, isoamyl  
407 acetate and butanal, in coffee bean during simulated fermentation. This predictive model  
408 highlighted the complexity of the mechanisms involved during fermentation and the  
409 significant impact of the evolving resistance of the parchment, the interaction of certain  
410 molecules with yeast cell walls and the degradation reactions in the coffee bean on the  
411 concentration of aromatic molecules in the beans. The transfer of higher alcohol was

412 accurately predicted by this model, while the accumulation of isoamyl acetate and butanal  
413 was more complex to describe because of two regime reactions and was predicted with less  
414 accuracy. To improve the model performance, other experiments should be conducted, and  
415 parameters should be implemented to take into account more mechanisms that affect the  
416 transfer of these molecules and the evolution of their concentrations in coffee beans, such  
417 as the partition coefficient and the complex mechanisms of germination. The numerical  
418 values of the coefficients are, however, specific to each molecule and can vary with the  
419 modulation of certain fermentation parameters such as temperature and yeast strain.  
420 Furthermore, this study highlighted that the three molecules, belonging to three different  
421 groups, have a different behavior during their transfer into the coffee beans. It will be  
422 important to extend this study to other molecules of interest and to make a scan of the  
423 different existing behaviors. Classifying these behaviors and modelling them afterwards  
424 will allow a more general model to be developed in order to test the different levers to  
425 modulate the final aromatic profile.

426 The understanding of the mechanisms involved during fermentation through this model  
427 could open new perspectives for the development of innovative strategies to modulate the  
428 aroma profile of coffee via fermentation to produce specialty coffees. Moreover, this will  
429 help to draw an approximate aromatic profile of the coffee beans during the fermentation  
430 process. The study of these strategies can be the subject of prospective studies and that  
431 need to be validated before application in the industry.

432

433 **Acknowledgement**

434 The authors acknowledge their financial support from the Lallemand SAS Company (Toulouse,  
435 France).

436

437

438

439

440

441

442

443

444

445

446

447

448

#### 449 **References**

450 Avallone, S., Guiraud, J.-P., Guyot, B., Olguin, E., & Brillouet, J.-M. (2001). Fate of Mucilage Cell

451 Wall Polysaccharides during Coffee Fermentation. *Journal of Agricultural and Food*

452 *Chemistry*, 49(11), 5556-5559. <https://doi.org/10.1021/jf010510s>

453 Bressani, A. P. P., Martinez, S. J., Evangelista, S. R., Dias, D. R., & Schwan, R. F. (2018).

454 Characteristics of fermented coffee inoculated with yeast starter cultures using

455 different inoculation methods. *LWT*, 92, 212-219.

456 <https://doi.org/10.1016/j.lwt.2018.02.029>

457 Briones, R. M., & Sarmah, A. K. (2019). Modelling degradation kinetics of metformin and  
458 guanylurea in soil microcosms to derive degradation end-points. *Environmental*  
459 *Pollution*, 245, 735-745. <https://doi.org/10.1016/j.envpol.2018.11.045>

460 Chalier, P., Angot, B., Delteil, D., Doco, T., & Gunata, Z. (2007). Interactions between aroma  
461 compounds and whole mannoprotein isolated from *Saccharomyces cerevisiae*  
462 strains. *Food Chemistry*, 100(1), 22-30.  
463 <https://doi.org/10.1016/j.foodchem.2005.09.004>

464 Comuzzo, P., Tat, L., Fenzi, D., Brotto, L., Battistutta, F., & Zironi, R. (2011). Interactions  
465 between yeast autolysates and volatile compounds in wine and model solution. *Food*  
466 *Chemistry*, 127(2), 473-480. <https://doi.org/10.1016/j.foodchem.2011.01.026>

467 De Castro, R. D., & Marraccini, P. (2006). Cytology, biochemistry and molecular changes  
468 during coffee fruit development. *Brazilian Journal of Plant Physiology*, 18(1),  
469 175-199. <https://doi.org/10.1590/S1677-04202006000100013>

470 Elhalis, H., Cox, J., Frank, D., & Zhao, J. (2021). Microbiological and biochemical  
471 performances of six yeast species as potential starter cultures for wet fermentation  
472 of coffee beans. *LWT*, 137, 110430. <https://doi.org/10.1016/j.lwt.2020.110430>

473 Evangelista, S. R., Silva, C. F., Miguel, M. G. P. da C., Cordeiro, C. de S., Pinheiro, A. C. M.,  
474 Duarte, W. F., & Schwan, R. F. (2014). Improvement of coffee beverage quality by  
475 using selected yeasts strains during the fermentation in dry process. *Food Research*  
476 *International*, 61, 183-195. <https://doi.org/10.1016/j.foodres.2013.11.033>

477 Hadj Salem, F., Lebrun, M., Mestres, C., Sieczkowski, N., Boulanger, R., & Collignan, A. (2020).  
478 Transfer kinetics of labeled aroma compounds from liquid media into coffee beans



479 during simulated wet processing conditions. *Food Chemistry*, 322, 126779.  
480 <https://doi.org/10.1016/j.foodchem.2020.126779>

481 Hameed, A., Hussain, S. A., Ijaz, M. U., Ullah, S., Pasha, I., & Suleria, H. A. R. (2018). Farm to  
482 Consumer : Factors Affecting the Organoleptic Characteristics of Coffee. II:  
483 Postharvest Processing Factors. *Comprehensive Reviews in Food Science and Food*  
484 *Safety*, 17(5), 1184-1237. <https://doi.org/10.1111/1541-4337.12365>

485 Knopp, S., Bytof, G., & Selmar, D. (2006). Influence of processing on the content of sugars in  
486 green Arabica coffee beans. *European Food Research and Technology*, 223(2),  
487 195-201. <https://doi.org/10.1007/s00217-005-0172-1>

488 Lee, L. W., Cheong, M. W., Curran, P., Yu, B., & Liu, S. Q. (2015). Coffee fermentation and  
489 flavor – An intricate and delicate relationship. *Food Chemistry*, 185, 182-191.  
490 <https://doi.org/10.1016/j.foodchem.2015.03.124>

491 Lee, L. W., Tay, G. Y., Cheong, M. W., Curran, P., Yu, B., & Liu, S. Q. (2017). Modulation of the  
492 volatile and non-volatile profiles of coffee fermented with *Yarrowia lipolytica* : I.  
493 Green coffee. *LWT*, 77, 225-232. <https://doi.org/10.1016/j.lwt.2016.11.047>

494 Martinez, S. J., Bressani, A. P. P., Dias, D. R., Simão, J. B. P., & Schwan, R. F. (2019). Effect of  
495 Bacterial and Yeast Starters on the Formation of Volatile and Organic Acid  
496 Compounds in Coffee Beans and Selection of Flavors Markers Precursors During Wet  
497 Fermentation. *Frontiers in Microbiology*, 10.  
498 <https://doi.org/10.3389/fmicb.2019.01287>

499 Neto, D. P. D. C., Pereira, G. V. D. M., Finco, A. M. O., Rodrigues, C., Carvalho, J. C. D., & Soccol,  
500 C. R. (2020). Microbiological, physicochemical and sensory studies of coffee beans

501 fermentation conducted in a yeast bioreactor model. *Food Biotechnology*, 34(2),  
502 172-192. <https://doi.org/10.1080/08905436.2020.1746666>

503 Neto, D. P. de C., Pereira, G. V. de M., Finco, A. M. O., Letti, L. A. J., da Silva, B. J. G.,  
504 Vandenberghe, L. P. S., & Soccol, C. R. (2018). Efficient coffee beans mucilage layer  
505 removal using lactic acid fermentation in a stirred-tank bioreactor : Kinetic,  
506 metabolic and sensorial studies. *Food Bioscience*, 26, 80-87.  
507 <https://doi.org/10.1016/j.fbio.2018.10.005>

508 Otero, J., Argüello, R., Oviedo, J. D., & Ramírez, M. (2018). Explaining coffee price  
509 differentials in terms of chemical markers : Evidence from a pairwise approach.  
510 *Economic Modelling*, 72, 190-201. <https://doi.org/10.1016/j.econmod.2018.01.017>

511 Pereira, G. V. de M., Neto, D. P. de C., Magalhães Júnior, A. I., Vásquez, Z. S., Medeiros, A. B. P.,  
512 Vandenberghe, L. P. S., & Soccol, C. R. (2019). Exploring the impacts of postharvest  
513 processing on the aroma formation of coffee beans – A review. *Food Chemistry*, 272,  
514 441-452. <https://doi.org/10.1016/j.foodchem.2018.08.061>

515 Pereira, G. V. de M., Neto, E., Soccol, V. T., Medeiros, A. B. P., Woiciechowski, A. L., & Soccol, C.  
516 R. (2015). Conducting starter culture-controlled fermentations of coffee beans  
517 during on-farm wet processing : Growth, metabolic analyses and sensorial effects.  
518 *Food Research International*, 75, 348-356.  
519 <https://doi.org/10.1016/j.foodres.2015.06.027>

520 Pereira, G. V. de M., Soccol, V. T., Brar, S. K., Neto, E., & Soccol, C. R. (2017). Microbial ecology  
521 and starter culture technology in coffee processing. *Critical Reviews in Food Science  
522 and Nutrition*, 57(13), 2775-2788.  
523 <https://doi.org/10.1080/10408398.2015.1067759>

524 Ramírez-Martínez, A., Salgado-Cervantes, M. A., Rodríguez-Jimenes, G. C., García-Alvarado,  
525 M. A., Cherblanc, F., & Bénet, J. C. (2013). Water transport in parchment and  
526 endosperm of coffee bean. *Journal of Food Engineering*, 114(3), 375-383.  
527 <https://doi.org/10.1016/j.jfoodeng.2012.08.028>

528 Selmar, D., Bytof, G., Knopp, S.-E., & Breitenstein, B. (2006). Germination of Coffee Seeds and  
529 its Significance for Coffee Quality. *Plant Biology*, 8(2), 260-264.  
530 <https://doi.org/10.1055/s-2006-923845>

531 Siddharth, M., & Karthiayani, A. (2014). Physical properties of fresh and partially fermented  
532 coffee parchment. *INTERNATIONAL JOURNAL OF AGRICULTURAL ENGINEERING*,  
533 7(2), 446-449. <https://doi.org/10.15740/HAS/IJAE/7.2/446-449>

534 Sunarharum, W. B., Williams, D. J., & Smyth, H. E. (2014). Complexity of coffee flavor : A  
535 compositional and sensory perspective. *Food Research International*, 62, 315-325.  
536 <https://doi.org/10.1016/j.foodres.2014.02.030>

537

538

539

540

541

542

543

544

545

546

547

548

549

550

551

552

553 **Tables**

554 **Table 1.** Data used in the experiments and  
555 numerical simulations.

Parameter	Value	555
$C_{e0}$	$0.04 \text{ kg/m}^3$	
$V_w$	$10^{-5} \text{ m}^3$	556
$V_c$	$2.2 \times 10^{-7} \times n_c \text{ m}^3$	557
$n_c$	63	
$V$	1.408	558

559

560

561

562

563

564  
565  
566  
567  
568  
569  
570  
571  
572  
573

574 **Table 2.** Model parameters and statistical measures for mass transfer kinetics of 2-  
575 phenylethanol in coffee beans using SMT, MTR and MTER models.

<b>Model / Medium* / Molecule</b>	<b>Parameter</b>	<b>Value</b>
SMT /M1/2-phenylethanol	K h <sup>-1</sup>	0.037
	RMSE	0.001
	SSE	0.478
	r <sup>2</sup>	0.89
MTR /M2/2-phenylethanol	K h <sup>-1</sup>	0.037
	R	0.027
	RMSE	0.0019
	SSE	0.935
	r <sup>2</sup>	0.80
	df	4
MTER /M2/2-phenylethanol	K <sub>1</sub> h <sup>-1</sup>	0.031
	K <sub>2</sub> h <sup>-1</sup>	0.008
	p	-0.056
	RMSE	8.05 × 10 <sup>-5</sup>
	SSE	0.0387
	r <sup>2</sup>	0.98
	df	3

F-statistic	69.48
F-critical	9.26

576 \* Study media used for parametric estimation.

577

578

579

580

581

582

583

584 **Table 3.** Model parameters and statistical measures for mass transfer kinetics of 2-phenyl-  
585 ethanol in coffee beans using SMT-FOR, SMT-DFORP and MTER-DFORP models.

Model / Medium*	Parameter	Isoamyl acetate	Butanal
SMT-FOR /M1	K h <sup>-1</sup>	0.014	0.003
	k <sub>d</sub> h <sup>-1</sup>	0.327	0.094
	RMSE	2.7×10 <sup>-7</sup>	2.2×10 <sup>-8</sup>
	SSE	1.31×10 <sup>-5</sup>	1.09×10 <sup>-6</sup>
	r <sup>2</sup>	0.31	0.26
SMT-DFORP/M1	K h <sup>-1</sup>	0.0047	0.011
	k <sub>d1</sub> h <sup>-1</sup>	0.424	0.125
	k <sub>d2</sub> h <sup>-1</sup>	0.088	0.277
	g	0.5	0.52
	RMSE	9.6×10 <sup>-10</sup>	1×10 <sup>-8</sup>
	SSE	4.7×10 <sup>-8</sup>	4.9×10 <sup>-7</sup>
	r <sup>2</sup>	0.95	0.76

	df		2
MTER-DFORP/M2	K <sub>1</sub> h <sup>-1</sup>	0.0035	2.5×10 <sup>-5</sup>
	K <sub>2</sub> h <sup>-1</sup>	0.001	6.7×10 <sup>-5</sup>
	p	-9.7×10 <sup>-7</sup>	-0.009
	k <sub>d1</sub> h <sup>-1</sup>	0.424	0.125
	k <sub>d2</sub> h <sup>-1</sup>	0.088	0.277
	g	0.5	0.52
	RMSE	5.07×10 <sup>-9</sup>	2.5×10 <sup>-7</sup>
	SSE	9.5×10 <sup>-8</sup>	1.1×10 <sup>-6</sup>
	r <sup>2</sup>	0.86	0.20
	df		1
	F-statistic	0.505	0.554
	F-critical	199.5	199.5

586 \* Study media used for parametric estimation.

587 **Table 4.** Selected parameters used for validation on M3 and M4 media.

Parameter	2-phenyethanol	Isoamyl acetate	Butanal
L	1	1	1 (M3); 0.4 (M4)
K <sub>1</sub> h <sup>-1</sup>	0.031	0.0047	0.011
K <sub>2</sub> h <sup>-1</sup>	0.008	0	0
p	-0.056	0	0
k <sub>d1</sub> h <sup>-1</sup>	0	0.424	0.125
k <sub>d2</sub> h <sup>-1</sup>	0	0.088	0.277
g	0	0.5	0.52
r <sup>2</sup> (M3)	0.98	0.74	0.79
r <sup>2</sup> (M4)	0.97	0.66	0.67

588

589

590

591

592

593

594 **Figures**

595

596

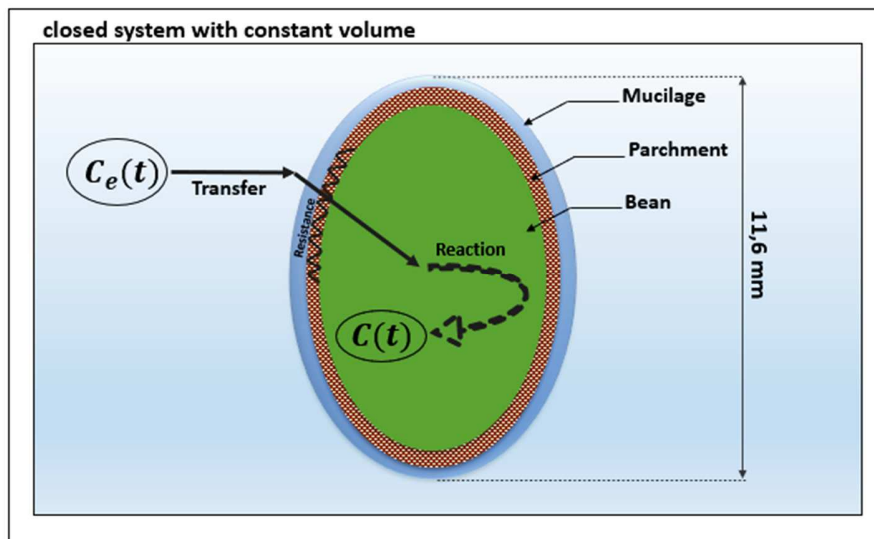
597

598

599

600

601



602

**Fig. 1.** Schematic representation of simplified transfer mechanisms of volatiles during simulated coffee bean fermentation.

603

604

605

606

607

608

609

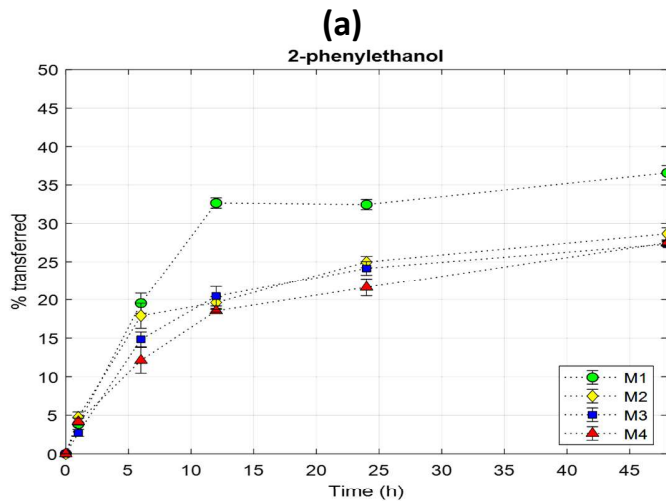


610

611

612

613



614

615

616

617

618

619

620

621

622

623

624

625

626

627

628

629

630

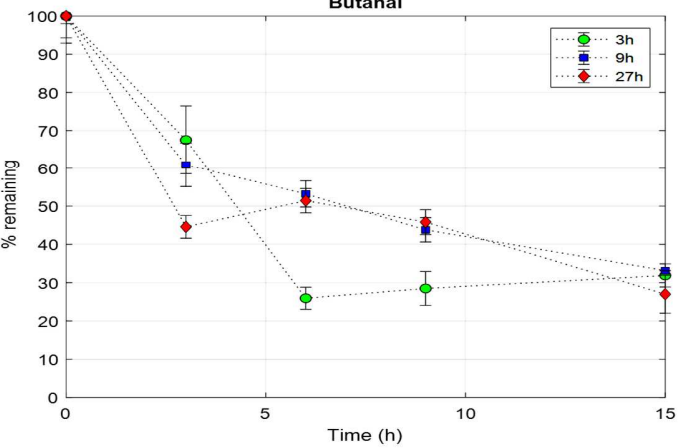
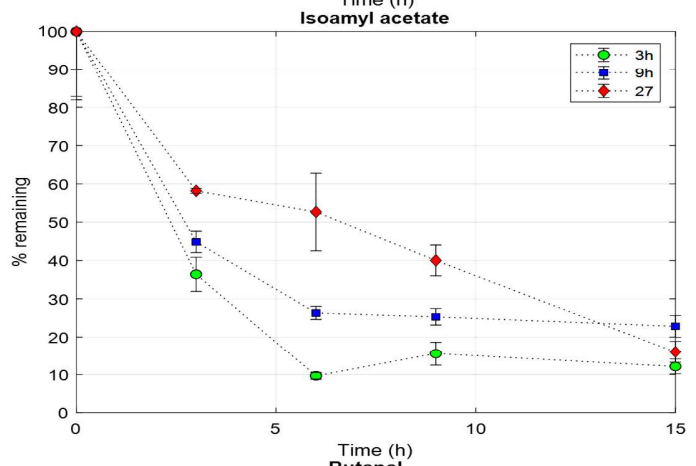
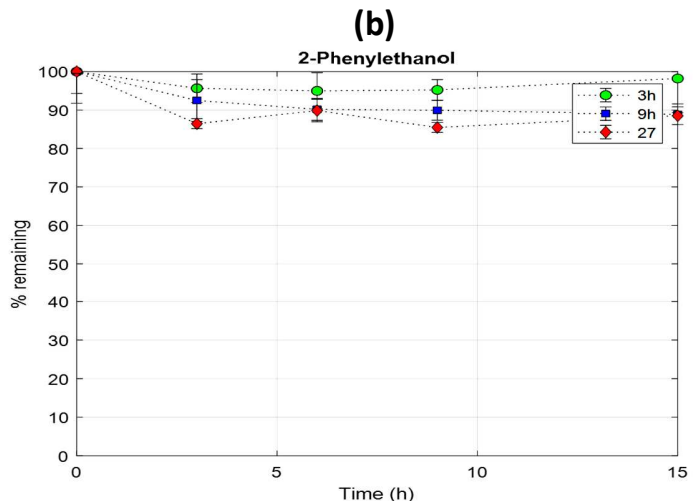
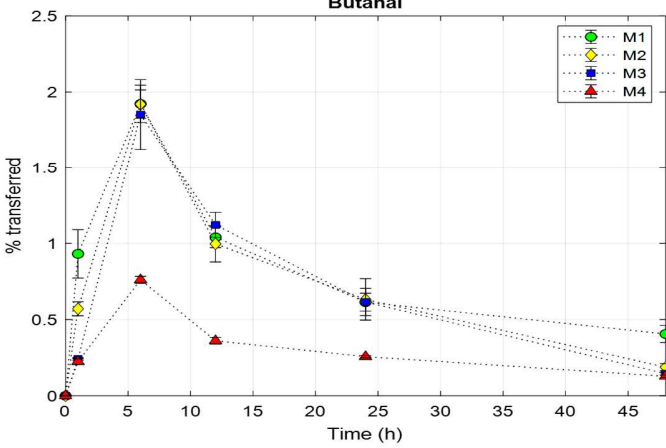
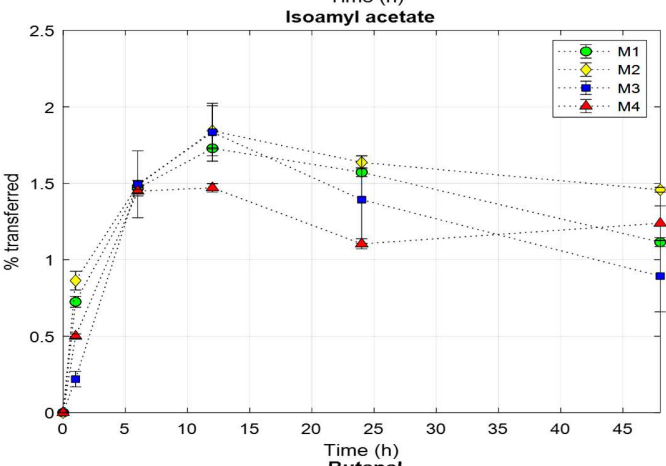
631

632

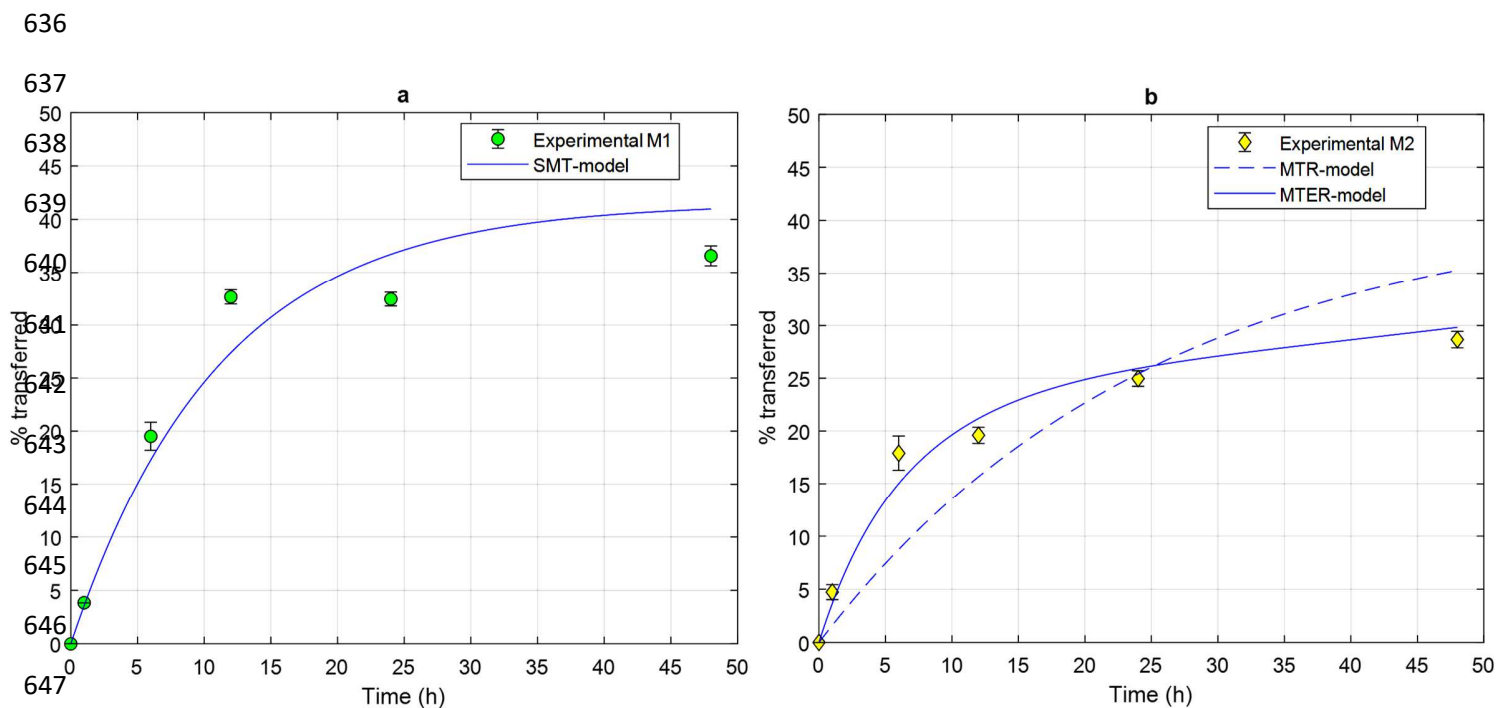
633

634

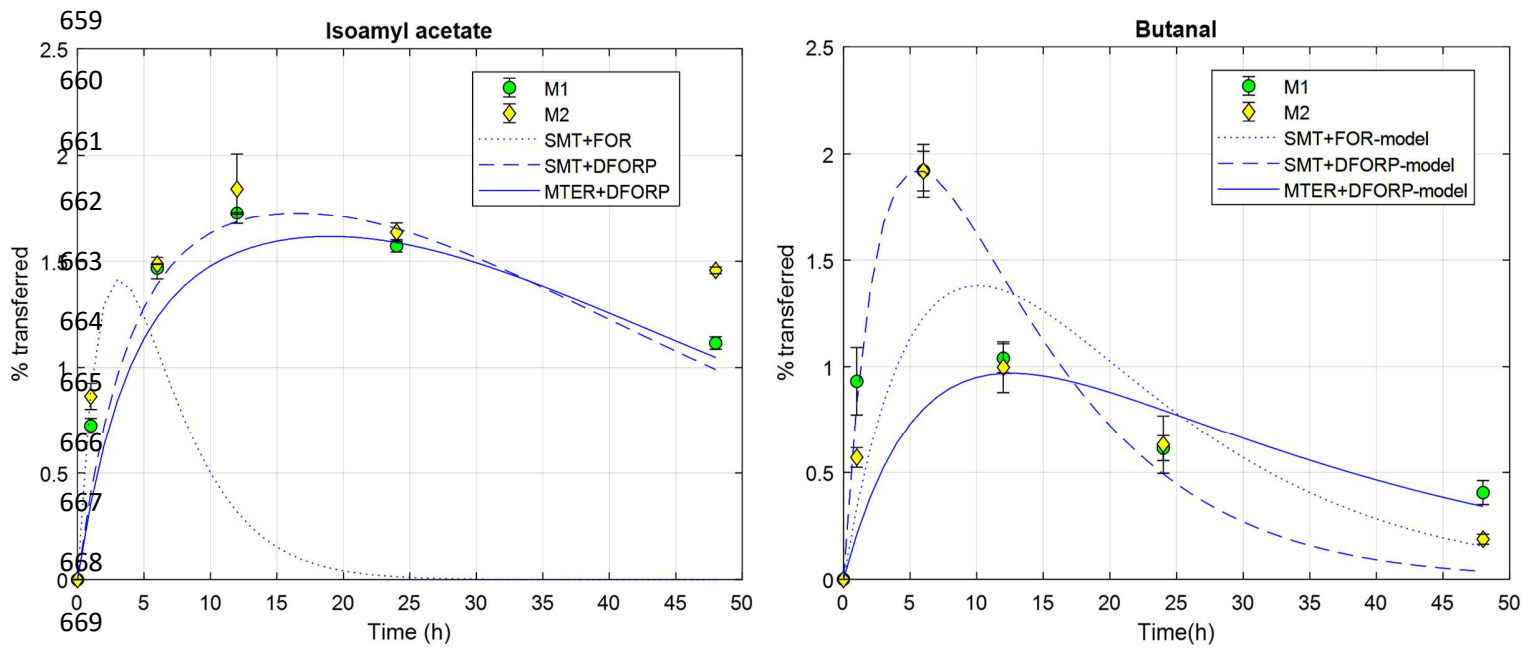
635



**Fig. 2.** Experimental data, (a) mass transfer kinetics of labeled compound in coffee beans during fermentation, M1 media with coffee beans without parchment; M2 media with coffee bean with parchment; M3 media with depulped coffee beans; M4 media with depulped coffee beans inoculated with yeast; (b) degradation reaction of transferred labeled molecules into coffee after 3, 9 and 27h.

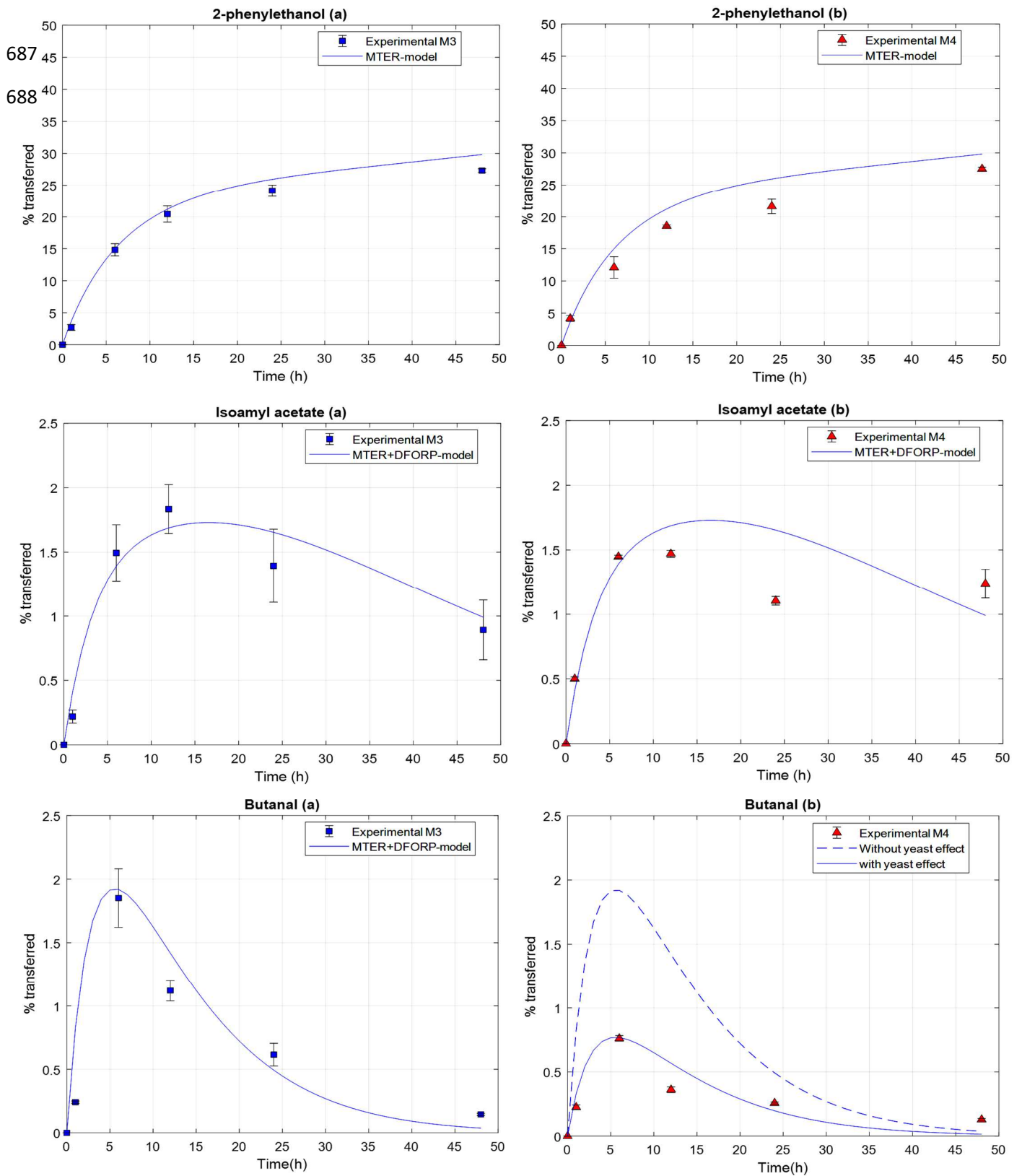


**Fig. 3.** Transferred concentration of 2-phenylethanol (% transferred) into coffee beans (a) using M1 media with fit for SMT model (continuous blue line), (b) using M2 media with fit for MTR (discontinuous blue line) and MTER (continuous blue line) models.



670 **Fig. 4.** Transferred concentration of isoamyl acetate (a) and butanal (b) (% transferred) into  
 671 coffee beans using M1 media (green circle) with fit for SMT-FOR model (dotted blue line) and  
 672 SMT-DFORP model (discontinuous blue line); and using M2 media (yellow diamond) with fit for

673  
 674  
 675  
 676  
 677  
 678  
 679  
 680  
 681  
 682  
 683  
 684  
 685  
 686



**Fig. 5.** Transferred concentration of 2-phenylethanol, isoamyl acetate and butanal (% transferred) into coffee beans. Superposition of the experimental results with M3 (a) and M4(b) with the values calculated by the model (blue line).