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## Highlights

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5 • Non-isothermal adsorption in near-critical binary mixtures was investigated by  
6 numerical simulations.

7 • The adsorption behavior near solvent's critical point has been analyzed.

8 • The effect of divergent properties and the piston effect were highlighted.

9 • A strong dependence to temperature and pressure variations in the vicinity of the  
10 critical point was depicted.

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24 Numerical study of non-isothermal adsorption of Naphthalene  
25 in supercritical CO<sub>2</sub> : behavior near critical point

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31 **Abstract**

32

33 In this study, adsorption in a model binary mixture is investigated near the critical point in a  
34 side-heated cavity. The diverging behavior of the equilibrium constant and the Piston effect  
35 are taken into account and their influence on the adsorption process is pointed to. The  
36 modeling is based on numerical integration of the differential equations, considering the  
37 Navier-Stokes equations coupled with the energy and mass diffusion balances. By means of  
38 this model, the temperature, density and adsorbed concentration profiles are drawn at different  
39 times. Some fundamental concepts about the system's response to the heating are illustrated.  
40 The results reveal that the adsorption process is influenced by the combined effect of several  
41 parameters, such as the gravity and the proximity to the critical point. In particular, the  
42 adsorbed amount exhibits a reversed dependency on the wall heating very close to the critical  
43 point, which confirms the complexity of such a process in binary systems near critical  
44 conditions.

45 **Keywords:** Supercritical fluids; Adsorption; Piston effect; Numerical analysis

46

47 1. Introduction

48 The supercritical state was first reported in 1822 by Baron Gagniard de la Tour [1], but  
49 only one hundred years later, supercritical techniques have received increased attention and  
50 have been used in analytical and on an industrial scale. This state is achieved when the  
51 temperature and the pressure of a substance is set over their critical values. So the properties

52 of a supercritical fluid range between those of a liquid and a gas and the distinction between  
53 the liquid and the gas phases is not possible. Some of the properties of a supercritical fluid are  
54 more liquid-like, whereas others are more gas-like.

55 Moreover, very close to the critical point, some properties diverge and others tend to  
56 zero. In fact, a small raise in pressure remarkably increases the fluid density and this effect  
57 diminishes with increasing distance from the critical point. On the other hand, a supercritical  
58 fluid has a higher diffusion coefficient and lower viscosity and surface tension than a liquid  
59 solvent, which leads to a more favorable mass transfer. Supercritical fluids exhibit very  
60 interesting qualities with regard to their physicochemical properties as well as ecology and  
61 economy. They are used as an alternative to organic liquid solvents in several applications  
62 such as cleanings [2-4]. Adsorption technologies using supercritical fluids have been also  
63 focused due to their potential applications including analytical extractions, activated carbon  
64 regeneration and soil remediation. Several studies have investigated the supercritical  
65 adsorption characteristics of many systems [5-12]. When adsorption is concerned,  
66 thermodynamic and kinetic aspects should be involved to know more details about its  
67 performance and mechanisms.

68 In the framework of isothermal supercritical adsorption, there have been numerous  
69 publications in literature dealing with the modeling of adsorption equilibrium using the most  
70 common adsorption isotherm models, i.e. the Langmuir, the Freundlich and the Redlich-  
71 Peterson models [6-7, 13-16]. All the experimental conditions used correspond to  
72 thermodynamic states relatively beyond the critical point because the adsorption equilibrium  
73 is influenced by the system temperature, pressure and by the supercritical fluid properties in  
74 the vicinity of the critical point. In contrast, supercritical adsorption systems close to the  
75 solvent's critical point have received much less explicit attention in the open literature. The  
76 experimental studies in this area are scarce. A thermodynamic analysis of near critical binary

77 mixtures was established by Afrane and Chimowitz [17]. The authors studied the adsorption  
78 thermodynamics of dilute solutes adsorbing from high pressure supercritical fluid using the  
79 Henry's law. However, set under high pressures, the results showed an extremely weak  
80 dependence to pressure and to the composition of the supercritical solvent phase. In  
81 chromatography, the proximity to the critical point was early reviewed by Van Wasen et al.  
82 [20]. The authors pointed out the unusual behavior of equilibrium partition coefficients in the  
83 near-critical region. Many other works also showed interesting features of data in this region  
84 [21-22]; in particular, papers by Schmitz et al. [23] and Klesper and Schmitz [24] provided  
85 striking evidence of the highly nonlinear behavior of equilibrium coefficients with respect to  
86 pressure and temperature variations, as the critical point of the fluid phase is approached. We  
87 believe that an adequate explanation of the thermodynamic basis of these phenomena in  
88 adsorption process taking into account both temperature and pressure effects is necessary.  
89 And it is also important to show the influence of the divergent character of thermodynamic  
90 properties and transport coefficients in near-critical systems on adsorption system behavior.

91 This is precisely the aim of this paper. For this purpose, adsorption of a model solute  
92 from supercritical CO<sub>2</sub> was investigated in a small side-heated cavity by means of 2D  
93 numerical simulations. Naphthalene was chosen as a model solute because its phase equilibria  
94 with CO<sub>2</sub> has been thoroughly studied [18-19]. There are extensive data available for this  
95 system that have been confirmed. The first section of the paper is devoted to the mathematical  
96 modeling of the problem and the numerical method used for the simulations. The modeling of  
97 the adsorption reaction at the solid boundaries is exposed in details. Then, the effect of the  
98 mass fraction and the proximity to the critical point are discussed for wide temperature and  
99 pressure conditions. The results show a strong dependence to temperature and pressure  
100 variations when the critical point is approached. We ended up with the effect of Damköhler  
101 number on the adsorbed mass fraction.

102

## 103 2. Mathematical modeling

## 104 2.1 Problem under investigation

105 The problem we consider is that of a dilute solute (Naphthalene in this case, named  
106 species 2) in supercritical CO<sub>2</sub> (named species 1). The physical properties of each pure  
107 compound are given in Table 1. The Naphthalene-CO<sub>2</sub> mixture is enclosed in a square cavity  
108 of height  $H=1\text{mm}$  and subjected to the earth gravitational field  $g$ . The cavity vertical walls are  
109 made of activated carbon (see Fig. 1). The activated carbon was chosen as a model adsorbent  
110 for this problem allowing as considering an adsorption reaction at the solid-fluid interface.  
111 Here, we emphasize that the chosen mixture as the adsorbent material is only generic since  
112 the aim of this study is to qualitatively investigate the influence of the proximity to the critical  
113 point on an adsorption reaction. Initially, the fluid is considered in thermodynamic  
114 equilibrium at a constant temperature  $T_i$  slightly above the mixture critical temperature  
115  $T_{cm} = 307.65\text{ K}$  such that  $T_i = (1 + \varepsilon) T_{cm}$ , where  $\varepsilon$  defines the dimensionless proximity to  
116 the critical point ( $\varepsilon \ll 1$ ), and the density is equal to the mixture critical density  
117  $\rho_{cm} = 470\text{ kg}\cdot\text{m}^{-3}$ . The critical properties,  $T_{cm}$  and  $\rho_{cm}$  correspond to the LCEP (“Lower  
118 Critical EndPoint”) of the mixture and are slightly above the critical point of CO<sub>2</sub>  
119 ( $T_{c1} = 304.21\text{ K}$ ,  $\rho_{c1} = 467.8\text{ kg}\cdot\text{m}^{-3}$ ). A weak gradually heating is then applied at the solid  
120 plate ( $x=0$ ). The hot temperature is noted  $T_h = T_i + \delta T$  where  $\delta T$  is about hundreds mK, while  
121 maintaining the other side at its initial temperature  $T_i$  (noted  $T_{co}$ ). An adiabatic boundary  
122 condition was applied to the non-reactive walls.

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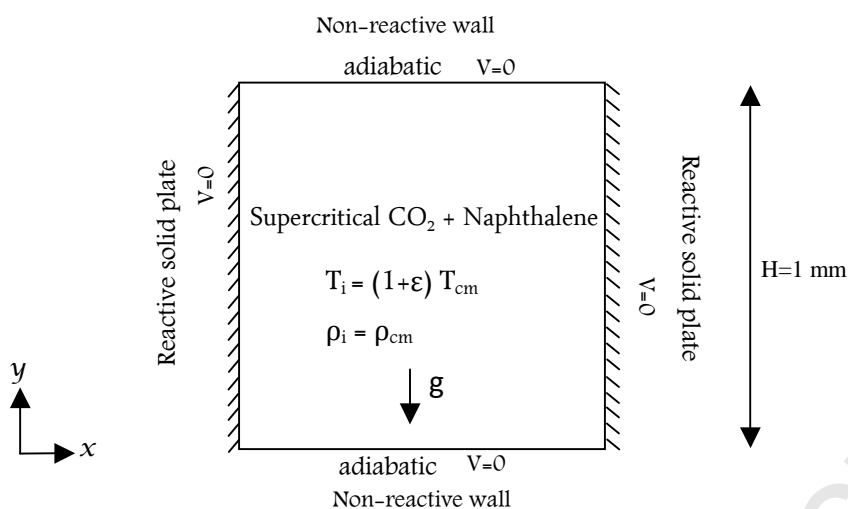


Fig. 1. Physical configuration

**Table 1**  
Pure component properties

	$T_c$ (K)	$\rho_c$ (kg.m <sup>-3</sup> )	$P_c$ (bar)	$M$ (kg.mol <sup>-1</sup> )	$\omega$	$v_b$ (cm <sup>3</sup> .mol <sup>-1</sup> )	$E_a$ (J mol <sup>-1</sup> )
<b>CO<sub>2</sub> (1)</b>	304.21	467.8	73.8	$4.401 \cdot 10^{-2}$	0.225	-	-
<b>Naphthalene (2)</b>	748.40	314.9	40.5	$1.282 \cdot 10^{-1}$	0.302	155	101.4

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138

## 139 2.2 Governing equations

140 The mathematical model is based on the 2D time-dependent and compressible Navier-  
141 Stokes equations, coupled with energy and mass diffusion equations including the  
142 supplemental Peng-Robinson equation of state. In order to reduce computational costs, a low  
143 Mach number approximation is used [25]. This approximation is valid since Mach numbers  
144 about  $10^{-4}$  are obtained. Thus, the total pressure is split into two parts: a homogeneous  
145 thermodynamic part  $P_{th}(t)$ , which appears in the equation of state and in the energy equation  
146 and only depends on time  $t$ , and a non-homogeneous dynamic part  $P_{dyn}(x, y, t)$ , appearing in  
147 the momentum equation and which varies with time and space. In this study, the dynamic  
148 pressure is strongly smaller than the thermodynamic part. Consequently, the total pressure is  
149 little different from the thermodynamic pressure and the evolution of  $P_{th}$  governs that of the



150 total pressure. In [38], a modification of the Low Mach number Approximation was proposed  
 151 to account for the strong stratification of fluids near the critical point. We tested this  
 152 modification and we noted that, for the present problem, the results obtained with and without  
 153 the modification were the same. Therefore, the original approximation [25] was used for the  
 154 simulations reported in this paper.

**Table 2**

Initial parameters

$T_i$ (K)	$\rho_i$ (kg.m <sup>-3</sup> )	$\lambda_i$ (W.m <sup>-1</sup> .K <sup>-1</sup> )	$C_{v_i}$ (J.kg <sup>-1</sup> .K <sup>-1</sup> )	$\mu_i$ (Pa.s)	$(D_{21})_i$ (m <sup>2</sup> .s <sup>-1</sup> )
307.75	470	0.098332532	1325.839	$3.33828 \times 10^{-5}$	$2.19525 \times 10^{-8}$
308.15	470	0.096196327	1306.27	$3.34016 \times 10^{-5}$	$2.19686 \times 10^{-8}$
309.15	470	0.091343811	1269.32	$3.34485 \times 10^{-5}$	$2.20090 \times 10^{-8}$
311.15	470	0.083368892	1214.86	$3.35423 \times 10^{-5}$	$2.20895 \times 10^{-8}$
318.15	470	0.066814297	1074.57	$3.38700 \times 10^{-5}$	$2.23679 \times 10^{-8}$

155  
 156 The dimensionless formulation was obtained using  $T_{cm}$  as characteristic temperature,  $\rho_i$  as  
 157 characteristic density,  $\rho_i (R / M_1) T_{cm}$  (with R is the perfect gas constant ( $R=8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ )  
 158 <sup>1</sup>) as characteristic pressure,  $H$  as characteristic length, the time scale of the piston effect as  
 159 characteristic time,  $t_{PE} = \frac{t_d}{(\gamma_m - 1)^2}$ , where  $t_d$  is the characteristic time of thermal diffusion,  
 160  $\gamma_m$  the capacity ratio of the mixture (see Appendix A) and  $H/t_{PE}$  was taken as the  
 161 characteristic velocity. The transport properties such as the dynamic viscosity  $\mu$ , the isochoric  
 162 specific heat capacity  $C_v$ , the thermal conductivity  $\lambda$  and the diffusion coefficient  $D_{21}$  were  
 163 dimensionless, relative to their respective initial values  $(\mu_i, \lambda_i, C_{v_i}, (D_{21})_i)$ . Thus, the  
 164 governing equations in a dimensionless form are:

$$165 \quad \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{V}) = 0 \quad (1)$$

$$166 \quad \rho \frac{\partial \mathbf{V}}{\partial t} + \rho \mathbf{V} \cdot \nabla \mathbf{V} = -\nabla P_{dyn} + \frac{1}{\text{Re}} \Delta \mathbf{V} + \frac{1}{3\text{Re}} \nabla (\nabla \cdot \mathbf{V}) + \frac{1}{Fr} \rho \quad (2)$$

$$\begin{aligned}
\rho \frac{\partial T}{\partial t} + \rho \mathbf{V} \cdot \nabla T &= - \frac{C_{v0}}{C_{vi}} (\gamma_0 - 1) \left[ P_{th} - T \left( \frac{\partial P_{th}}{\partial T} \right)_{\rho w} \right] (\nabla \cdot \mathbf{V}) \\
167 \quad &+ \frac{\gamma}{\text{RePr}} \nabla \cdot (\lambda^* \nabla T) - \left[ (\bar{U}_2^* - \bar{U}_1^*) + \frac{C_{v0}}{C_{vi}} (\gamma_0 - 1) \left( P_{th} - T \left( \frac{\partial P_{th}}{\partial T} \right)_{\rho w} \right) (\bar{V}_2^* - \bar{V}_1^*) \right] \times \\
&\frac{1}{(\gamma - 1)^2 Le} \nabla \cdot (\rho D_{21}^* \nabla w)
\end{aligned} \tag{3}$$

$$168 \quad \rho \frac{\partial w}{\partial t} + \rho \mathbf{V} \cdot \nabla w = \frac{1}{(\gamma - 1)^2 Le} \nabla \cdot (\rho D_{21}^* \nabla w) \tag{4}$$

169  $\mathbf{V}$  is the velocity of components  $u$  and  $v$  in the  $x$ - and  $y$ -directions respectively,  $w$  is the mass  
170 fraction,  $\gamma$  is the ratio of the isobaric and isochoric specific heats calculated from the  
171 equation of state (see Appendix A) with  $\gamma_0$  and  $C_{v0}$  corresponding to the values for a perfect  
172 gas ( $\gamma_0 = 1.3$ ,  $C_{v0} = 3R / M_1$ ). The value of  $C_{vi}$  for the initial state was taken from the NIST  
173 (see Table 2). The dimensionless numbers are respectively, the Mach number  $Ma$ , the  
174 Reynolds number  $Re$ , the Froude number  $Fr$ , the Prandtl number  $Pr$  and the Lewis number  $Le$   
175 and are defined as:

$$176 \quad Ma = \frac{V_{PE}}{c_0}, \quad Re = \frac{\rho_i V_{PE} H}{\mu_i}, \quad Fr = \frac{V_{PE}^2}{g H}, \quad Pr = \frac{\mu_i \gamma C_{vi}}{\lambda_i}, \quad Le = \frac{\lambda_i}{\rho_i \gamma C_{vi} (D_{21})_i}$$

177 where  $c_0 = \sqrt{\gamma_0 (R / M_1) T_{cm}}$  is the sound speed and  $V_{PE} = H / t_{PE}$  is the characteristic velocity

178 of the piston effect.

**Table 3**  
Characteristic times (piston effect  $t_{PE}$ , thermal diffusion  $t_d$ , mass diffusion  $t_{Md}$ , adsorption  $t_{ad}$ )

$T_i$ (K)	$t_{PE}$ (s)	$t_d$ (s)	$t_{Md}$ (s)	$t_{ad}$ (s)
307.75	0.1999	115.6989	45.5530	45.5530 $\times 10^5$
308.15	0.2367	106.9022	45.5194	45.5194 $\times 10^5$
309.15	0.3333	91.1253	45.4359	45.4359 $\times 10^5$
311.15	0.5404	73.0746	45.2704	45.2704 $\times 10^5$
318.15	1.2621	49.2332	44.7069	44.7069 $\times 10^5$

179

180 In Eq. (3),  $\bar{U}_k^*$  and  $\bar{V}_k^*$  are respectively the dimensionless partial molar internal energy and  
 181 partial molar volume expressed as follow:

$$182 \quad \bar{U}_k^* = \bar{U}_k / (M_2 C_{vi} T_{cm}) \quad \text{and} \quad \bar{V}_k^* = \bar{V}_k / (M_2 / \rho_i) \quad \text{for } k=1,2.$$

183 The expressions of  $\bar{U}_k$  and  $\bar{V}_k$  calculated using the Peng Robinson equation of state are  
 184 given in Appendix B.

185 The following relationship is used for  $\theta(w)$  :

$$186 \quad \theta(w) = 1 - \left(1 - \frac{M_1}{M_2}\right) w$$

187 with  $M_1$  and  $M_2$  ( $\text{kg mol}^{-1}$ ) are respectively, the molecular weight of  $\text{CO}_2$  and Naphthalene  
 188 (see Table 1).

189 The superscript (\*) refers to dimensionless parameters.

190 For thermal conductivity  $\lambda$  ( $\text{W.m}^{-1}.\text{K}^{-1}$ ), the following correlation is used [26]:

$$191 \quad \lambda(T, \rho) = \lambda_0(T) + \lambda_e(\rho) + \Delta\lambda_c(T, \rho),$$

192 The first term  $\lambda_0(T)$  corresponds to the limit of small densities and is expressed as follow:

$$193 \quad \lambda_0(T) = -7.6683 \times 10^{-3} + 8.0321 \times 10^{-5} T$$

194 The second term  $\lambda_e(\rho)$  is the excess property and is expressed as follow:

$$195 \quad \lambda_e(\rho) = 3.0990 \times 10^{-5} \rho + 5.5782 \times 10^{-8} \rho^2 + 2.5990 \times 10^{-17} \rho^5,$$

196 And the third term is the critical enhancement:

$$197 \quad \Delta\lambda_c(T, \rho) = \left( \frac{1.6735}{T - 291.4686} - 0.2774 + 7.4216 \times 10^{-4} T \right) \times \exp\left(-C^2 (\rho - \rho_{c1})^2\right)$$

198 with  $\begin{cases} C = 6.7112 \times 10^{-3} & \text{if } \rho < \rho_{c1} \\ C = 6.9818 \times 10^{-3} & \text{if } \rho > \rho_{c1} \end{cases}$

199 The binary mass diffusion coefficient,  $D_{21}$  ( $\text{m}^2 \text{s}^{-1}$ ), is calculated with the Wilke-Chang  
200 equation [27]:

201 
$$D_{21} = 7.4 \times 10^{-15} \frac{T \sqrt{\Phi 10^3 M_1}}{\mu v_{b2}^{0.6}},$$

202 with  $v_{b2}$  ( $\text{cm}^3 \text{mol}^{-1}$ ) the molar volume of Naphthalene at boiling point,  $\Phi$  the association  
203 factor ( $\Phi = 1$  for  $\text{CO}_2$ ).

204 The thermodynamic state of the mixture is described by the Peng-Robinson equation of state  
205 in the framework of the one-fluid theory. We can then compute the thermodynamic pressure  
206 as follow:

207 
$$P_{th} = \frac{T \rho \theta(w)}{1 - b^*(w) \rho / \theta(w)} - \frac{a^*(T, w) \rho^2}{1 + 2b^*(w) \rho / \theta(w) - b^*(w)^2 \rho^2 / \theta(w)^2} \quad (5)$$

208 Where:

209 
$$a^*(T, w) = a_1^*(T) (1-w)^2 + 2a_{12}^*(T) w (1-w) + a_2^*(T) w^2,$$

210 
$$b^*(w) = b_1^* (1-w)^2 + 2b_{12}^* w (1-w) + b_2^* w^2,$$

211 
$$a_1^*(T) = 1.487422 \frac{T_{c1}}{T_{cm}} \frac{\rho_i}{\rho_{c1}} \left[ 1 + \beta_1 \left( 1 - \sqrt{T (T_{cm} / T_{c1})} \right) \right]^2$$

212 
$$a_2^*(T) = 1.487422 \frac{M_1 T_{c2}}{M_2 T_{cm}} \frac{\rho_i}{\rho_{c2}} \left[ 1 + \beta_2 \left( 1 - \sqrt{T (T_{cm} / T_{c2})} \right) \right]^2$$

213 
$$b_j^* = 0.253076 \left( \frac{\rho_i}{\rho_{cj}} \right) \text{ with } j=(1,2)$$

$$214 \quad a_{12}^*(T) = \sqrt{a_1^*(T)a_2^*(T)}(1 - k_{12}),$$

$$215 \quad b_{12}^* = \frac{1}{2} \left( b_1^* \frac{M_1}{M_2} + b_2^* \right) (1 - l_{12}),$$

$$216 \quad \beta_j = 0.37464 + 1.54226\omega_j - 0.26992\omega_j^2 \quad (j=1,2)$$

217 with  $\omega$  the acentric factor (Table 1). The binary interaction parameters  $k_{12}$  and  $l_{12}$  are

218 determined so as to minimize the error between the calculated and experimental solubility  
 219 data. These two parameters are temperature dependent and they are obtained through these  
 220 formulae [28]:

$$221 \quad k_{12} = k_{12}' + k_{12}'' \left( \frac{308.15}{T} - 1 \right),$$

$$222 \quad l_{12} = l_{12}' + l_{12}'' \left( \frac{308.15}{T} - 1 \right)$$

223 The values of the binary interaction parameters predicted by a least square method are then:

$$224 \quad k_{12}' = 0.0395, \quad k_{12}'' = 0.0114, \quad l_{12}' = -0.1136 \quad \text{and} \quad l_{12}'' = -0.3103.$$

225

226 As it can be noted, the equations (1) – (5) are coupled for a given time step. This coupling  
 227 can be reduced by using an explicit scheme to evaluate the convective terms in Eq. (3). But  
 228 the energy source term involving  $\nabla \cdot V$  must be implicitly evaluated because it accounts for  
 229 the piston effect, namely the thermoacoustic effect responsible for fast heat transfer near the  
 230 liquid-gas critical point. So in order to decouple the energy equation (Eq. (3)) and the Navier-

231 Stokes equations (Eqs. (1)- (2)), the velocity divergence, must be calculated using only the  
 232 thermodynamic variables as explained by [29-30].

233 As part of the low Mach number approximation and for the dimensionless equations and if we  
 234 consider the equation of state written in the general form  $P_{th}=F(T, \rho, w)$ , the total derivative  
 235 of  $F$  with respect to time  $t$  leads to the relation:

236

$$237 \frac{dT}{dt} = \frac{-\left(\frac{\partial F}{\partial \rho}\right)_{T,w} \frac{d\rho}{dt} + \frac{dP_{th}}{dt} - \left(\frac{\partial F}{\partial w}\right)_{T,\rho} \frac{dw}{dt}}{\left(\frac{\partial F}{\partial T}\right)_{\rho,w}} \quad (6)$$

238 Moreover, the continuity equation (1) can also be written in the following form:

239

$$240 \frac{d\rho}{dt} = -\rho(\nabla \cdot \mathbf{V}) \quad (7)$$

241

242 Then, inserting Eq. (6) in the energy equation Eq. (3) using Eq. (7) for the computation of  
 243  $d\rho/dt$  and Eq. (4) for the computation of  $dw/dt$ , lead finally to the following expression for the  
 244 velocity divergence:

$$245 \nabla \cdot \mathbf{V} = \frac{\left\{ \rho \frac{dP_{th}}{dt} - \frac{\gamma}{\text{Re Pr}} \left(\frac{\partial F}{\partial T}\right)_{\rho,w} \nabla \cdot (\lambda^* \nabla T) - \left[ \left(\frac{\partial F}{\partial w}\right)_{T,\rho} - \frac{1}{\theta(w)} A(\bar{U}^*, \bar{V}^*) \left(\frac{\partial F}{\partial T}\right)_{\rho,w} \right] \right\} \times \left[ \frac{1}{(\gamma-1)^2 Le} \nabla \cdot (\rho D_{21}^* \nabla w) \right]}{1} \quad (8)$$

$$\frac{C_{v,0}}{C_{v,i}} (\gamma_0 - 1) \left(\frac{\partial F}{\partial T}\right)_{\rho,w} \left( P_{th} - T \left(\frac{\partial P_{th}}{\partial T}\right)_{\rho,w} \right) - \rho^2 \left(\frac{\partial F}{\partial \rho}\right)_{T,w}}$$

246 with  $A(\bar{U}^*, \bar{V}^*) = (\bar{U}_2^* - \bar{U}_1^*) + \frac{C_{v,0}}{C_{v,i}} (\gamma_0 - 1) \left[ P_{th} - T \left(\frac{\partial P_{th}}{\partial T}\right)_{\rho,w} \right] \times (\bar{V}_2^* - \bar{V}_1^*)$

247 The expressions of  $\left(\frac{\partial F}{\partial T}\right)_{\rho,w}$ ,  $\left(\frac{\partial F}{\partial w}\right)_{T,\rho}$  and  $\left(\frac{\partial F}{\partial \rho}\right)_{T,w}$  are reported in Appendix C.

248 Thanks to Eq. (8), we are now able to solve the governing equations in two uncoupled  
 249 steps, namely the energy equation and the equation of state on the one hand and the Navier-  
 250 Stokes equations on the other hand. The algorithm is detailed in section 2.4.

251 In this study, only the gravity effect was considered, the stratification of the fluid was not  
 252 taken into account, because we have tested several cases with stratification and no effect was  
 253 observed.

254 The initial and boundary conditions in dimensionless form are:

255 *CI:  $t = 0$*

$$T_i = 1 + \varepsilon$$

$$\rho_i = 1$$

256  $w_i$  fixed

$$P_i = \frac{(1 + \varepsilon)\theta(w_i)}{1 - b^*(w_i)/\theta(w_i)} - \frac{a^*(1 + \varepsilon, w_i)}{1 + 2b^*(w_i)/\theta(w_i) - b^*(w_i)^2/\theta(w_i)^2}$$

257 *BC:*

258 *No-slip walls* were considered so  $u = v = 0$  at the two plates.

259 At  $x=0$   $T_h = 1 + \varepsilon + \delta T^*$

260 with  $\delta T^* = \delta T / T_{cm}$

261 At  $x=l$   $T_{co} = 1 + \varepsilon$

262 At  $y=0, l$   $\frac{\partial T}{\partial y} = 0$  (adiabatic walls)

263

264 *2.3 Modeling of the adsorption reaction*

265 At the interfaces  $x=0$  and  $H$ , an adsorption reaction of Naphthalene on activated  
 266 carbon is considered. The choice of such adsorption system can be explained by the extensive  
 267 use of activated carbon as new-type high-efficiency adsorbent due to its high adsorption  
 268 capacities and high mass transfer rates. However, the model description can be applied to any  
 269 other adsorption system. The main objective here is to see how a supercritical mixture  
 270 behaves in the vicinity of reactive wall. So, we will focus essentially on the fluid side rather  
 271 than on what happens in the solid itself.

272 The species diffusion equation, (Eq. (4)), can be written in this form:

$$273 \quad \rho \frac{\partial w}{\partial t} + \rho u \frac{\partial w}{\partial x} + \rho v \frac{\partial w}{\partial y} = \nabla \cdot (\rho D_{21} \nabla w)$$

274 where  $u$  and  $v$  are the velocity of components in the  $x$ - and  $y$ -directions respectively.

275 The boundary conditions are:

276 *At the horizontal non-reactive walls*

$$277 \quad \frac{\partial w}{\partial y} = 0 \quad \text{for } y=0 \text{ and } y=H$$

278 *At the vertical reactive walls*, a first order kinetic adsorption model is used:

$$279 \quad D_{21} \frac{\partial w}{\partial n} = K_a w$$

280 where  $n$  is the normal to the surface at  $x=0$  and  $x=H$  and  $K_a = k_a / S_{ac}$  with  $k_a$  the adsorption rate  
 281 constant ( $\text{m}^3 \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$ ) and  $S_{ac}$  the specific surface area of activated carbon ( $\text{m}^2 \cdot \text{kg}^{-1}$ ).

282 Assuming small variations of temperature and pressure,  $K_a$  can be approximated by the first-  
 283 order term of its Taylor series in the vicinity of  $(T_i, P_i)$ :

$$284 \quad K_a = K_a(T_i, P_i) + \left( \frac{\partial K_a}{\partial T} \right)_P (T - T_i) + \left( \frac{\partial K_a}{\partial P} \right)_T (P - P_i) \quad (9)$$



285 The adsorption rate constant  $k_a$  can be computed by  $k_a = K_2 \cdot k_d$  where  $K_2$  is the adsorption  
 286 equilibrium constant ( $\text{m}^3 \cdot \text{kg}^{-1}$ ) and  $k_d$  is the desorption rate constant obtained through the  
 287 Arrhenius law:

$$288 \quad k_d = A \exp\left(-\frac{E_a}{RT}\right)$$

289 with  $E_a$  the activation energy and  $A$  the pre-exponential factor of Arrhenius.

290 The first term of Eq. (9) can be then considered as:

$$291 \quad K_{ai} = K_a(T_i, P_i) = \frac{k_d(T_i) K_2(T_i, P_i)}{S_{ac}}$$

292 The partial derivatives of  $K_a$  with respect to temperature and pressure are written as follow:

$$293 \quad \left(\frac{\partial K_a}{\partial T}\right)_p = \frac{1}{S_{ac}} \left(\frac{\partial k_a}{\partial T}\right)_p = \frac{k_d(T_i) K_2(T_i, P_i)}{S_{ac}} \left[ \frac{E_a}{RT^2} + \left(\frac{\partial \ln K_2}{\partial T}\right)_p \right]$$

$$294 \quad \left(\frac{\partial K_a}{\partial P}\right)_T = \frac{1}{S_{ac}} \left(\frac{\partial k_a}{\partial P}\right)_T = \frac{k_d(T_i) K_2(T_i, P_i)}{S_{ac}} \left(\frac{\partial \ln K_2}{\partial P}\right)_T$$

295 Thus Eq. (9) becomes:

$$296 \quad K_a(T, P) = K_{ai} \left\{ 1 + \left[ \frac{E_a}{RT^2} + \left(\frac{\partial \ln K_2}{\partial T}\right)_p(T_i, P_i) \right] (T - T_i) + \left(\frac{\partial \ln K_2}{\partial P}\right)_T(T_i, P_i) (P - P_i) \right\} \quad (10)$$

297 The partial derivatives of  $K_2$  with respect to temperature and pressure are obtained by  
 298 equating differentials of the logarithm of the solute fugacity in the fluid and solid phases  
 299 [31]:

$$300 \quad \left(\frac{\partial \ln K_2}{\partial T}\right)_p = \frac{\left(h_2^{IG} - \bar{h}_2^m\right) + \Delta H_2^{ads}}{RT^2} + \alpha^m \quad (11)$$

$$301 \quad \left( \frac{\partial \ln K_2}{\partial P} \right)_T = \frac{\bar{v}_2^{\infty,m}}{RT} - \kappa^m \quad (12)$$

302 where  $\Delta H_2^{ads} = \bar{h}_2^s - h_2^{IG}$  is the heat of adsorption of the solute on the solid plate,  $\bar{h}_2^m$  and  
 303  $\bar{h}_2^s$  are the infinite-dilution partial molar enthalpies of solute in the mobile and stationary  
 304 phases, respectively,  $h_2^{IG}$  is the enthalpy of the solute in the ideal gas state,  $\bar{v}_2^{\infty,m}$  is the infinite-  
 305 dilution partial molar volume of the solute in mobile phase and  $\alpha^m$ ,  $\kappa^m$  are respectively, the  
 306 volume expansivity and the isothermal compressibility.

307 The infinite-dilution residual partial molar enthalpy ( $h_2^{IG} - \bar{h}_2^m$ ) of the solute,  $\alpha^m$ ,  $\kappa^m$  and  
 308  $\bar{v}_2^{\infty,m}$  are obtained using the Peng-Robinson equation of state and they are reported in  
 309 Appendix D.

310 As shown by Eq. (10), the derivatives of the equilibrium adsorption constant,  $K_2$ , with respect  
 311 to temperature and pressure are directly involved in the definition of the boundary condition  
 312 at the solid-fluid interface. So, it is important to assess the effect of temperature and pressure  
 313 on these derivatives. A strong sensitivity to temperature and pressure can be guessed from  
 314 Eqs. (11) – (12) since the infinite-dilution residual partial molar enthalpy, ( $h_2^{IG} - \bar{h}_2^m$ ), the  
 315 infinite dilution partial molar volume of the solute,  $\bar{v}_2^{\infty,m}$ , the isothermal compressibility,  $\kappa^m$ ,  
 316 and the volume expansivity,  $\alpha^m$ , diverge near the solvent critical point. This assumption is  
 317 confirmed by Fig. 2 which shows the  $K_2$  derivative profiles as a function of pressure for  
 318 different temperatures. The profiles show a sharp minimum which becomes more important  
 319 when the critical temperature is approached. Then this minimum is shifted to the high  
 320 pressure domain and becomes less significant away from the critical point especially for  
 321  $T=318.15$  K. In this region (high pressure domain), the effect of the temperature on the  
 322 isothermal derivative is less pronounced. In the same way, the isobaric derivative of the

323 equilibrium constant as a function of temperature is shown in Fig. 3 for different pressures.  
 324 For pressures close to the critical one, namely  $P \leq 8.909$  MPa, a divergence of the derivative is  
 325 observed as the critical temperature is approached. Then, from 9 MPa, a behavior change can  
 326 be depicted with the appearance of a maximum which decreases and is shifted to the high  
 327 temperature domain when the pressure increases. One can also notice a similar trend for high  
 328 pressures and high temperatures. Therefore beyond the critical point the effect of the pressure  
 329 and temperature is no longer noticed.

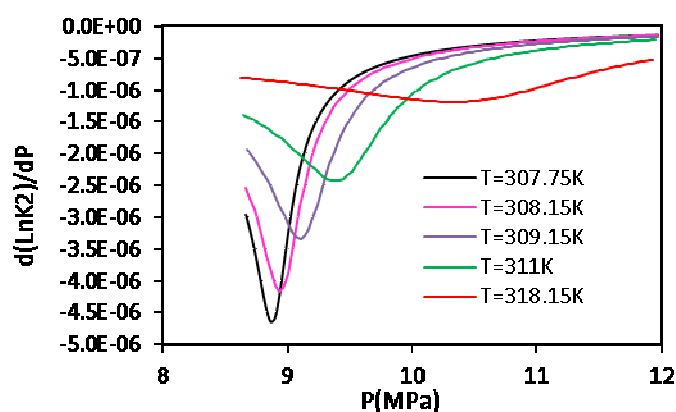


Fig. 2. Equilibrium constant derivative vs. pressure

330

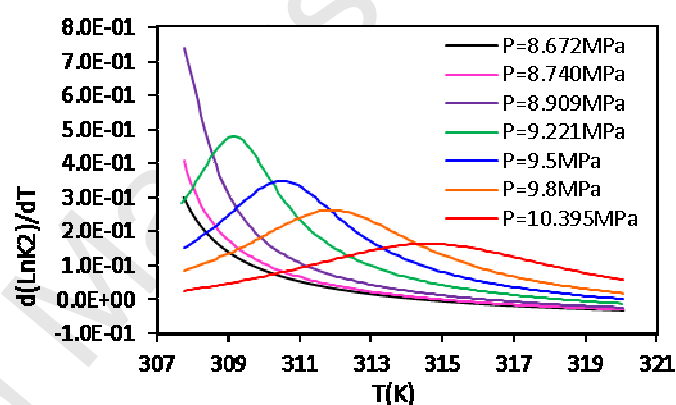


Fig 3. Equilibrium constant derivative vs. temperature

331 For this reason, a particular attention was paid to the effects of temperature and pressure on  
 332 the equilibrium adsorption constant in this study because a wide range of temperature and  
 333 pressure were considered. Moreover, changes near and far from the critical point will help us  
 334 to explain our results later.

336 It must be noted that the divergence of the infinite-dilution properties (residual partial molar  
 337 enthalpy and partial molar volume) of the solute is not specific of Naphthalene but it is a  
 338 universal behavior for dilute mixtures [32-33]. Therefore, the results obtained in this paper for  
 339 Naphthalene in supercritical  $\text{CO}_2$  are likely to be observed in all dilute binary mixtures, at  
 340 least on a qualitative point of view. Moreover, the nature of the adsorbent material appears

341 only through the heat of adsorption,  $\Delta H_2^{ads}$ , in Eq. (11), and therefore just for the variation of  
 342  $K_2$  with respect to temperature. We compared the evolutions of  $d(\text{Ln}K_2)/dT$  for soil ( $\Delta H_2^{ads} =$   
 343  $-46054.8 \text{ J/mol}$ ) and for activated carbon ( $\Delta H_2^{ads} = -83736 \text{ J/mol}$ ) as adsorbent material. The  
 344 same variations were observed in both cases with maxima occurring for the same  
 345 temperatures but with slightly different values: for example, the maximum for  $P = 9.221 \text{ MPa}$   
 346 was equal to  $0.52383 \text{ K}^{-1}$  for soil and  $0.47643 \text{ K}^{-1}$  for activated carbon. These identical  
 347 variations can be explained by the fact that the evolution of  $d(\text{Ln}K_2)/dT$  is governed by the  
 348 very large values of the infinite-dilution residual partial molar enthalpy,  $(h_2^{IG} - \bar{h}_2^m)$ , and of  
 349 the volume expansivity,  $\alpha^m$ , near the critical point. And these two properties are completely  
 350 independent of the characteristics of the adsorbent material. Consequently, the results  
 351 presented in this paper for adsorption on activated carbon are also relevant for any other  
 352 adsorbent material.

353 In the framework of the Low Mach number approximation, the boundary condition for the  
 354 mass fraction  $w$  on  $x=0$  and  $H$  can then be expressed as:

$$355 \quad D_{21} \frac{\partial w}{\partial n} = K_{ai} D_k (T, P_{th}) w$$

$$356 \quad \text{with } D_k (T, P_{th}) = 1 + \left[ \frac{E_a}{RT^2} + \left( \frac{\partial \text{Ln}K_2}{\partial T} \right)_P (T_i, P_i) \right] (T - T_i) + \left( \frac{\partial \text{Ln}K_2}{\partial P} \right)_T (T_i, P_i) (P - P_i)$$

357 In the dimensionless form, it will be written as:

$$358 \quad -\frac{D_{21}^*}{Da} \frac{1}{D_k} \frac{\partial w^*}{\partial n} = 1 - w^* \quad (13)$$

359 with  $D_{21}^* = D_{21} / (D_{21})_i$ ,  $w^* = (w - w_i) / w_i$  and Da is the Damköhler number defined as the  
 360 ratio of the characteristic fluidic time scale (diffusion characteristic time) and chemical time  
 361 scale (adsorption characteristic time):

$$362 \quad Da = \frac{HK_{ai}}{(D_{21})_i}$$

363 Eq. (13) leads to two Robin-type boundary conditions at  $x=0$  and  $x=1$ :

$$364 \quad \text{At } x=0 \quad w^* + \frac{D_{21}^*}{Da} \frac{1}{D_k} \frac{\partial w^*}{\partial x} = 1 \quad (14)$$

365 At  $x=1$ , the wall is maintained at the initial temperature, thus,  $D_{21}^*=1$ :

$$366 \quad w^* - \frac{1}{Da} \frac{1}{D_k} \frac{\partial w^*}{\partial x} = 1 \quad (15)$$

#### 367 2.4 Numerical method

368 The numerical integration of the model equations has been carried out using a second  
 369 order semi-implicit scheme [34]: the convective terms are evaluated by an Adams-Bashforth  
 370 scheme, and then the time integration of the resulting differential equations has been done  
 371 with an implicit second order backward Euler scheme. The space approximation is performed  
 372 using the Chebyshev-collocation method with Gauss-Lobatto points. For the computation of  
 373 the convective terms, the derivatives are calculated in the spectral space and the products are  
 374 performed in the physical one; the connection between the spectral and the physical spaces is  
 375 realized through a FFT algorithm. On the other hand, the spectral differentiation matrices are  
 376 used for the derivatives in the diffusive terms.

377 The computation of the velocity divergence by Eq. (8) allowed a decoupling between the  
 378 thermodynamic variables  $T$ ,  $\rho$ ,  $P_{th}$ ,  $w^*$  and that of the dynamic field. Consequently, the  
 379 discretized equations can be solved in two successive steps: first, the thermodynamic  
 380 variables are computed through the algorithm proposed by Ouazzani and Garrabos [29] and

381 then the Navier-Stokes equations are solved using the modified projection method developed  
382 in [35] and extended to variable density flows. These two steps are detailed bellow.

### 383 2.4.1 Computation of the thermodynamic variables ( $T, \rho, P_{th}, w^*$ )

384

385 The discretised energy and diffusion equations can be written as Helmholtz equations with  
386 time-dependent coefficients. In order to solve them using the diagonalization technique  
387 developed in [36] for Helmholtz equations with constant coefficients, the density and the  
388 transport coefficients  $\lambda^*$  and  $D_{21}^*$  are split into a constant part equal to the initial value and a  
389 time-dependent part:

$$390 \alpha^{n+1} = 1 + (\alpha^{n+1} - 1) \text{ for } \alpha = \rho, \lambda^*, D_{21}^*$$

391 So, the discretized energy equation for example obtained as Helmholtz equation with constant  
392 coefficients is written as follow:

$$\begin{aligned}
 \frac{\gamma}{\text{Re Pr}} \Delta T^{n+1} - \frac{3}{2\delta t} T^{n+1} &= \frac{3}{2\delta t} (\rho^{n+1} - 1) T^{n+1} - \frac{\gamma}{\text{Re Pr}} \nabla \cdot ((\lambda^{*n+1} - 1) \nabla T^{n+1}) \\
 &+ \rho^{n+1} \left( \frac{-4T^n + T^{n-1}}{2\delta t} \right) + AB(\rho \mathbf{V} \cdot \nabla T)^{n,n-1} \\
 &+ \frac{C_{v,0}}{C_{v,i}} (\gamma_0 - 1) \left[ P_{th}^{n+1} - T^{n+1} \left( \frac{\partial P_{th}}{\partial T} \right)_{\rho,w}^{n+1} \right] (\nabla \cdot \mathbf{V})^{n+1} \\
 &- \frac{w_i}{\theta(w^{n+1})} A \left( \bar{U}^{*n+1}, \bar{V}^{*n+1} \right) \frac{1}{(\gamma-1)^2 Le} \nabla \cdot (\rho^{n+1} D_{21}^{*n+1} \nabla w^{*n+1})
 \end{aligned} \tag{16}$$

394 where  $\delta t$  is the time-step and the notation  $AB(\cdot)$  means an Adams-Bashforth evaluation of the  
395 quantity:

$$396 AB(\phi)^{n,n-1} = 2\phi^n - \phi^{n-1}.$$

397 The diagonalization process of the Helmholtz operator with constant coefficients is executed  
398 only once in a preprocessing stage. After that, at each time step, the solution of Eq. (16) is  
399 reduced to matrix products, leading to a very efficient solution technique.

400 Thus, the solution of the energy Eq. (16), the diffusion equation and the equation of state  
401 is performed through the following iterative algorithm:

402 1. The variables  $T^{k-1}$ ,  $P_{th}^{k-1}$ ,  $\rho^{k-1}$ ,  $w^{*(k-1)}$  and  $(\nabla \cdot V)_T^{k-1}$  are initialized at their values at the  
403 previous time step  $n$ ;

404 2. The temperature  $T^k$  is obtained by the solution of the Helmholtz equation:

405

$$\begin{aligned} \frac{\gamma}{\text{Re Pr}} \Delta T^k - \frac{3}{2\delta t} T^k &= \frac{3}{2\delta t} (\rho^{k-1} - 1) T^{k-1} - \frac{\gamma}{\text{Re Pr}} \nabla \cdot ((\lambda^{k-1} - 1) \nabla T^{k-1}) \\ &+ \rho^{k-1} \left( \frac{-4T^n + T^{n-1}}{2\delta t} \right) + AB (\rho \mathbf{V} \cdot \nabla T)^{n,n-1} \\ &+ \frac{C_{v0}}{C_{vi}} (\gamma_0 - 1) \left[ P_{th}^{k-1} - T^{k-1} \left( \frac{\partial P_{th}}{\partial T} \right)_{\rho,w}^{k-1} \right] (\nabla \cdot V)^{k-1} \\ &- \frac{w_i}{\theta(w^{k-1})} A \left( \bar{U}^{*k-1}, \bar{V}^{*k-1} \right) \frac{1}{(\gamma-1)^2 Le} \nabla \cdot (\rho^{k-1} D_{21}^{*k-1} \nabla w^{*k-1}) \end{aligned}$$

406

407 3. The mass fraction  $w^{*k}$  is obtained by the solution of the Helmholtz equation:

408

$$\begin{aligned} \frac{1}{(\gamma-1)^2 Le} \Delta w^{*k} - \frac{3}{2\delta t} w^{*k} &= \frac{3}{2\delta t} (\rho^{k-1} - 1) w^{*k-1} - \frac{1}{(\gamma-1)^2 Le} \nabla \cdot ((\rho^{k-1} D_{21}^{*k-1} - 1) \nabla w^{*k-1}) \\ &+ \rho^{k-1} \left( \frac{-4w^{*n} + w^{*n-1}}{2\delta t} \right) + AB (\rho V \nabla w^*)^{n,n-1} \end{aligned}$$

409

410 with the following Robin boundary conditions on adsorbing walls:

411

$$412 \quad w^{*k} + \frac{1}{Da} \frac{\partial w^{*k}}{\partial x} = 1 + \left( \frac{1}{Da} - \frac{D_{21}^{*k-1}}{Da} \frac{1}{D_k^{k-1}} \right) \frac{\partial w^{*(k-1)}}{\partial x} \quad \text{for } x=0$$

$$413 \quad w^{*k} - \frac{1}{Da} \frac{\partial w^{*k}}{\partial x} = 1 - \frac{1}{Da} \left( 1 - \frac{1}{D_k^{k-1}} \right) \frac{\partial w^{*(k-1)}}{\partial x} \quad \text{for } x=1$$

414 4. The couple  $(P_{th}^k, \rho^k)$  is computed from the constraint of global mass conservation and the

415 equation of state. This computation must be performed through an iterative process;

416 5. The thermal conductivity  $\lambda^{*k}$  and the diffusion coefficient  $D_{21}^{*k}$  are updated.

417 6. The velocity divergence  $(\nabla \cdot \mathbf{V})_T^k$  is computed by Eq. (8).

418 The steps 2 to 6 are repeated until convergence is achieved on temperature, thermodynamic  
 419 pressure, density and mass fraction. The convergence criterion used is  $\text{Max}(Res_T, Res_\rho, Res_w,$   
 420  $Res_{P_{th}}) < 10^{-11}$ , with  $Res = \text{Max}((\phi^k - \phi^{k-1}) / \phi^{k-1})$  for  $\phi = T, \rho, w, P_{th}$ , and the maximum number of  
 421 iterations is fixed to 250.

422

#### 423 2.4.2 Solution of the Navier-Stokes equations

424

425 The second step is the solution of the Navier-Stokes equations. At the current time step  
 426  $(n+1)$ , temperature, density and velocity divergence are known. A projection-type algorithm  
 427 such as those developed for the solution of incompressible Navier-Stokes equations can then  
 428 be used. In the present work, the original projection method of Hugues and  
 429 Randriamampianina [35] was modified to account for variable density flows [30, 39]. The  
 430 advantage of this method compared to other projection methods is that it allows improving the  
 431 accuracy on pressure and reducing the slip velocity. It consists in solving the Navier-Stokes  
 432 equations by three successive steps.

#### 433 1<sup>st</sup> Step: Computation of a preliminary pressure

434 The preliminary pressure  $\bar{P}_{dyn}^{n+1}$  is computed from a Poisson equation, derived from the  
 435 discretized momentum equation, with Neumann boundary conditions obtained by the normal  
 436 projection of the momentum equation on the boundary:

437



$$\begin{cases}
\Delta \bar{P}_{dyn}^{n+1} = \nabla \cdot \left[ -AB (\rho \mathbf{V} \cdot \nabla \mathbf{V})^{n,n-1} + \rho^{n+1} \left( \frac{4\mathbf{V}^n - \mathbf{V}^{n-1}}{2\delta t} \right) + \frac{1}{Fr} \rho^{n+1} g \right] & \text{in } \Omega \\
+ \frac{4}{3Re} \Delta (\nabla \cdot \mathbf{V})_T^{n+1} + \frac{3}{2\delta t} \left( \frac{3\rho^{n+1} - 4\rho^n + \rho^{n-1}}{2\delta t} \right) & \\
\frac{\partial \bar{P}_{dyn}^{n+1}}{\partial n} = n \cdot \left[ -AB (\rho \mathbf{V} \cdot \nabla \mathbf{V})^{n,n-1} - \rho^{n+1} \left( \frac{3\mathbf{V}_B^{n+1} - 4\mathbf{V}^n + \mathbf{V}^{n-1}}{2\delta t} \right) + \frac{1}{Fr} \rho^{n+1} g \right] & \text{on } \partial\Omega \\
+ \frac{4}{3Re} \nabla (\nabla \cdot \mathbf{V})_T^{n+1} - \frac{1}{Re} AB (\nabla \times (\nabla \times \mathbf{V}))^{n,n-1} &
\end{cases} \quad (17)$$

439

440 with  $\Omega$  the computational domain ( $\Omega = ]-1,+1[ \times ]-1,+1[$ ),  $\partial\Omega$  its boundary,  $\mathbf{V}_B^{n+1}$  the boundary  
441 conditions of the velocity  $\mathbf{V}^{n+1}$ ,  $\partial/\partial n$  the normal derivative and  $\nabla \cdot \mathbf{V}$  is calculated from  
442 thermodynamic variables and noted  $(\nabla \cdot \mathbf{V})_T$ .

443 In Eq. (17), the term  $\Delta \mathbf{V}^{n+1}$  was decomposed in the boundary condition using the formula:

444

$$445 \quad \Delta \mathbf{V}^{n+1} = \nabla (\nabla \cdot \mathbf{V}^{n+1}) - \nabla \times (\nabla \times \mathbf{V}^{n+1})$$

446

447 and the rotational term was evaluated using an Adams-Bashforth scheme.

448

449 2<sup>nd</sup> Step: Computation of a predicted velocity  $\mathbf{V}^*$

450

451 The predicted velocity field  $\mathbf{V}^*$  is computed implicitly from the momentum equation with  
452 the gradient of the preliminary pressure instead of that of the actual pressure  $P_{dyn}^{n+1}$ . The  
453 predicted velocity therefore satisfies the following problem:

454

$$\begin{cases}
\rho^{n+1} \frac{3\mathbf{V}^* - 4\mathbf{V}^n + \mathbf{V}^{n-1}}{2\delta t} + AB (\rho \mathbf{V} \cdot \nabla \mathbf{V})^{n,n-1} = -\nabla \bar{P}_{dyn}^{n+1} + \frac{1}{Re} \Delta \mathbf{V}^* + \frac{1}{3Re} \nabla (\nabla \cdot \mathbf{V})_T^{n+1} + \frac{1}{Fr} \rho^{n+1} g & \text{in } \Omega \\
\mathbf{V}^* = \mathbf{V}_B^{n+1} & \text{on } \partial\Omega
\end{cases} \quad (18)$$

456

457

458 Here again, we have to solve Helmholtz equations with variable coefficients for each  
 459 velocity component. As for energy and mass diffusion equations, the density  $\rho^{n+1}$  is split into  
 460 a constant part and a time-dependent part and the following Helmholtz equation with constant  
 461 coefficient is solved iteratively:

$$\begin{aligned}
 \frac{1}{\text{Re}} \Delta \mathbf{V}^{*,l} - \frac{3}{2\delta t} \rho_0 \mathbf{V}^{*,l} &= \frac{3}{2\delta t} (\rho^{n+1} - \rho_0) \mathbf{V}^{*,l-1} + \nabla \bar{P}_{dyn}^{n+1} \\
 -\rho^{n+1} \left( \frac{4\mathbf{V}^n - \mathbf{V}^{n-1}}{2\delta t} \right) &+ AB (\rho \mathbf{V} \cdot \nabla \mathbf{V})^{n,n-1} \\
 -\frac{1}{3\text{Re}} \nabla (\nabla \cdot \mathbf{V})_T^{n+1} - \frac{1}{Fr} \rho^{n+1} \mathbf{g} &
 \end{aligned} \quad (19)$$

463  
 464 The convergence is achieved when  $\text{Max}(Res_u, Res_v) < 10^{-13}$ , with  $Res = \text{Max}((\cdot)^{l-1})^{l-1}$  for  
 465  $=u, v$ . Only 3 or 4 iterations are necessary.

466  
 467 3<sup>rd</sup> Step: Correction step

468 The converged velocity field  $\mathbf{V}^*$  is then corrected by taking into account the pressure  
 469 gradient at the current time step ( $n+1$ ) so that the final velocity field satisfies the continuity  
 470 equation:

$$\begin{cases}
 \frac{3}{2\delta t} (\rho^{n+1} \mathbf{V}^{n+1} - \rho^{n+1} \mathbf{V}^*) = -\nabla (P_{dyn}^{n+1} - \bar{P}_{dyn}^{n+1}) & \text{in } \Omega \cup \partial\Omega \\
 \mathbf{V}^{n+1} \cdot \mathbf{n} = \mathbf{V}_B^{n+1} \cdot \mathbf{n} & \text{on } \partial\Omega \\
 \frac{3\rho^{n+1} - 4\rho^n + \rho^{n-1}}{2\delta t} + \nabla \cdot (\rho^{n+1} \mathbf{V}^{n+1}) = 0 & \text{in } \Omega
 \end{cases} \quad (20)$$

473  
 474 This system is solved through the following Poisson problem for the intermediate  
 475 variable  $\varphi = 2\delta t (P_{dyn}^{n+1} - \bar{P}_{dyn}^{n+1})/3$ :

476

$$\begin{cases} \Delta \varphi = \nabla \cdot (\rho^{n+1} \mathbf{V}^*) + \frac{3\rho^{n+1} - 4\rho^n + \rho^{n-1}}{2\delta t} & \text{in } \Omega \\ \frac{\partial \varphi}{\partial n} = 0 & \text{on } \partial\Omega \end{cases} \quad (21)$$

478

479 The actual velocity field and pressure at the current time step ( $n+1$ ) are finally calculated in

480  $\Omega \cup \partial\Omega$  by the formulae:

$$481 \quad \mathbf{V}^{n+1} = \mathbf{V}^* - \frac{1}{\rho^{n+1}} \nabla \varphi \quad (22)$$

$$482 \quad P_{dyn}^{n+1} = \bar{P}_{dyn}^{n+1} + \frac{3}{2\delta t} \varphi \quad (23)$$

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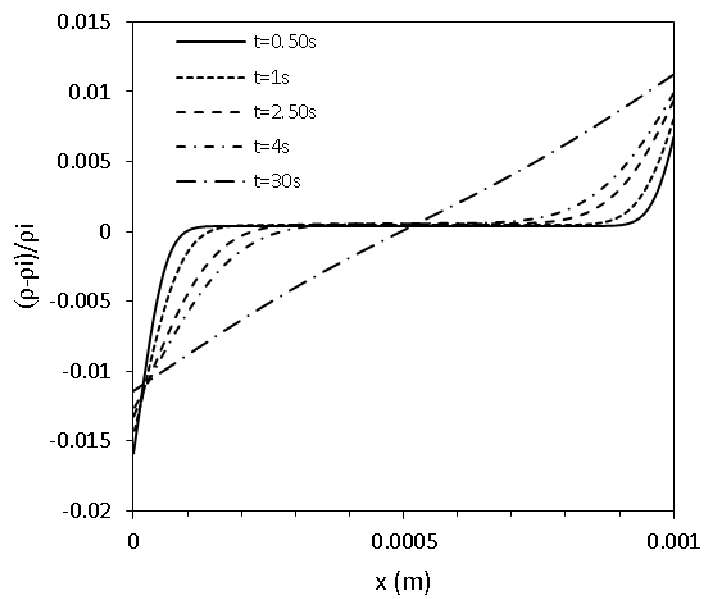
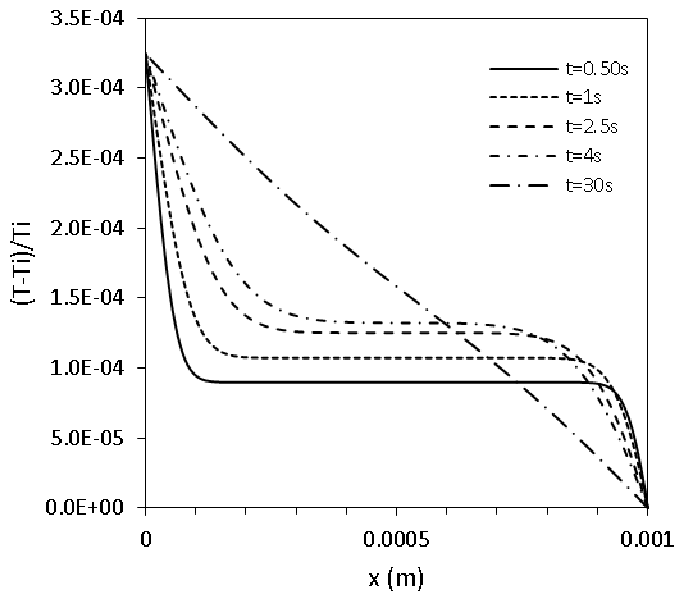
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## 498 3. Results and discussions



499

500

501 Fig. 4. Profiles of the temperature perturbation at several  
502 times for  $T_i=308.15$  K and  $\Delta T=100$  mK in the case  $g=0$ 

503

504

505 Fig. 5. Profiles of the density perturbation at several  
506 times for  $T_i=308.15$  K and  $\Delta T=100$  mK

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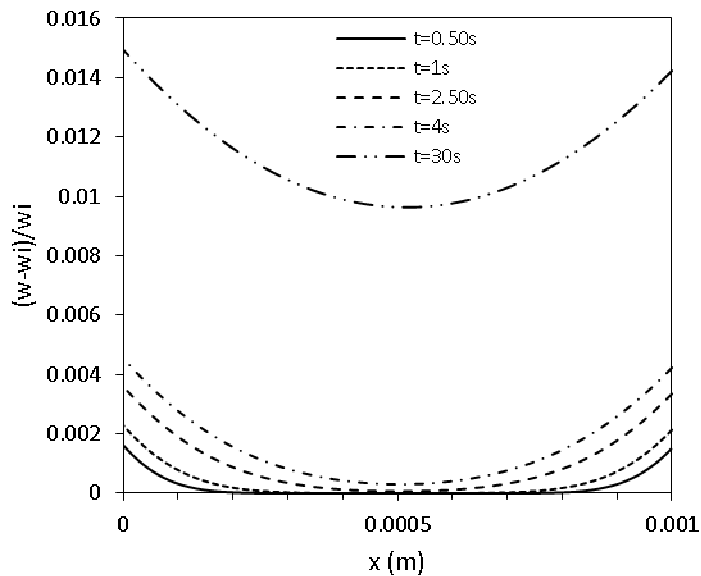
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530 Fig. 6. Profiles of the mass fraction perturbation at several  
531 times for  $T_i=308.15$  K and  $\Delta T=100$  mK in the case  $g=0$ 

530 The system's response to the heating of the left vertical wall is explained in this

531 section. The analysis below is based on simulations carried out at various initial temperatures

532  $T_i$  ranging from 307.75 K to 318.15 K and which correspond to dimensionless distances  $\epsilon$  to  
 533 the critical point ranging from  $3.25 \times 10^{-4}$  to  $3.41 \times 10^{-2}$ . The values of the different  
 534 characteristic times of the problem are given in Table 3. It can be noted that, as the critical  
 535 temperature is approached, the thermal diffusion and mass diffusion times strongly increase  
 536 whereas the characteristic time of piston effect decreases. For all the simulations, the left side  
 537 of the cavity (at  $x=0$ ) is gradually heated following a cosine law expressed as:

$$538 \quad \delta T(t) = \begin{cases} 0.5 \Delta T \left( 1 - \cos \left( \pi \frac{t}{t_{\text{heat}}} \right) \right) & \text{if } t \leq t_{\text{heat}} \\ \Delta T & \text{if } t \geq t_{\text{heat}} \end{cases}$$

539 where  $\Delta T$  is the temperature increase and  $t_{\text{heat}}$  is the heating phase time corresponding to 200  
 540 time steps. The influence of  $\Delta T$  will be discussed later for different cases ( $\Delta T = 50, 100, 150$   
 541 and 200 mK).

### 542 3.1 General description

543 In the first part, the case of  $T_i = 308.15$  K and  $\Delta T = 100$  mK, is discussed. The  
 544 Damköhler number is fixed to  $Da = 10^{-5}$  and the initial mass fraction  $w_i$  corresponds to the  
 545 solubility of Naphthalene in  $\text{CO}_2$ .

546 The evolution of temperature and density distributions between the walls and at the cavity  
 547 mid-height are illustrated in Figs. 4 and 5 for several times ( $t = 0.5$  s, 1 s, 2.5 s, 4 s and 30 s)  
 548 in the absence of gravity. Because of the very small thermal diffusivity near the critical point,  
 549 the heating of the wall causes ultra-thin boundary layers at the wall-fluid interface. Due to the  
 550 high isothermal compressibility, the fluid close to the heated side expands upward and  
 551 converts some of the kinetic energy into thermal energy. This results in compressing  
 552 adiabatically the rest of the fluid and leading to a quick increase of the thermodynamic  
 553 pressure which induces a fast and homogeneous heating of the cavity bulk by thermo-acoustic

554 effects (piston effect). During the heating phase, temperature, and therefore density, at the  
555 heated wall change at each time step and, as a consequence, temperature and density gradients  
556 near this wall increase more and more. As the bulk temperature grows, and since the right wall  
557 (at  $x=H$ ) temperature is maintained at its initial value, a cold boundary layer settles near the  
558 right wall where the fluid contracts. The contraction causes an expansion of the bulk and  
559 reduces the bulk temperature. The behavior of the fluid is the result of these two competing  
560 processes, heating by hot boundary layer and cooling by cold boundary layer. The  
561 temperature field is then divided into three distinct zones: two thermal boundary layers  
562 associated with large density gradients (Fig. 5) along the vertical walls and the isothermal  
563 cavity bulk. Therefore, the temperature and the density profiles exhibit the same behavior,  
564 dominated by the piston effect, as in pure fluid [45-46]. In the rest of the paper, we denote as  
565 bulk the fluid region, which does not include the boundary layers. The homogeneous bulk  
566 temperature and density fields of a supercritical fluid occur at a time that is much shorter than  
567 the thermal diffusion time ( $t_{PE}=0.23$  s and  $t_d=107$ s). They are the signature of the piston effect  
568 which was identified a long time ago as responsible for fast heat transport in near-critical pure  
569 fluids [47-49]. However, the piston effect plays an important role only for short times because  
570 of the disappearance of sharp temperature gradients due to the action of thermal diffusivity.  
571 For an advanced time (30s), the system's response, is then markedly different from that  
572 observed for shorter times. A similar trend to that of a perfect gas characterized by  
573 equilibrium can be depicted. It must be noted that temperature equilibrium is achieved on a  
574 time much shorter than the diffusion time. This is probably a consequence of the evolution of  
575 mass fraction in the cavity bulk, since  $w$  influences the temperature evolution as a source term  
576 of the energy equation.

577 The mass fraction field exhibits a different aspect as shown in Fig. 6. In order to explain the  
578 typical behavior of the supercritical mixture near the two reactive walls, we focus on the

579 boundary conditions developed in section 2.3. The dependence to temperature and pressure of  
580 the adsorption rate can be depicted from Eq. (10). Since the partial derivative of  $K_2$  with  
581 respect to pressure is negative (see Fig. 2), the pressure term tends to reduce  $K_a$  and as a  
582 result, to diminish the adsorbed amount. On the left heated wall, the effect of the temperature  
583 increase is amplified by the diverging derivative of  $K_2$  with respect to temperature (see Fig.  
584 3), leading to an important amount of Naphthalene adsorbed at the warm side.

585 The phenomenon occurring at the isothermal right wall is totally different. The strong density  
586 gradient near the boundary  $x=H$  (Fig. 5), generated by the piston effect, goes along with an  
587 increase of the amount of Naphthalene neat this reactive wall leading to an increase of the  
588 adsorbed quantity. Finally, the strong and homogeneous increase of the pressure, induced by  
589 the piston effect in the whole cavity, reduces the adsorbed amount at both reactive walls.

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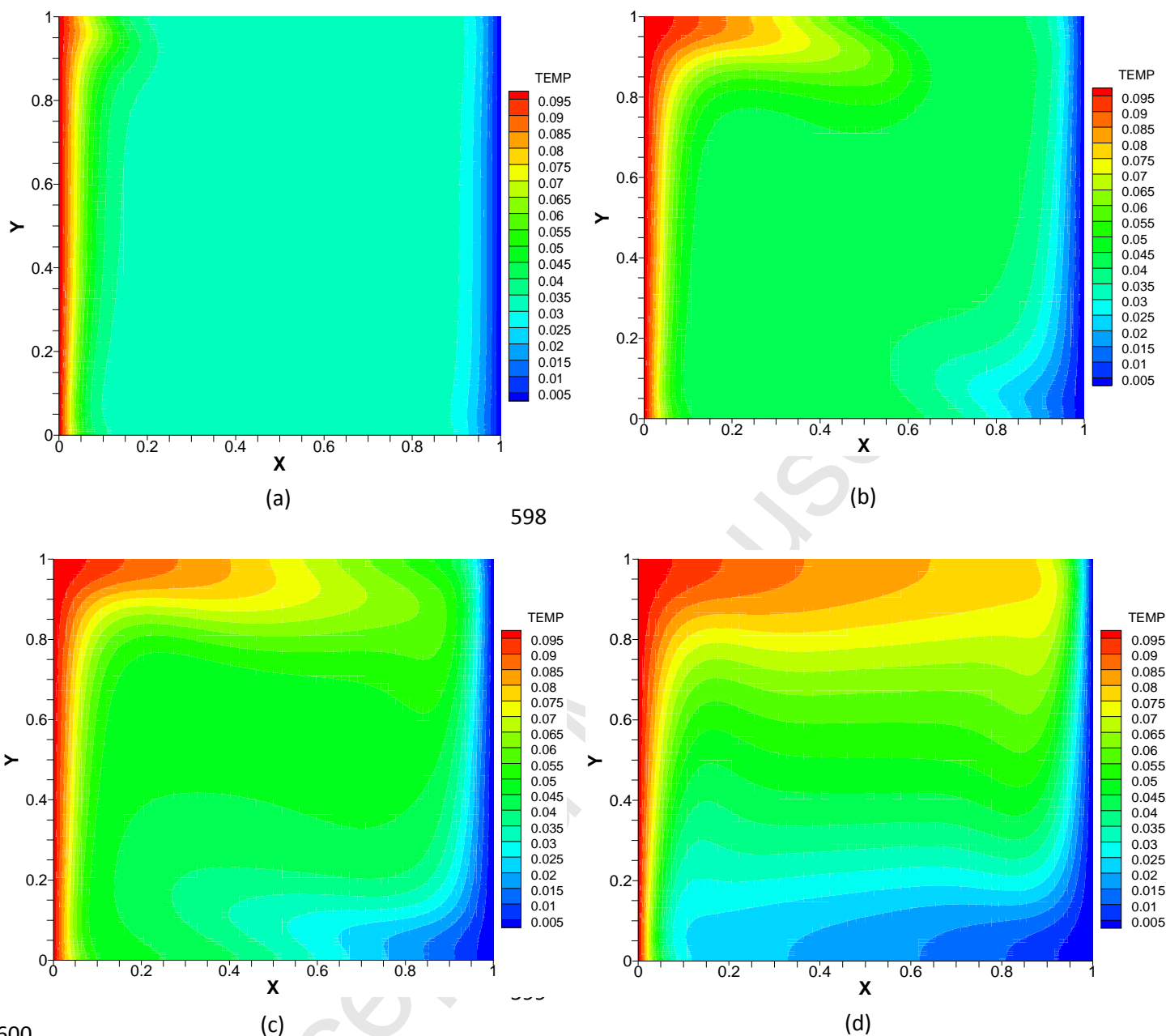
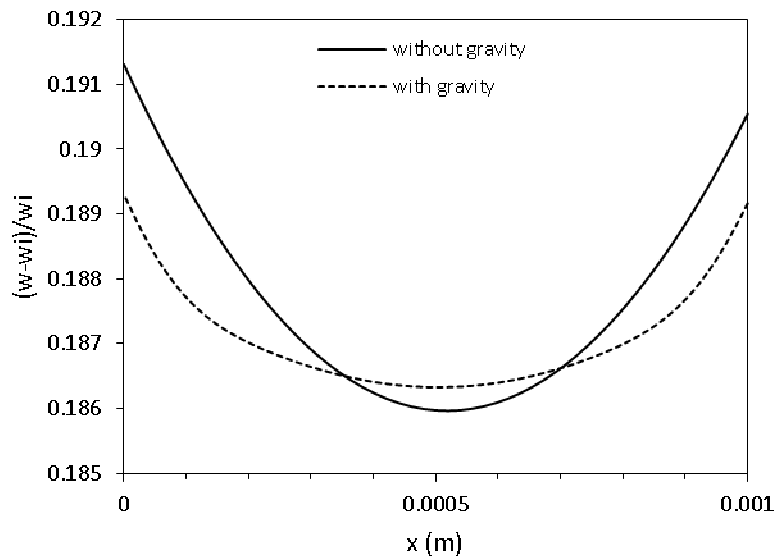


Fig. 7. Isosurfaces of the temperature variation for several times (a) 1s, (b) 2.5s, (c) 4s and (d) 30s, for  $T_i=308.15$  K and  $\Delta T=100$ mK in the presence of gravity

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 603 We consider now the case when the mixture is subjected to the gravity. In this case,  
 604 side heating initiates gravity-driven convection in the fluid phase and the temperature and  
 605 density fields obtained are completely two-dimensional on the contrary to the mainly 1D  
 606 solutions previously observed in the absence of gravity. In Fig. 7, instantaneous temperature  
 607 fields are plotted in the (x,y) plan for several times (1 s, 2.5 s, 4 s and 30 s). During a short  
 608 time, the cavity bulk is heated rapidly due to the piston effect. As a result, upstream rises near



609 the left warm surface and a hot spot at the left corner of the cavity can be depicted after 1s and  
 610 then it is convected progressively along the top wall for longer times. As in Fig. 4 for  $g=0$ , a  
 611 cool boundary layer forms near the right isothermal wall, due to the piston effect. As a result,  
 612 a jet moving down appears near the right wall from 2.5 s. The hot and cold thermal plumes  
 613 along the top and the bottom sides develop progressively in time as shown in Fig. 7. We can  
 614 clearly see the homogenous increase of the bulk temperature induced by the piston effect.  
 615 This aspect is different from the perfect gas case where thermal boundary layer is formed only  
 616 near heated side which leads to a single stream [50].



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Fig. 8. The effect of the gravity on the mass fraction perturbation  
 for  $T_i=308.15$  K and  $\Delta T=100$  mK at  $t=500$ s

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For the sake of comparison and in order to highlight the effect of Earth's gravity, we

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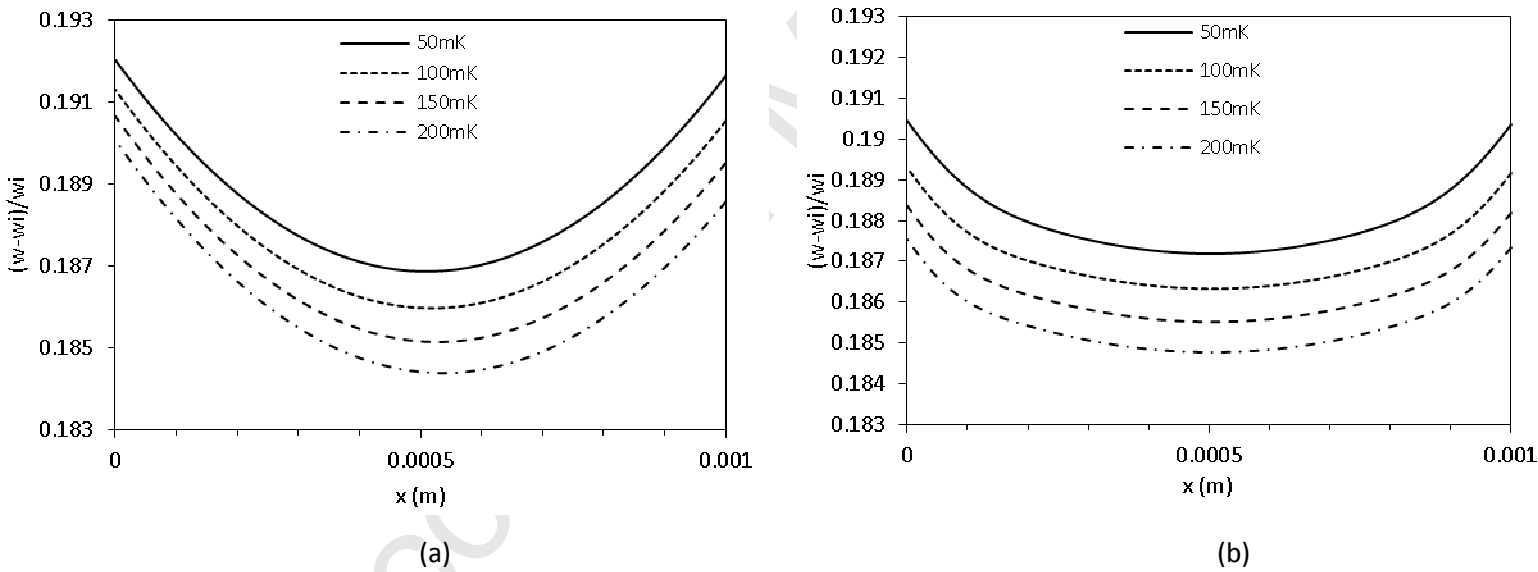
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analyze in the following the Naphthalene mass fraction evolution with and without gravity  
 (Fig. 8). The difference previously observed between the hot wall and the cold wall has  
 disappeared. Gravity in this case tends to balance both sides. Conversely, the amount  
 adsorbed is remarkably lower at the two sides (hot and cold) compared to the case without  
 gravity. On the other hand, the mass fraction at the cavity centre has increased. These  
 observations can be explained as follow:

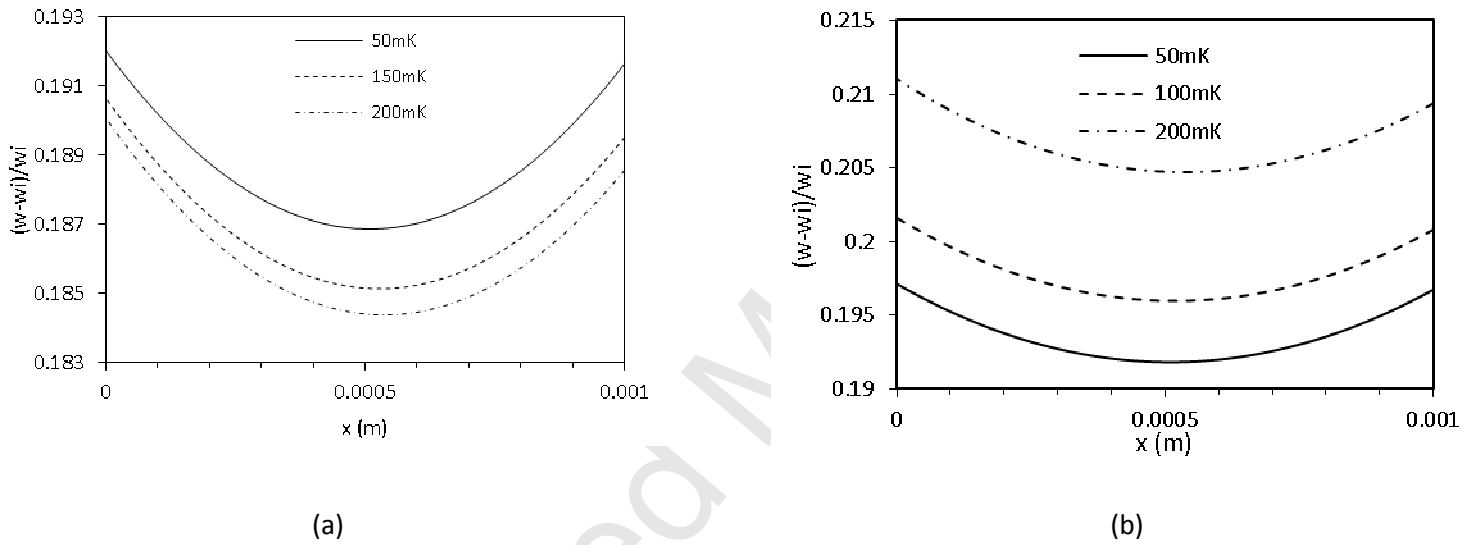
627 For the case without gravity, thermal diffusion process is the only highlighted. The  
 628 characteristic time of thermal diffusion is much higher than the time scale of the piston effect.  
 629 Such a long process allows keeping a high temperature in the vicinity of the heated wall.  
 630 Consequently, as seen above, the divergence of the partial derivative of the equilibrium  
 631 constant with respect to temperature near the critical point is believed to affect the mass  
 632 fraction rate at the hot side. However, in the case with gravity, density variations generate a  
 633 plume which expands upwardly (as shown in Fig. 7). This intensive plume moves hot fluid to  
 634 the top boundary and thus decreases the temperature near the warm side. Therefore, the effect  
 635 of the derivative with respect to temperature is reduced. Such a phenomenon can explain the  
 636 reduction of the mass fraction when gravity is taken into account.



637 Fig. 9. The effect of the solid plate temperature on the mass fraction perturbation without gravity (a) and with gravity (b) for  
 638  $T_i=308.15$  K at  $t=500$ s

639 The effect of heating intensity is highlighted in Fig. 9 with and without gravity. For the same  
 640 proximity to the critical point and the same time, Fig. 9 shows a comparison of the mass  
 641 fraction profiles at the cavity mid-height obtained for four values of the temperature rise  $\Delta T=$   
 642 50mK, 100mK, 150mK and 200mK: the mass fraction decreases with increasing heating. In  
 643 the case without gravity, a stronger heating reduces remarkably the mass fraction throughout  
 644 the entire volume while keeping the asymmetry of adsorbed amount between the hot and the

645 cold walls (Fig. 9(a)). It can be noted that this asymmetry increases with the heating. A  
 646 similar trend can be observed with gravity (Fig. 9(b)). This surprising result can be explained  
 647 by the negative pressure term in the adsorption rate  $K_a$  (Eq. (10)). Indeed, a stronger heating  
 648 of the wall induces a larger thermodynamic pressure increase by the piston effect and, as a  
 649 result, a larger value of the pressure term which reduces the parameter  $K_a$ . The reduction of  
 650 the adsorbed amount at the walls then leads to a smaller mass fraction in the whole cavity.



651  
 652 Fig. 10. Influence of the piston effect on the mass fraction perturbation without gravity with (a)  $d\text{Ln}K_2/dp \neq 0$  and  
 653  $d\text{Ln}K_2/dp = 0$  in Eq. (10) for  $T_i = 308.15$  K and  $t = 500$ s.

654 This explanation is confirmed by Fig. 10 where a case without the pressure term in Eq.  
 655 (10) was tested. We can then observe that with the sole presence of the temperature term, a  
 656 stronger heating increases the mass fraction in the entire volume (Fig. 10(b)). Consequently,  
 657 the pressure term plays a major role in the expression of the adsorption rate  $K_a$  (Eq. (10)) near  
 658 the critical point. The evolution of the mass fraction profiles as a function of heating depicted  
 659 in Fig. 10(a) is then directly attributable to the piston effect which is responsible for the strong  
 660 and homogeneous increase of the pressure in the cavity.

### 661 3.2 Effect of initial mass fraction

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**Table 4**

The effect of the initial mass fraction for  $T_i=308.15$  K,  $\Delta T=100$  mK and  $\Delta T=50$  mK at  $t=30$ s and without gravity

$\Delta T=100$ mK			
$w_i$	$w-w_i(x=0)$	$w-w_i(x=H)$	$(w_{x=0}-w_{x=H})/w_{x=0}$
$7.6751 \times 10^{-3}$	$3.93 \times 10^{-4}$	$3.88 \times 10^{-4}$	$1.48 \times 10^{-2}$
$4.22 \times 10^{-3}$	$1.65 \times 10^{-4}$	$1.62 \times 10^{-4}$	$1.97 \times 10^{-2}$
$2.11 \times 10^{-3}$	$7.16 \times 10^{-5}$	$6.99 \times 10^{-5}$	$2.28 \times 10^{-2}$
$9.35 \times 10^{-4}$	$2.95 \times 10^{-5}$	$2.87 \times 10^{-5}$	$2.46 \times 10^{-2}$
$7.6751 \times 10^{-4}$	$2.39 \times 10^{-5}$	$2.34 \times 10^{-5}$	$2.49 \times 10^{-2}$
$\Delta T=50$ mK			
$w_i$	$w-w_i(x=0)$	$w-w_i(x=H)$	$(w_{x=0}-w_{x=H})/w_{x=0}$
$7.6751 \times 10^{-3}$	$3.94 \times 10^{-4}$	$3.91 \times 10^{-4}$	$7.44 \times 10^{-3}$
$4.22 \times 10^{-3}$	$1.65 \times 10^{-4}$	$1.64 \times 10^{-4}$	$9.88 \times 10^{-3}$
$2.11 \times 10^{-3}$	$7.15 \times 10^{-5}$	$7.07 \times 10^{-5}$	$1.15 \times 10^{-2}$
$9.35 \times 10^{-4}$	$2.94 \times 10^{-5}$	$2.91 \times 10^{-5}$	$1.24 \times 10^{-2}$
$7.6751 \times 10^{-4}$	$2.39 \times 10^{-5}$	$2.36 \times 10^{-5}$	$1.25 \times 10^{-2}$

667

**Table 5**

The effect of the initial mass fraction for  $T_i=308.15$  K,  $\Delta T=100$  mK and  $\Delta T=50$  mK at  $t=30$ s and with gravity

$\Delta T=100$ mK			
$w_i$	$w-w_i(x=0)$	$w-w_i(x=H)$	$(w_{x=0}-w_{x=H})/w_{x=0}$
$7.6751 \times 10^{-3}$	$3.78 \times 10^{-4}$	$3.77 \times 10^{-4}$	$2.78 \times 10^{-3}$
$4.22 \times 10^{-3}$	$1.56 \times 10^{-4}$	$1.56 \times 10^{-4}$	$3.11 \times 10^{-3}$
$2.11 \times 10^{-3}$	$6.70 \times 10^{-5}$	$6.67 \times 10^{-5}$	$3.42 \times 10^{-3}$
$9.35 \times 10^{-4}$	$2.74 \times 10^{-5}$	$2.73 \times 10^{-5}$	$3.63 \times 10^{-3}$
$7.6751 \times 10^{-4}$	$2.22 \times 10^{-5}$	$2.22 \times 10^{-5}$	$3.66 \times 10^{-3}$
$\Delta T=50$ mK			
$w_i$	$w-w_i(x=0)$	$w-w_i(x=H)$	$(w_{x=0}-w_{x=H})/w_{x=0}$
$7.6751 \times 10^{-3}$	$3.82 \times 10^{-4}$	$3.81 \times 10^{-4}$	$1.83 \times 10^{-3}$
$4.22 \times 10^{-3}$	$1.58 \times 10^{-4}$	$1.57 \times 10^{-4}$	$2.00 \times 10^{-3}$
$2.11 \times 10^{-3}$	$6.76 \times 10^{-5}$	$6.75 \times 10^{-5}$	$2.17 \times 10^{-3}$
$9.35 \times 10^{-4}$	$2.77 \times 10^{-5}$	$2.76 \times 10^{-5}$	$2.28 \times 10^{-3}$
$7.6751 \times 10^{-4}$	$2.25 \times 10^{-5}$	$2.24 \times 10^{-5}$	$2.30 \times 10^{-3}$

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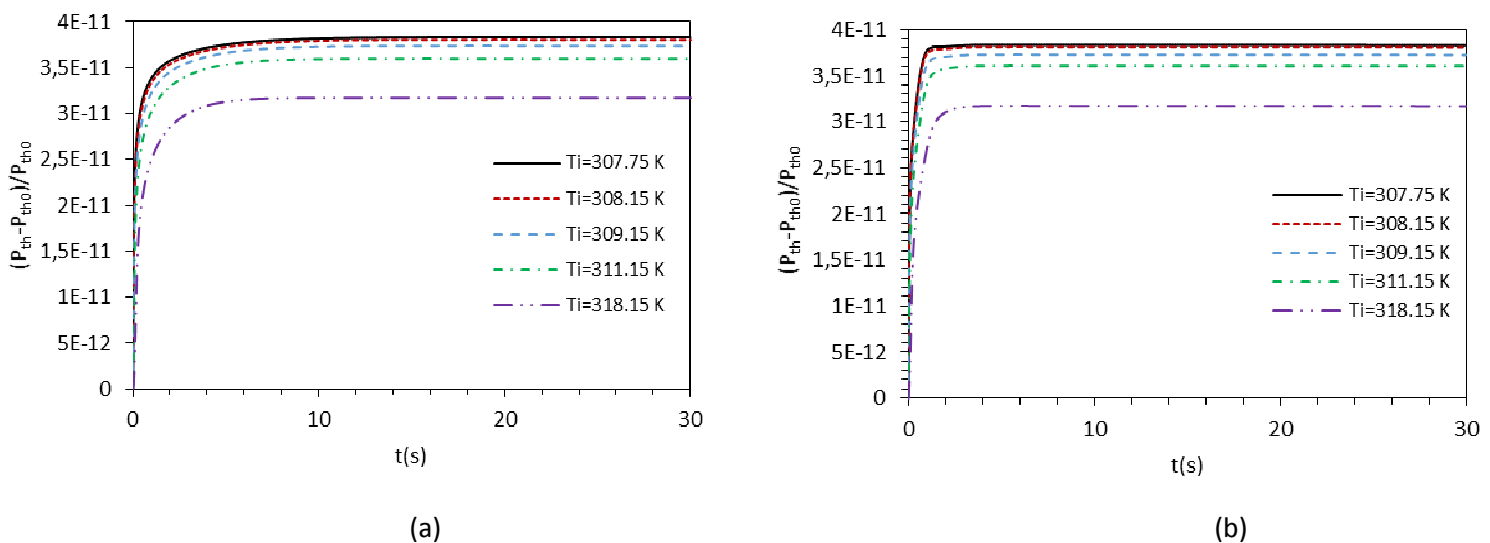
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The effect of the initial mass fraction on the adsorbed amount at the two walls is reported in Tables 4 and 5 for cases with and without gravity and for two temperature increases  $\Delta T=50$ mK and  $100$ mK. The maximum value of  $w_i$  corresponds to the solubility of Naphthalene in  $\text{CO}_2$ . We note that the difference between the left and right sides observed in Fig. 8 without gravity can be quantified for each initial mass fraction and for the two temperature increase. Then, the effect of the gravity is confirmed in Table 5 where equilibrium is established between the two sides and only a slight difference can be observed between the heated and the isothermal plates. A detailed analysis of Tables 4 and 5 reveals

678 that, as could be expected, the mass fraction variation at both sides decreases with the initial  
 679 mass fraction. To better quantify the difference between the hot and the cold sides, the relative  
 680 variation  $w_{x=0} - w_{x=H} / w_{x=0}$  is reported in the third column. In the first case, without gravity  
 681 and for  $\Delta T=100\text{mK}$ , a difference of 1.5% can be depicted for the greater initial mass fraction.  
 682 Then this difference evolves to 2.5% for the lowest value of  $w_i$ . When the heating decreases to  
 683 50mK, the difference between the heated and isothermal sides is reduced (0.7% and 1.2% for  
 684 high and low initial mass fraction respectively). However, it can be noted that, for both values  
 685 of  $\Delta T$ , the relative difference of adsorbed amount between the hot and cold sides increases  
 686 when  $w_i$  decreases and the increase is larger for the smaller heating, (71% for  $\Delta T=50\text{mK}$  and  
 687 66% for  $\Delta T=100\text{mK}$ ). Table 5 shows that the gravity not only lowers the difference between  
 688 the two walls (only 0.27% and 0.36% of difference can be observed for higher and lower  
 689 initial mass fraction for  $\Delta T=100\text{mK}$  and 0.18% and 0.23% for  $\Delta T=50\text{mK}$ ) but also reduces  
 690 the effect of the initial mass fraction: the increase between the largest and the smallest values  
 691 of  $w_i$  is about 31% for  $\Delta T=100\text{mK}$  and 26% for  $\Delta T=50\text{mK}$ . These results then confirm the  
 692 balancing influence of the gravity previously depicted by Fig. 8.

### 693 3.3 Proximity of the LCEP

694



695 Fig. 11. The effect of the proximity to the critical temperature without (a) and with (b) gravity at  $\Delta T=100\text{ mK}$ .

696

697 The results presented in this section were obtained with an initial mass fraction  $w_i$   
 698 corresponding to the solubility of Naphthalene in  $\text{CO}_2$  at temperature  $T_i$  and density  $\rho_i$ . The  
 699 values of  $w_i$  and the initial pressure  $P_{\text{thi}}$  calculated using the Peng-Robinson equation are  
 700 reported in Table 6.

**Table 6**Initial mass fraction  $w_i$  and pressure  $P_{\text{thi}}$ 

$T_i$ (K)	$\rho_i$ (kg.m <sup>-3</sup> )	$w_i$	$P_{\text{thi}}$ (MPa)
307.75	470	$7.6751 \times 10^{-3}$	8.67158154
308.15	470	$4.22 \times 10^{-3}$	8.73970242
309.15	470	$2.11 \times 10^{-3}$	8.90942413
311.15	470	$9.35 \times 10^{-4}$	9.22114740
318.15	470	$7.6751 \times 10^{-4}$	10.3949472

701

702 A Similar behavior to that described in section 3.1 was observed for the mass fraction for  
 703 different initial temperatures  $T_i$  and temperature increases  $\Delta T$ . However, when we move away  
 704 from the critical point, the partial derivatives of the equilibrium constant  $K_2$  with respect to  
 705 temperature and pressure decrease (Figs. 2 and 3) and thus, the mass fraction at the heated and  
 706 isothermal sides are influenced. Moreover, it must be noted that, since the initial mass fraction  
 707  $w_i$  is fixed to the value corresponding to the solubility at  $T_i$  and  $\rho_i$ , the resulting pressure gets  
 708 higher as the initial temperature moves away from the critical one. As a consequence, the  
 709 initial pressure belongs to the high pressure range where the derivative of  $K_2$  with respect to  
 710 pressure is smaller. For all the initial temperatures ( $T_i=307.75$  K to  $T_i=318.15$  K), the piston  
 711 effect generated by the boundary heating induces a fast and strong pressure rise in the entire  
 712 volume before the pressure reaches a steady value. When the system is subjected to the  
 713 Earth's gravity, convection accelerates the pressure increase (Fig. 11(b)). Yet, with or without  
 714 gravity, above the critical point the piston effect becomes less effective and the pressure  
 715 plateau for a given  $\Delta T$  gradually decreases. For  $T_i=318.15$  K, steady value is much smaller

716 showing that far enough from the critical point the previously observed effects on temperature  
717 and mass fraction will be reduced.

718 The effect on temperature and density can actually be observed in Figs. 12 and 13  
719 comparing the instantaneous temperature and density fields near and far from the critical point  
720 (for  $T_i=307.75$  K and  $T_i=318.15$  K). For these two initial temperatures, the characteristic time  
721 scales of the piston effect are  $t_{PE}=0.19$  s and  $t_{PE}=1.26$  s respectively. On the other hand, the  
722 characteristic time of thermal diffusion is  $t_d=115.7$  s for  $T_i=307.75$  K and  $t_d=49.23$  s for  
723  $T_i=318.15$  K. Therefore, far from the critical point, the piston effect decreases in favor of the  
724 thermal diffusion as clearly shown by the temperature field in Fig. 12(b). The boundary layers  
725 become thicker and the thermal plumes are larger (Figs 12(b) and 13(b)). The figures also  
726 show that, near the critical point ( $T_i=307.75$  K), top and bottom plumes reach the opposite  
727 plate while the reduction of the piston effect away from the critical point reduces this  
728 phenomenon.

729 The lessening of the piston effect depicted by Fig. 11 is confirmed by Tables 7 and 8 which  
730 show that the pressure value corresponding to the equilibrium state after  $t=30$ s decrease when  
731 moving away from the critical point for both temperature increases of 50mK and 100mK and  
732 for the two cases with and without gravity effect. It can be also noted that the gravity has a  
733 very little influence on the pressure evolution, since very close values are obtained for the  
734 pressure with and without gravity. Tables 7 and 8 also show how the proximity to the critical  
735 point affects the adsorbed amount at the two reactive walls. In the two cases, with or without  
736 gravity, a change in the variation of the mass fraction as a function of initial temperature can  
737 be observed for the farthest value of  $T_i$ . Indeed, the mass fraction at the heated and isothermal  
738 plates regularly decreases when the system moves away from the critical temperature up to  
739  $T_i=311.15$  K. Then, a strong increase of the mass fraction is observed at  $T_i=318.15$  K. A  
740 similar behavior change at the highest temperature can also be noted on the relative gap of

741 mass fraction between the two sides. For example, for  $\Delta T=100\text{mK}$ , the difference between the  
 742 two reactive walls increases from about 1.4% at  $T_i=307.75\text{ K}$  to 1.6% at  $T_i=311.15\text{ K}$  and  
 743 then decreases to 1% at  $T_i=318.15\text{ K}$ . This abrupt behavior change can be attributed both to  
 744 the reduction of the piston effect (leading to a smaller pressure increase) and to the decrease  
 745 of the derivative of the equilibrium constant  $K_2$  with respect to pressure. These two  
 746 phenomena lead to a decrease of the negative pressure term in the adsorption rate expression  
 747 (Eq. (10)).

748 **Table 7**  
 The effect of the proximity to the critical temperature for  $\Delta T=100\text{ mK}$  and  $\Delta T=50\text{ mK}$  at  $t=30\text{s}$  and without gravity

100 mK				
$T_i\text{ (K)}$	$w-w_i\text{ (x=0)}$	$w-w_i\text{ (x=H)}$	$(w_{x=0}-w_{x=H})/w_{x=0}$	$(P_{th}-P_{th0})/P_{th0}$
307.75	$4.09 \times 10^{-4}$	$4.03 \times 10^{-4}$	$1.3885 \times 10^{-2}$	$3.8347 \times 10^{-11}$
308.15	$3.93 \times 10^{-4}$	$3.88 \times 10^{-4}$	$1.4824 \times 10^{-2}$	$3.8053 \times 10^{-11}$
309.15	$3.75 \times 10^{-4}$	$3.69 \times 10^{-4}$	$1.6061 \times 10^{-2}$	$3.7326 \times 10^{-11}$
311.15	$3.71 \times 10^{-4}$	$3.65 \times 10^{-4}$	$1.6067 \times 10^{-2}$	$3.6028 \times 10^{-11}$
318.15	$4.77 \times 10^{-4}$	$4.72 \times 10^{-4}$	$1.0726 \times 10^{-2}$	$3.1747 \times 10^{-11}$
50 mK				
$T_i\text{ (K)}$	$w-w_i\text{ (x=0)}$	$w-w_i\text{ (x=H)}$	$(w_{x=0}-w_{x=H})/w_{x=0}$	$(P_{th}-P_{th0})/P_{th0}$
307.75	$4.10 \times 10^{-4}$	$4.07 \times 10^{-4}$	$6.9607 \times 10^{-3}$	$1.9197 \times 10^{-11}$
308.15	$3.94 \times 10^{-4}$	$3.91 \times 10^{-4}$	$7.4364 \times 10^{-3}$	$1.9046 \times 10^{-11}$
309.15	$3.75 \times 10^{-4}$	$3.72 \times 10^{-4}$	$8.0633 \times 10^{-3}$	$1.8675 \times 10^{-11}$
311.15	$3.70 \times 10^{-4}$	$3.67 \times 10^{-4}$	$8.0684 \times 10^{-3}$	$1.8016 \times 10^{-11}$
318.15	$4.76 \times 10^{-4}$	$4.73 \times 10^{-4}$	$5.3793 \times 10^{-3}$	$1.5852 \times 10^{-11}$

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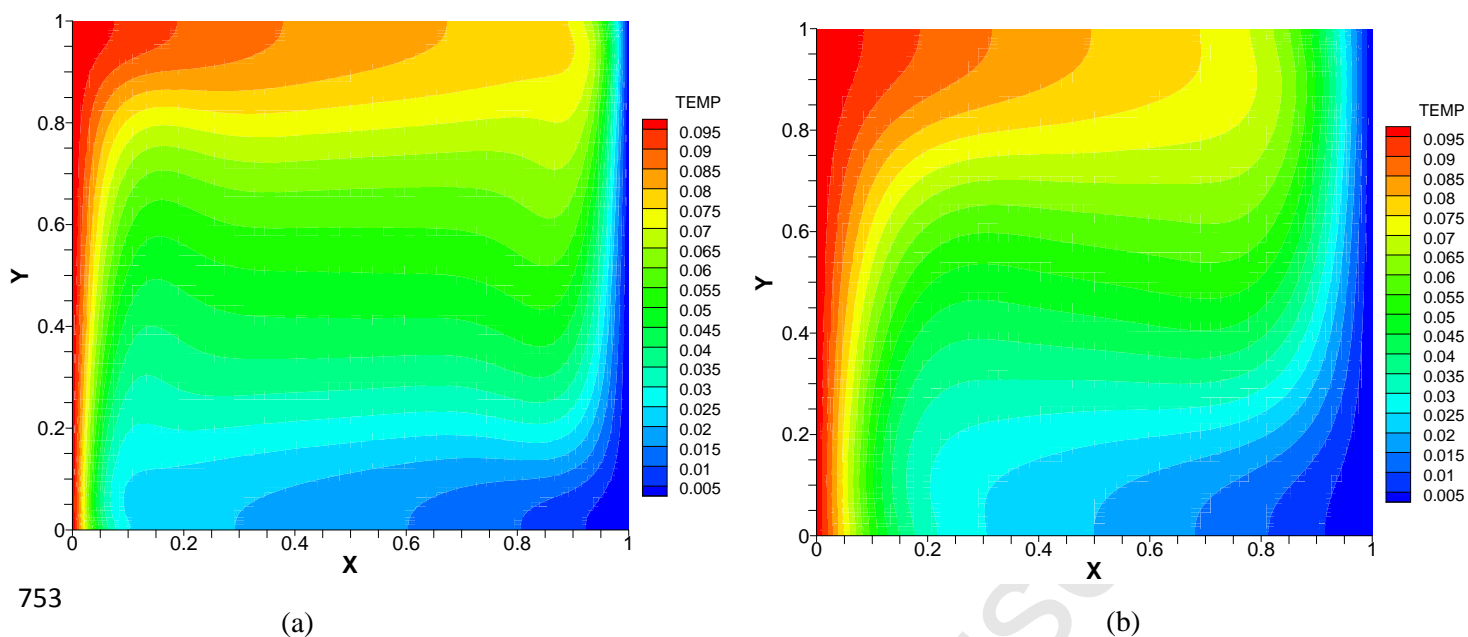
750 **Table 8**  
 The effect of the proximity to the critical temperature  $\Delta T=100\text{ mK}$  and  $\Delta T=50\text{ mK}$  at  $t=30\text{s}$  and with gravity

100 mK				
$T_i\text{ (K)}$	$w-w_i\text{ (x=0)}$	$w-w_i\text{ (x=H)}$	$(w_{x=0}-w_{x=H})/w_{x=0}$	$(P_{th}-P_{th0})/P_{th0}$
307.75	$3.94 \times 10^{-4}$	$3.93 \times 10^{-4}$	$2.6531 \times 10^{-3}$	$3.8326 \times 10^{-11}$
308.15	$3.78 \times 10^{-4}$	$3.77 \times 10^{-4}$	$2.7778 \times 10^{-3}$	$3.8036 \times 10^{-11}$
309.15	$3.58 \times 10^{-4}$	$3.57 \times 10^{-4}$	$2.9648 \times 10^{-3}$	$3.7315 \times 10^{-11}$
311.15	$3.53 \times 10^{-4}$	$3.52 \times 10^{-4}$	$3.0537 \times 10^{-3}$	$3.6024 \times 10^{-11}$
318.15	$4.56 \times 10^{-4}$	$4.55 \times 10^{-4}$	$2.3868 \times 10^{-3}$	$3.1752 \times 10^{-11}$
50 mK				
$T_i\text{ (K)}$	$w-w_i\text{ (x=0)}$	$w-w_i\text{ (x=H)}$	$(w_{x=0}-w_{x=H})/w_{x=0}$	$(P_{th}-P_{th0})/P_{th0}$
307.75	$3.98 \times 10^{-4}$	$3.97 \times 10^{-4}$	$1.7511 \times 10^{-3}$	$1.9199 \times 10^{-11}$
308.15	$3.82 \times 10^{-4}$	$3.81 \times 10^{-4}$	$1.8280 \times 10^{-3}$	$1.9049 \times 10^{-11}$
309.15	$3.62 \times 10^{-4}$	$3.61 \times 10^{-4}$	$1.9335 \times 10^{-3}$	$1.8679 \times 10^{-11}$
311.15	$3.56 \times 10^{-4}$	$3.55 \times 10^{-4}$	$1.9657 \times 10^{-3}$	$1.8020 \times 10^{-11}$
318.15	$4.59 \times 10^{-4}$	$4.58 \times 10^{-4}$	$1.5165 \times 10^{-3}$	$1.5860 \times 10^{-11}$

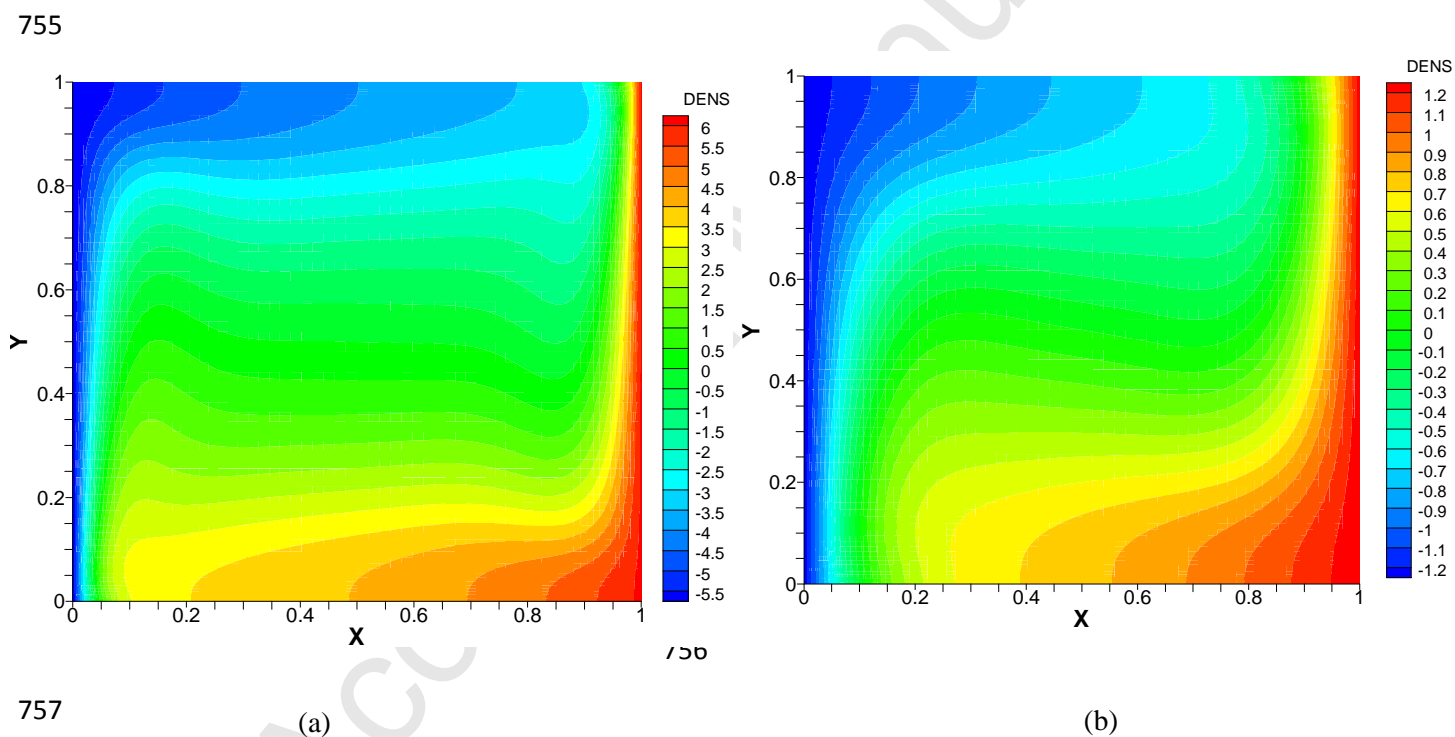
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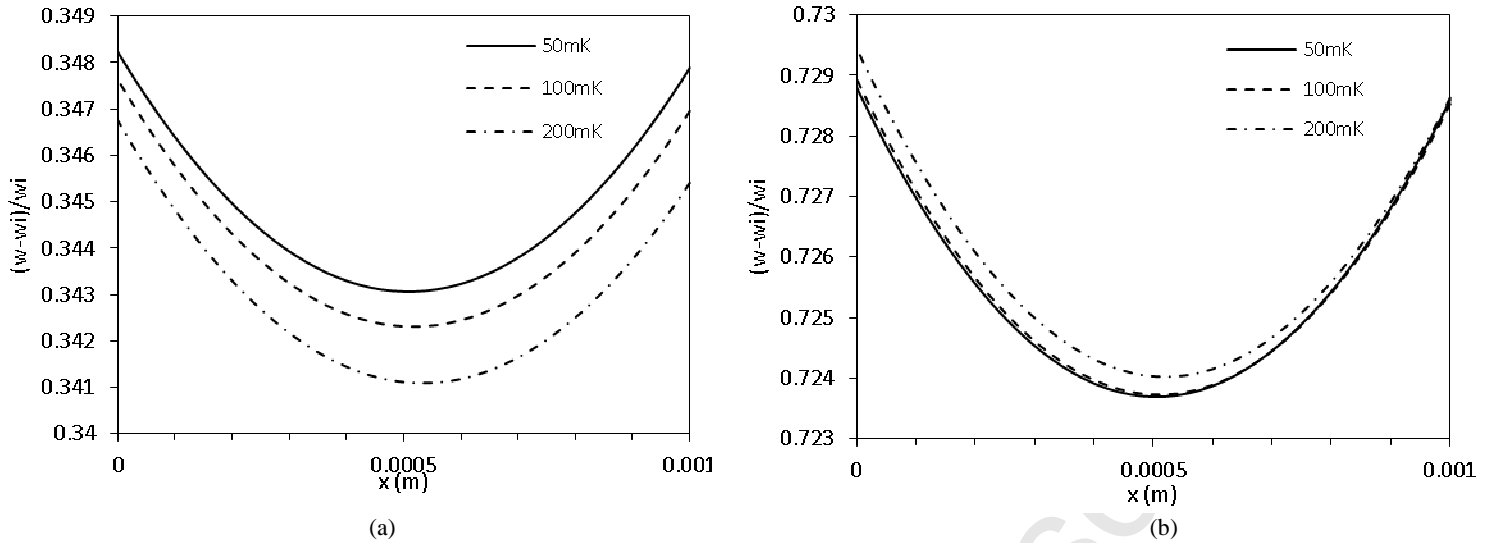


754 Fig. 12. Isosurfaces of temperature with gravity for (a)  $T_i=307.75$  K and (b) 318.15 K for  $\Delta T=100$  mK at  $t=500s$ .



757

758 Fig. 13. Isosurfaces of density with gravity for (a)  $T_i=307.75$  K and (b) 318.15 K for  $\Delta T=100$  mK at  $t=500s$



759 Fig. 14. Evolution of the mass fraction with the heating intensity for (a)  $T_i=311.15$  K at  $t=500$ s and (b)  $T_i=318.15$  K at  $t=500$ s

760 The consequence of this decrease of the pressure term in Eq. (10) at the highest initial  
 761 temperature is depicted by Fig. 14 which shows the mass fraction variation between the two  
 762 plates for three temperature increases ( $\Delta T=50, 100$  and  $200$ mK) and two initial temperatures  
 763 ( $T_i=311.15$  K and  $318.15$  K). Though the tendency for  $T_i=311.15$  K is similar to that shown in  
 764 Fig. 10 for  $T_i=308.15$  K, the behavior of the mass fraction distribution for  $T_i=318.15$  K is  
 765 reversed: a stronger heating of the left side increases the mass fraction. The effect is more  
 766 remarkable at the heated side than at the isothermal one where the profiles of  $\Delta T=50$ mK and  
 767  $100$ mK merge. This behavior change is due to the competition between the derivatives of the  
 768 equilibrium constant  $K_2$  with respect to temperature and pressure. Far away from the critical  
 769 point, the diverging behaviors of the isothermal compressibility and of the volume expansivity  
 770 disappear leading to smaller variations of the derivatives  $(\partial \ln K_2 / \partial T)_p$  and  $(\partial \ln K_2 / \partial P)_T$   
 771 (see Appendix D). Moreover, for a given heating intensity, the pressure increase generated by  
 772 the piston effect is much lower for the highest initial temperature. As a result, the negative  
 773 pressure term in Eq. (10) becomes negligible and only the temperature effect is highlighted  
 774 and causes the enhancement of mass fraction with heating increase.

775

776

777 *3.4 Influence of the Damköhler number*778 **Table 9**779 The effect of the Damköhler number on the mass fraction perturbation for  $T_i=308.15$  K and  $\Delta T=100$  mK

<b>Da</b>	<b><math>10^{-4}</math></b>	<b><math>10^{-5}</math></b>	<b><math>10^{-12}</math></b>
<b>w-w<sub>i</sub> (en x=H)</b>	3.88 x10 <sup>-3</sup>	3.88 x10 <sup>-4</sup>	2.37 x10 <sup>-10</sup>
<b>w-w<sub>i</sub> (en x=0)</b>	3.94 x10 <sup>-3</sup>	3.93 x10 <sup>-4</sup>	2.33 x10 <sup>-10</sup>

780

781 The results presented up to now were obtained for a Damköhler number fixed to  $10^{-5}$ .  
 782 With reference to literature studies, it has been found that the Damköhler number for the  
 783 adsorption of Naphthalene and other solutes such as toluene or benzene can vary from  $10^{-3}$  to  
 784  $10^{-14}$  [40-44]. The Damköhler number was estimated using the available data in each research  
 785 work. For the sake of comparison, three values of the Damköhler number were tested. Similar  
 786 behaviors to those reported in the previous sections were found for temperature, pressure and  
 787 mass fraction distribution. Only the mass fraction variations at the heated left side and the  
 788 isothermal right one are presented in Table 9. The same tendency was found with high mass  
 789 fraction at the heated plate for all the Damköhler numbers. Whereas the Naphthalene mass  
 790 fraction is found to be very much smaller for the smallest Damköhler number, increasing Da  
 791 by a decade results in an increase by a decade of the mass fraction for the larger values of Da.

792 **4. Conclusion**

793

794 In this paper we have presented new results and a detailed analysis of adsorption in a  
 795 model binary dilute mixture, the Naphthalene-CO<sub>2</sub> mixture, very close to the critical point.  
 796 The results of this study revealed that sufficiently close to the mixture critical point, the  
 797 increase of the wall heating remarkably affects the adsorbed amount at the two reactive  
 798 boundaries and the mass fraction inside the cavity. More precisely, the adsorbed amount, as  
 799 the bulk mass fraction, is reduced by increasing the wall heating. This peculiar behavior is  
 800 attributed to the Piston effect, coupled with the divergent character of the derivative of the

801 adsorption equilibrium constant with respect to pressure. Far enough from the critical point,  
802 the Piston effect weakens and a classical behavior is observed. Our results also showed that  
803 this retrograde adsorption is obtained with and without gravity. However, in the presence of  
804 gravity, convection induces large thermal plumes along the hot and cold boundaries and tends  
805 to reduce the temperature gradients near the two walls leading to more symmetric profiles of  
806 the mass fraction. Finally, the effect of the Damköhler number was studied. The same  
807 behavior was found for all the values considered.

808 All the results presented in this paper were obtained for the Naphthalene-CO<sub>2</sub> model  
809 mixture. However, we believe that this study can be relevant for many dilute binary mixtures.  
810 Indeed, the phenomena observed are due to the divergence of the solvent transport properties  
811 (namely the isothermal compressibility and the thermal expansion coefficient) near the critical  
812 point leading to the appearance of the Piston effect and to the divergence of the solute  
813 thermodynamic properties (such as infinite dilution partial molar volume). And these  
814 divergent behaviors occur in a universal way for large classes of systems. Therefore, similar  
815 results should be obtained for all binary dilute mixtures involving a non-volatile solute near  
816 the solvent's critical point and this kind of dilute mixtures is relevant for many adsorption  
817 processes.

818

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820 National d'Etudes Spatiales).

## 821 Appendix A

822

823 The ratio of the isobaric and isochoric specific heats for pure CO<sub>2</sub>,  $\gamma$ , and for mixture,  $\gamma_m$ ,  
824 are calculated from the equation of state as follow:

$$825 \quad \gamma = 1 + \frac{T_i}{C_v \rho_i^2} \left( \frac{\partial P}{\partial T} \right)_\rho^2 \left( \frac{\partial \rho}{\partial P} \right)_T \quad (\text{A.1})$$

826 The derivatives are calculated using the Peng-Robinson equation for pure CO<sub>2</sub>:

$$827 \quad \left( \frac{\partial P}{\partial T} \right)_\rho = \frac{(R/M)\rho}{1-b\rho} - f(\rho) \frac{d a}{d T} \quad (\text{A.2})$$

$$828 \quad \text{with } f(\rho) = \frac{\rho^2}{1+2b\rho-b^2\rho^2} \quad \text{and} \quad \frac{d a}{d T} = -1.487422 \frac{(R/M)\beta}{\rho_c} \sqrt{\frac{T_c}{T}} \left[ 1 + \beta \left( 1 - \sqrt{T/T_c} \right) \right]$$

$$829 \quad \left( \frac{\partial \rho}{\partial P} \right)_T = \frac{(1-b\rho)^2}{(R/M)T - a(T)(1-b\rho)^2} \frac{d f}{d \rho} \quad (\text{A.3})$$

$$830 \quad \text{with } \frac{d f}{d \rho} = \frac{2\rho(1+b\rho)}{(1+2b\rho-b^2\rho^2)^2}$$

831 In Eqs. (A2) and (A3),  $a(T)$  and  $b$  are the coefficients of the Peng-Robinson equation of  
832 state written for mass variable in dimensional form.

$$a_i(T) = 1.487422 \frac{(R/M_i)T_{ci}}{\rho_{ci}} \left[ 1 + \beta_i \left( 1 - \sqrt{T/T_{ci}} \right) \right]^2$$

$$833 \quad b_i = 0.253076 \frac{1}{\rho_{ci}}$$

for  $i = 1, 2$

834 In a similar way, the capacity ratio of the mixture,  $\gamma_m$  is calculated as follow:

$$835 \quad \gamma_m = 1 + \frac{T_i}{C_v \rho_i^2} \left( \frac{\partial P}{\partial T} \right)_{\rho,w}^2 \left( \frac{\partial \rho}{\partial P} \right)_{T,w} \quad (\text{A.4})$$

836 where the derivatives are calculated using the Peng-Robinson equation of state for the  
837 mixture:

$$838 \quad \left( \frac{\partial P}{\partial T} \right)_{\rho,w} = \frac{(R/M_1)\rho \theta(w)}{1-b(w)\rho/\theta(w)} - f(\rho,w) \left( \frac{\partial a}{\partial T} \right)_w \quad (\text{A.5})$$

$$839 \quad \text{with } f(\rho,w) = \frac{\rho^2}{1+2b(w)\rho/\theta(w) - b(w)^2\rho^2/\theta(w)^2}$$

$$840 \quad \text{and } \left( \frac{\partial a}{\partial T} \right)_w = \frac{d a_1}{d T} (1-w)^2 + 2 \frac{d a_{12}}{d T} w (1-w) + \frac{d a_2}{d T} w^2$$

841 in which the derivatives  $da_i/dT$  are calculated as described above for pure component.

$$842 \quad \left( \frac{\partial \rho}{\partial P} \right)_{T,w} = \frac{(1-b(w)\rho/\theta(w))^2}{(R/M_1)T\theta(w) - a(T,w)(1-b(w)\rho/\theta(w))^2 \left( \frac{\partial f}{\partial \rho} \right)_w} \quad (\text{A.6})$$

$$843 \quad \text{with} \quad \left( \frac{\partial f}{\partial \rho} \right)_w = \frac{2\rho(1+b(w)\rho/\theta(w))}{(1+2b(w)\rho/\theta(w) - b(w)^2\rho^2/\theta(w)^2)^2}$$

#### 844 Appendix B

845 The difference of the partial molar internal energies of the two components is expressed by:

$$846 \quad \bar{U}_2(T, \vartheta, y) - \bar{U}_2(T, \vartheta, y) = H_2^0(T_0) - H_1^0(T_0) + Cp_2^0 - Cp_1^0 + \frac{1}{2\sqrt{2b}}COF1 \\ Ln \left( \frac{\vartheta + (1-\sqrt{2})\bar{b}}{\vartheta + (1+\sqrt{2})\bar{b}} \right) + \frac{COF2}{\vartheta^2 + 2\vartheta\bar{b} - \bar{b}^2} \quad (\text{B.1})$$

847 with  $H_2^0(T_0)$  and  $H_1^0(T_0)$  the perfect gas enthalpy of the two components at  $T_0=298.15$  K  
848 and  $y$  the mole fraction of component 2, calculated from the mass fraction by the formula:

$$849 \quad y = \frac{\left( \frac{M_1}{M_2} \right)_w}{\theta(w)}$$

850  $Cp_2^0$  and  $Cp_1^0$  are the isobaric heat capacities of components 2 and 1 respectively as perfect  
851 gas and their difference is expressed by:

$$852 \quad Cp_2^0 - Cp_1^0 = (A_2 - A_1)(T - T_0) + \frac{1}{2}(B_2 - B_1)(T^2 - T_0^2) + \frac{1}{3}(C_2 - C_1)(T^3 - T_0^3) \\ + \frac{1}{4}(D_2 - D_1)(T^4 - T_0^4)$$

853 Finally:

$$854 \quad COF1 = \left\{ -\frac{1}{b} \frac{db}{dy} \left[ \bar{a} - T \left( \frac{\partial \bar{a}}{\partial T} \right)_y \right] + \left( \frac{\partial \bar{a}}{\partial y} \right)_T - T \left( \frac{\partial}{\partial y} \left( \frac{\partial \bar{a}}{\partial T} \right)_y \right)_T \right\}$$

855

$$856 \quad COF2 = \frac{1}{b} \left[ \bar{a} - T \left( \frac{\partial \bar{a}}{\partial T} \right)_y \right] \left[ \bar{b}(\bar{V}_2 - \bar{V}_1) + \vartheta \frac{d\bar{b}}{dy} \right]$$

$$\frac{d\bar{b}}{dy} = -2\bar{b}_1(1-y) + 2\bar{b}_{12}(1-2y) + 2\bar{b}_2y$$

$$857 \quad \left(\frac{\partial \bar{a}}{\partial y}\right)_T = -2\bar{a}_1(1-y) + 2\bar{a}_{12}(1-2y) + 2\bar{a}_2y$$

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial \bar{a}}{\partial T}\right)_y\right)_T = -2\frac{d\bar{a}_1}{dT}(1-y) + 2\frac{d\bar{a}_{12}}{dT}(1-2y) + 2\frac{d\bar{a}_2}{dT}y$$

858 where  $\bar{a}$ ,  $\bar{b}$ ,  $\bar{a}_i$ ,  $\bar{b}_i$ ,  $\bar{a}_{12}$  and  $\bar{b}_{12}$  are the coefficients of the Peng-Robinson equation of state  
859 written in molar variables and they are defined by:

$$860 \quad \bar{a}(T, y) = \bar{a}_1(T)(1-y)^2 + 2\bar{a}_{12}(T)y(1-y) + \bar{a}_2(T)y^2$$

$$\bar{b}(y) = \bar{b}_1(1-y)^2 + 2\bar{b}_{12}y(1-y) + \bar{b}_2y^2$$

861 with

$$\bar{a}_i(T) = 1.487422 \frac{RT_{ci}}{(\rho_{ci}/M_i)} \left[1 + \beta_i \left(1 - \sqrt{T/T_{ci}}\right)\right]^2$$

$$862 \quad \bar{b}_i = 0.253076 \frac{1}{(\rho_{ci}/M_i)}$$

$$\bar{a}_{12}(T) = \sqrt{\bar{a}_1(T)\bar{a}_2(T)}(1-k_{12})$$

$$\bar{b}_{12} = \frac{1}{2}(\bar{b}_1 + \bar{b}_2)(1-l_{12})$$

863 In the expression of COF2, the difference of volumes of Naphthalene and CO<sub>2</sub> is expressed  
864 by:

$$865 \quad \bar{V}_2 - \bar{V}_1 = (1-2y) \frac{\left[ \frac{RT}{(\vartheta - \bar{b})^2} + \frac{2\bar{a}(\vartheta - \bar{b})}{(\vartheta^2 + 2\bar{b}\vartheta - \bar{b}^2)^2} \right] \frac{d\bar{b}}{dy} - \left(\frac{\partial \bar{a}}{\partial y}\right)_T}{\frac{RT}{(\vartheta - \bar{b})^2} - \frac{2\bar{a}(\vartheta + \bar{b})}{(\vartheta^2 + 2\bar{b}\vartheta - \bar{b}^2)^2}} \quad (\text{B.2})$$

866 where  $\vartheta$  is the molar volume of mixture.

### 867 Appendix C

868 In the expression of the velocity divergence ( $\nabla \cdot V$ ) (Eq. (8)), the derivatives are calculated as  
869 follow:

$$870 \quad \left(\frac{\partial F}{\partial T}\right)_{\rho, w} = \frac{\rho \theta(w)}{1 - b^*(w) \rho / \theta(w)} - f^*(\rho, w) \left(\frac{\partial a^*}{\partial T}\right)_w \quad (\text{C.1})$$

$$871 \quad \text{with } f^*(\rho, w) = \frac{\rho^2}{1 + 2b^*(w)\rho/\theta(w) - b^*(w)^2\rho^2/\theta(w)^2}$$

872  $a^*$  and  $b^*$  are those defined for Eq. (5) and are calculated using  $a_i^*$  and  $b_i^*$  in dimensionless  
873 form (see section 2.2).

$$874 \quad \left(\frac{\partial F}{\partial \rho}\right)_{T,w} = - \frac{T\theta(w)}{(1 - b^*(w)\rho/\theta(w))^2} + a^*(T, w) \left(\frac{\partial f}{\partial \rho}\right)_w \quad (\text{C.2})$$

$$875$$

$$876 \quad \left(\frac{\partial F}{\partial w}\right)_{\rho,T} = - \frac{\rho T}{(1 - b^*(w)\rho/\theta(w))^2} \left[ \rho \frac{db^*}{dw} + (1 - 2b^*(w)\rho/\theta(w)) \left(\frac{M_1}{M_2} - 1\right) \right]$$

$$877 \quad + f(\rho, w) \left(\frac{\partial a^*}{\partial w}\right)_T - \frac{2a^*(T, w)f(\rho, w)^2}{\rho\theta(w)} \times (1 - b^*(w)\rho/\theta(w)) \times \left[ \frac{db^*}{dw} - \frac{b^*(w)(M_1/M_2 - 1)}{\theta(w)} \right]$$

$$878 \quad (\text{C.3})$$

## 879 Appendix D

880 In Eqs. (11)-(12), the volume expansivity,  $\alpha$ , the isothermal compressibility,  $\kappa$ , the partial  
881 molar volume,  $\bar{v}_2^m$  and the partial molar residual enthalpy,  $\bar{h}_2^m - h_2^{IG}$ , are given by:

$$882 \quad \alpha = \frac{1}{\bar{v}} \left(\frac{\partial \bar{v}}{\partial T}\right)_p = \frac{\frac{\partial \bar{a}}{\partial T} - \frac{R}{\bar{v}(\bar{v} - \bar{b})}}{2\bar{a}(\bar{v} + \bar{b}) - \frac{RT}{\bar{v}(\bar{v} - \bar{b})}} \quad (\text{D.1})$$

$$883 \quad \kappa = -\frac{1}{\bar{v}} \left(\frac{\partial \bar{v}}{\partial p}\right)_T$$

$$884 \quad = \frac{1}{\left(-2\bar{a}(\bar{v} + \bar{b})\bar{v} / (\bar{v}^2 + 2\bar{v}\bar{b} - \bar{b}^2)^2\right) + RT\bar{v} / (\bar{v} - \bar{b})^2} \quad (\text{D.2})$$

$$885 \quad \bar{v}_2^m = \kappa \bar{v} \left[ \frac{\bar{v} - \bar{b} + B}{(\bar{v} - \bar{b})^2} - \frac{(\bar{v}^2 + 2\bar{v}\bar{b} - \bar{b}^2)A - 2\bar{a}(\bar{v} - \bar{b})B}{(\bar{v}^2 + 2\bar{v}\bar{b} - \bar{b}^2)^2} \right] \quad (\text{D.3})$$

$$A = 2\bar{a}_{12}, B = 2\bar{b}_{12} - \bar{b}_1$$



$$\bar{h}_2^m - h_2^{IG} = P_{th} \bar{v}_2^m - RT + \frac{(T (\partial \bar{a} / \partial T) - \bar{a})(\vartheta B - \bar{b} \bar{v}_2^m)}{\bar{b}(\vartheta^2 + 2\vartheta \bar{b} - \bar{b}^2)} \quad (\text{D.4})$$

$$+ \frac{1}{2\sqrt{2}\bar{b}} \ln \left( \frac{\vartheta + (1 - \sqrt{2})\bar{b}}{\vartheta + (1 + \sqrt{2})\bar{b}} \right) \left[ 2 \frac{d\bar{a}_{12}}{dT} T - A - \frac{1}{\bar{b}} \left( T \frac{\partial \bar{a}}{\partial T} - \bar{a} \right) B \right]$$

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