

THE UNIVERSITY of EDINBURGH

Edinburgh Research Explorer

Ideal adsorbed solution theory solved with direct search minimisation

Citation for published version:

Santori, G, Luberti, M & Ahn, H 2014, 'Ideal adsorbed solution theory solved with direct search minimisation', Computers and Chemical Engineering, vol. 71, pp. 235-240. https://doi.org/10.1016/j.compchemeng.2014.07.027

Digital Object Identifier (DOI):

10.1016/j.compchemeng.2014.07.027

Link:

Link to publication record in Edinburgh Research Explorer

Document Version: Early version, also known as pre-print

Published In: Computers and Chemical Engineering

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.



1 Published in: Computers and Chemical Engneering (2014) 71:235

3 Ideal adsorbed solution theory solved with direct search minimisation

4 Giulio Santori^{a*}, Mauro Luberti^a, Hyungwoong Ahn^a 5

6 *corresponding author: Dr. Giulio Santori, <u>g.santori@ed.ac.uk</u>, tel: +4401316519043, fax: +4401316506551

^a The University of Edinburgh, School of Engineering, Institute for Materials and Processes, Sanderson
 Building, The King's Buildings, Mayfield Road, EH9 3JL, Edinburgh, Scotland, UK

10 Abstract

2

9

11 The ideal adsorbed solution theory (IAST) is the most widespread theory for multicomponent adsorption interpretation. It postulates the existence of an adsorbed phase which behaves as a Raoult ideal solution. The 12 13 theory results in a system of nonlinear algebraic equations which are solved to know the composition of the 14 adsorbed mixture at equilibrium. In this paper an investigation on an alternative method for the IAST 15 equations solution is proposed which is based on the minimisation of an objective function representing the 16 iso-spreading pressure condition. This approach to the solution of the IAST equations reduces in some cases 17 the computational effort and mitigate the issues of the currently adopted approaches (inversion of functions 18 and initial guess). For binary systems, direct search minimisation approach is faster than the classic IAST 19 equations solution approach up to 19.0 (Dual Langmuir isotherm) and 22.7 times (Toth isotherm). In ternary 20 systems, this difference decreases to 10.4 (O'Brien and Myers isotherm). Compared to FASTIAS approach, 21 direct search minimisation is up to 4.2 times slower in ternary systems 22

Keywords: ideal adsorbed solution theory; adsorption equilibria; adsorption thermodynamics; solution
 algorithm;

26 Introduction

27 Adsorption materials are increasingly attracting interest because they permit almost selectively the separation

of targeted compounds, often reducing energy consumption compared with traditional separation techniques. Thanks to their ability of selectively capturing single compounds from complex multicomponent mixtures (Minceva and Rodrigues, 2005) and the suitability of triggering the heat using a concentration swing (Yu et al., 2013), new adsorptive technologies are currently commercialized (Dawoud et al., 2012; Ramaswamy et al. 2013; Santori et al. 2013) or at R&D stage (Liu et al. 2011; Santori et al. 2014). In all cases, adsorption

thermodynamics plays a fundamental role in the system design.

In the majority of practical cases, the separation of a selected compound from a multicomponent mixtures is required and consequently multicomponent adsorption thermodynamic theories are regarded with a particular interest. Presently, the most widespread multicomponent adsorption theory is the ideal adsorbed solution theory (IAST) (Myers and Prausnitz, 1965). The reason of its success consists in the possibility to predict multicomponent adsorption equilibrium from single component adsorption isotherms.

In the IAST, an ideal gas phase and an adsorbed phase are in equilibrium. The adsorbed phase is considered an ideal solution following the Raoult's law. In several cases this is an acceptable assumption or can offer a useful initial result for a more refined interpretation (Cessford et al., 2012; Yun et al. 2002).

Multicomponent gaseous mixtures are considered in this paper, but the IAST can be applied similarly to
 liquid mixtures. The mathematical formulation of the problem consists in the solution of the following
 algebraic-integral equations:

45
$$P_{tot} y_i = P_i^0 x_i$$
 $i = 1, 2, ..., NC$ (1)

$$46 \qquad \sum_{i}^{NC} x_i = 1 \tag{2}$$

47
$$n_i = f_i(P_i^0, T)$$
 $i = 1, 2, ..., NC$ (3)

48
$$\frac{\pi_i A}{RT} = \int_0^{P_i^0} n_i d\left(\ln\left(P_i^0\right)\right) \quad i = 1, 2,NC$$
 (4)

49 where P_{tot} [kPa] is the total pressure of the gaseous mixture flowing on the adsorbent surface, y_i is the molar 50 fraction of the component i of the non-adsorbed mixture, x_i is the molar fraction of the component i in the adsorbed phase, NC is the total number of components, q_i^0 [mol/kg] is the specific adsorbed amount of the component i at equilibrium, P_i^0 [kPa] is the surface pressure of the component i, T [K] is the equilibrium temperature, π_i [kPa m] is the specific spreading pressure of the component i, A [m²/kg] is the specific surface area covered by the adsorbed mixture. For the solution of the eqns (1-4) the condition of thermodynamic equilibrium must be considered. The system is at equilibrium when the reduced spreading pressure ($\pi_i A/(RT)$) has the same value for each component. So the equilibrium condition is represented by the following iso-spreading pressure condition:

58
$$\frac{\pi_i A}{RT} = constant$$

63

64

65

(5)

- 59 The problem can be solved giving P_{tot} , y_i and the adsorption isotherms $f_i(P_i^0, T)$ with parameters computed by 60 single component adsorption equilibrium data. The unknowns of the system are x_i , π_i , P_i^0 and q_i^0 .
- An extensive review of the different approaches proposed for the solution of the problem above has been presented in [8], highlighting the following main issues of the described strategies:
 - 1) An inversion of the spreading pressure function is needed and only in few cases such inversion is analytical;
 - 2) An initial guess should be provided in order to find a solution.
- These issues are overcome following the method proposed in (Rubiera Landa et al., 2013). The only claimed limit of the procedure in (Rubiera Landa et al., 2013) consists in the computational load, which is comparable with the classical solution approaches (Do, 1998; Myers and Valenzuela 1986; Valenzuela and Myers 1989), making the method (FASTIAS) presented in (O'Brien and Myers, 1985) and successively refined in (O'Brien and Myers, 1988) still the quickest numerical method for the solution of IAST equations.
- In some cases explicit solution of the IAST equations can be formulated for binary systems. In (Le Van and Vermeulen, 1981) a method is presented for deriving explicit binary isotherms from simple single isotherm
- 73 (Langmuir and Freundlich) in form of series expansions.

i = 1, 2,*NC*

- 74 Assuming single isotherms fitted considering equal saturation capacities, binary adsorption isotherms have
- 75 been derived for Brunauer-Emmet-Teller (BET)-Langmuir, BET-BET, Langmuir-Langmuir, anti-Langmuir-
- 76 anti-Langmuir and quadratic-quadratic (Gritti and Guiochon, 2003a; Gritti and Guiochon, 2003b; Taradafer
- and Mazzotti, 2012). In addition, explicit isotherms have been derived also without the previous assumption
- 78 (Frey and Rodrigues, 1994; Ilic et al., 2010).
- 79 Integration of IAST equations with adsorptive bed dynamics equations is an additional issue. There are three 80 possibilities to couple IAST equations in adsorptive bed dynamics. Firstly, the spreading pressure can be 81 treated as a dependent variable of time and space and added to the differential system describing bed 82 dynamics (Mota and Rodrigo, 2000). This results in a strongly non-linear system of differential-algebraic 83 equations which is difficult to solve, computationally expensive and time consuming. For this reason the 84 most common methodology consists on the computation of the adsorption equilibrium separately to bed 85 dynamics in each time step. Also the approach is time consuming because it obliges to exit and enter continuously the IAST equations solver with new conditions. The third strategy is the use of the B-Spline 86 87 approach (Santos et al. 2011). It allows to pre-compute the equilibrium states and this can mitigate the issues 88 for the binary system case, but for more than two components the B-Spline approach results in additional 89 multidimensional fitting issues, losing its advantages.
- 90 This paper presents an investigation on the solution of the IAST equations using analytical expression of the 91 spreading pressures for the adsorbed components and a direct search minimisation approach for the iso-92 spreading pressure condition of eq. (5). The method is tested on a number of adsorption isotherms and on
- 93 binary and ternary systems.
- 94 The immediate way to implement direct search methods for adsorptive bed dynamics is the use of a separate 95 solver. The proposed investigation is not a contribution to the solution of these issues, which are still open.
- 96 On the basis of the reported results, direct search methods are expected to reduce the time spent for
- 97 equilibrium calculations in comparison with the traditional IAST method and consequently the overall bed
- 98 dynamics simulation times.99

100 2. Solution of the IAST equations through direct search minimisation methods

- 101 The IAST equation system can be reduced through successive substitution of variables to a smaller system of
- 102 iso-spreading pressure conditions. Table 1 shows the analytically integrated form of the spreading pressure
- for some adsorption isotherms. The spreading pressure are expressed in terms of molar fractions x_i through a
- 104 preliminary change of variable from \hat{P}_i^0 to x_i substituting the eq. (1) into eq. (4).

For sake of clarity, taking the Dual Langmuir isotherm, spreading pressure in terms of molar fraction isobtained by the following change of variable:

107
$$d\ln\left(\frac{P_{tot}y_i}{x_i}\right) = -\frac{1}{x_i}dx_i$$
(6)

108 Accordingly, the spreading pressure integral becomes:

$$\frac{\pi_{i}A}{RT} = \int -\left(\frac{q_{s1,i}b_{1,i}\left(\frac{P_{tot}y_{i}}{x_{i}}\right)}{x_{i} + x_{i}b_{1,i}\left(\frac{P_{tot}y_{i}}{x_{i}}\right)} + \frac{q_{s2,i}b_{2,i}\left(\frac{P_{tot}y_{i}}{x_{i}}\right)}{x_{i} + x_{i}b_{2,i}\left(\frac{P_{tot}y_{i}}{x_{i}}\right)}\right) dx_{i} = \\
= \int \left(-\frac{q_{s1,i} + q_{s2,i}}{x_{i}} + \frac{q_{s1,i}}{x_{i} + P_{tot}y_{i}b_{1,i}} + \frac{q_{s2,i}}{x_{i} + P_{tot}y_{i}b_{2,i}}\right) dx_{i} \qquad (7)$$

110

111 The integration of eq. (7) results in the expression listed in Table 1 for Dual Langmuir isotherm. An

additional result of this paper is represented by the analytical expression for spreading pressure of the Unilan

113 isotherm, which was deemed not computable (Do, 1998).

114

Table1: List of the analytical expressions of the spreading pressure for different adsorption isotherms

$$\frac{1}{1} \frac{b_{i,j}P}{b_{i,j}P} + q_{s2,j} \frac{b_{j,j}P}{1 + b_{i,j}P} + q_{s2,j} \frac{b_{j,j}P}{1 + b_{j,j}P} = -(q_{s1,j} + q_{s2,j}) \ln(x_i) + q_{s1,j} \ln(b_{l,j} y_i P_{tot} + x_i) + q_{s2,j} \ln(b_{2,j} y_i P_{tot} + x_i)$$

$$Toth \qquad q_i = q_{s,i} \frac{b_i P}{\left[1 + (b_i P)^i\right]^{1/i}} \qquad \qquad \frac{\pi_i A}{RT} = \frac{y_i P_{tot} b_i q_{s,j}}{x_i} {}_2 F_1\left(\frac{1}{t_i}; \frac{1}{t_i}; \left(1 + \frac{1}{t_i}\right); -\left(\frac{y_i P_{tot} b_j}{x_i}\right)^{t_j}\right)$$

$$where {}_2 F_1 is the Gauss hypergeometric function {}_2 F_1 is th$$

115

116 Using the spreading pressures listed in Table 1, the iso-spreading pressure condition can be set as a 117 minimisation problem. Using eq.(2), the objective function of the minimisation problem becomes for the 118 binary case:

119
$$f_{binary}(x_1) = \left| \frac{\pi_1(x_1)A}{RT} - \frac{\pi_2(x_1)A}{RT} \right|$$
 (8)

120 and for the ternary case:

121
$$f_{ternary}(x_1, x_2) = \left(\left| \frac{\pi_1(x_1)A}{RT} - \frac{\pi_2(x_2)A}{RT} \right| + \left| \frac{\pi_1(x_1)A}{RT} - \frac{\pi_3(x_1, x_2)A}{RT} \right| \right)$$
(9)

122 Considering the isotherms in Table 1, the resulting objective functions present only a minimum whose 123 coordinates correspond to the equilibrium condition. This feature makes the minimisation problem 124 particularly easy to solve even by direct search local minimisation algorithms.

The advantage in the change of the independent variable of the spreading pressure (from P_i^0 to x_i) consists in the chance of constraining the molar fractions x_i in their feasible interval (0,1). So for the more general ternary case, the optimization problem is stated as:

128

129 130

Minimize the objective function $f_{ternary}(x_1, x_2)$ subject to constraints $0 < x_1 < 1 - x_2$ and $0 < x_2 < 1 - x_1$

131 From the solutions of this problem the number of total adsorbed moles is calculated with:

132
$$\frac{1}{q_{tot}} = \sum_{i=1}^{3} \left(\frac{x_i}{n_i \left(P_i^0 \right)} \right)$$
 (10)

All the computations presented in this paper were performed with Nelder-Mead minimisation algorithm 133 (Nelder and Mead, 1965) operated with a working precision of 10⁻⁸, which resulted in final residuals ranging 134 between 10⁻⁷ and 10⁻⁹. The residuals are far beneath the accuracy of the experimental values and coherent 135 with the order of magnitude considered by other authors (O'Brien and Myers, 1985; O'Brien and Myers, 136 137 1998; Rubiera Landa et al, 2013). The comparisons presented in next sections aim to validate quantitatively 138 the proposed approach.

139

140 **3.** Application to single equilibrium conditions

141 The minimisation approach is applied only to few case studies due to the limited number of experimental 142 data for binary and ternary systems of acceptable quality. The parameters used for the single component 143 adsorption isotherms are reported in Table 2 and Table 3.

144

Table 2: Parameters of the single component adsorption isotherms for the binary system Methane(1)/Ethane(2) on activated carbon BPL at 301.4										
K (He et al., 2004)										
	Pressure Range		Dual La	angmuir		Toth				
	[kPa]	q_{s1}	\mathbf{b}_1	q_{s2}	b_2	q_s	b	t		
Methane	0-3220.7	0.894481	8.368828 10 ⁻³	4.921966	6.950138 10 ⁻⁴	7.912945	1.520872 10 ⁻³	0.5620853		
Ethane	0-791.98	4.698140	5.876234 10 ⁻³	1.173161	1.683690 10 ⁻¹	9.382593	4.406557 10 ⁻²	0.3808238		

145

Table 3: Parameters of the single component adsorption isotherms for the ternary system Methane(1)/Nitrogen(2)/Carbon Dioxide(3) on activated carbon Norit R1 at 298 K (Dreisbach et al., 1999) and ternary system Methane(1)/Ethane(2)/Ethylene(3) on activated carbon BPL at 301.4 K (O'Brien and Myers 1985)

	Pressure Range		Unilan	O'Brien-Myers			
	[kPa]	q_s	b	s	q_s	b	σ
Adsorbent: AC Norit R1							
Methane	0-5753	9.280873	7.544924 10 ⁻⁴	2.000000			
Nitrogen	0-5958		3.356512 10 ⁻⁴	1.707017			
Carbon Dioxide	rbon Dioxide 0-6000		1.560106 10 ⁻³	1.621091			
Adsorbent: AC BPL							
Methane	131.7-339.2				5.721	9.0023 10 ⁻⁴	0.8231
Ethane	131.7-339.2				5.639	$1.0186 \ 10^{-2}$	1.1927
Ethylene	131.7-339.2				5.900	6.4428 10 ⁻³	1.1737

146

147 **3.1 Binary systems**

148 The adsorption of the binary system Methane(1)/Ethane(2) in BPL activated carbon is analysed, regressing

149 the data with Dual Langmuir (DL) and Toth isotherms adopting parameters of Table 2. Table 4 shows a

150 comparison of the experimental data with the equilibria predicted by IAST using same isotherms (DL-DL or 151 Toth-Toth) for both the components.

152

Table 4: Methane(1)/Ethane(2) adsorption in BPL Activated Carbon at 301.4 K (He et al., 2004). Experimental data and results from the calculation of IAST equations using DL and Toth isotherms

							Calculation Times [s]				
		$q_1(x_1)$			q% (x%)	DL		Toth		
Pressure [kPa]	y1	exp. data	DL	Toth	DL	Toth	min IAST	trad. IAST	min IAST	trad. IAST	
52.02	0.716	0.158 (0.119)	0.166 (0.127)	0.165 (0.124)	-5.3 (-6.6)	-4.0 (-4.5)	0.032	0.438	0.047	0.566	
197.05	0.716	0.347 (0.139)	0.361 (0.149)	0.358 (0.144)	-4.1 (-6.9)	-3.0 (-3.5)	0.031	0.566	0.031	0.703	
682.61	0.716	0.673 (0.174)	0.649 (0.166)	0.624 (0.162)	3.6 (4.6)	7.8 (6.9)	0.031	0.660	0.062	0.701	
1397.62	0.716	0.853 (0.187)	0.801 (0.172)	0.799 (0.172)	6.1 (8.2)	6.7 (8.4)	0.031	0.548	0.047	0.665	
52.3	0.906	0.262 (0.317)	0.294 (0.338)	0.278 (0.328)	-12.4 (-6.8)	-5.7 (-3.7)	0.032	0.336	0.031	0.451	
683.68	0.906	1.319 (0.423)	1.289 (0.415)	1.258 (0.405)	2.3 (3.3)	4.9 (5.7)	0.032	0.609	0.047	0.699	
52.18	0.97	0.331 (0.531)	0.382 (0.623)	0.357 (0.604)	-15.4 (-17.3)	-7.2 (-13.8)	0.047	0.293	0.046	0.371	
195.85	0.97	0.850 (0.608)	0.909 (0.650)	0.905 (0.644)	-7.0 (-7.0)	-6.1 (-6.0)	0.032	0.375	0.031	0.478	
684.88	0.97	1.820 (0.692)	1.826 (0.691)	1.814 (0.683)	-0.3 (0.0)	0.3 (1.3)	0.047	0.461	0.047	0.574	
1396.82	0.97	2.539 (0.717)	2.511 (0.711)	2.467 (0.702)	1.1 (0.9)	2.9 (2.1)	0.032	0.540	0.062	0.575	
Materia											

Flot(acp⁺q_{cab})/q_{exp}; x%=100(x_{exp}-x_{cab})/x_{exp} min IAST= minimized IAST equations trad. IAST= IAST equations solved with the traditional approach (Do, 1998; Myers and Valenzuela 1986; Valenzuela and Myers, 1989)

153

154 These results are presented in order to evaluate the advantage of the proposed solution method compared 155 with the conventional approach of Myers (Myers and Valenzuela, 1986; Valenzuela and Myers, 1989) and

156 Do (Do, 1998) for the IAST equations solution. The main advantages of such new procedure are simplicity 157 and calculation times lower than the traditional approach of about one order of magnitude which make the 158 minimisation approach applied to binary systems adsorption comparable with the FASTIAS presented by

159 O'Brien and Myers in (O'Brien and Myers, 1988).

Approaching the solution of eq.(8) as a minimisation problem has the following advantages: (i) it mitigates the necessity of an initial guess to apply the Newton method, substituting it with a set of initial points. This

means that the solution is not affected by the closure of the initial condition to the final solution; (ii) the

163 inversion of the spreading pressure function; (iii) the solution of an algebraic nonlinear system of equations.

164 The problem is visualized in Figure 1 where the spreading pressure curves are plotted as a function of the

- 165 molar fraction of methane.
- 166



167

Figure 1: Reduced spreading pressure curves and reduced spreading pressure difference curve obtained using
 DL isotherms. The curves are calculated from the data of (He et al., 2004) for the binary system
 methane(1)/ethane(2) on BPL activated carbon at 301.4K, 683.68kPa and molar fraction y₁=0.906.

The equilibrium is represented by the value of the molar fraction where the spreading pressure difference curve has zero value. Because of high nonlinearity of the spreading pressure curves, it is more convenient to adopt a minimisation algorithm instead of trying to solve numerically the equation. Moreover, adopting eq. (8) instead of the difference curve the objective function assumes only one minimum. So even local optimization algorithms are suitable to find the correct solution.

177178 **3.2 Ternary systems**

Unilan and O'Brien and Myers (OM) isotherms are used for the calculation of adsorption equilibrium in ternary systems. The system Methane(1)/Ethane(2)/Ethylene(3) on activated carbon BPL (O'Brien and Myers, 1985) was studied with the OM isotherm and the system Methane(1)/Nitrogen(2)/Carbon Dioxide(3) on activated carbon Norit R1 (Dreisbach et al., 1999) with the Unilan isotherm. This first system enables a direct comparison between the FASTIAS solution method reported in (O'Brien and Myers, 1988) and the approach proposed here, in terms of calculation times. Table 5 collects the results of the calculations.

- 185
- 186
- 187 188
- 189
- 190
- 191
- 192

Table 5: Methane(1)/Ethane(2)/Ethylene(3) adsorption on BPL Activated Carbon at 301.4 K (O'Brien and Myers, 1985) and Methane(1)/Nitrogen(2)/Carbon Dioxide(3) on activated carbon Norit R1 at 298 K (Dreisbach et al., 1999). Experimental data and results from the calculation of IAST equations using Unilan and O'Brien and Myers isotherms.

Pressure [kPa]	y ₁	y ₂	$q_{1}(x_{1})$	$q_{2}(x_{2})$	$q_{1}(x_{1})$	$q_{2}(x_{2})$	Errors		Calculation times [s]		
	experimental data calculated values		ed values	$q_1\% (x_1\%)$	$q_2\% (x_2\%)$	min IAS	trad IAS	FASTIAS			
Methane(1)/Nitrogen(2)/Carbon Dioxide(3)	Vitrogen(2)/Carbon Dioxide(3) Unilan										
113	0.445	0.504	0.511 (0.553)	0.199 (0.215)	0.566 (0.612)	0.191 (0.181)	-10.8 (-10.7)	15.8 (15.8)	0.203	0.150	
433	0.535	0.125	1.469 (0.415)	0.060 (0.017)	1.200 (0.333)	0.071 (0.020)	18.3 (19.7)	-18.4 (-16.3)	0.249	0.343	
467	0.349	0.403	0.942 (0.298)	0.228 (0.072)	0.930 (0.291)	0.274 (0.086)	1.2 (2.3)	-20.3 (-18.9)	0.218	0.396	
1054	0.538	0.115	1.994 (0.361)	0.077 (0.014)	1.760 (0.310)	0.091 (0.016)	11.8 (14.2)	-17.5 (-14.2)	0.234	0.604	
Methane(1)/Ethane(2)/Ethylene(3)					O'Brien a	and Myers					
339.2	0.624	0.174	0.493 (0.156)	0.231 (0.469)	0.411 (0.134)	1.491 (0.484)	16.6 (14.4)	-0.6 (3.3)	0.156	0.613	0.037
124.1	0.2	0.192	0.049 (0.019)	0.014 (0.278)	0.064 (0.024)	0.821 (0.312)	-29.4 (27.0)	-14.3 (12.2)	0.156	0.422	0.043
131.7	0.23	0.52	0.059 (0.021)	0.044 (0.747)	0.068 (0.025)	2.055 (0.736)	-16.4 (16.8)	1.7 (1.4)	0.156	1.619	0.042
Notes:											

 $\begin{array}{l} q\% = 100(q_{exp}\text{-}q_{calc})/q_{exp} \\ x\% = 100(x_{exp}\text{-}x_{calc})/x_{exp} \end{array}$

193

193

Similarly to the binary equilibrium, the ternary equilibrium can be described by the objective function of eq. 194 195 (7). This objective function is a surface which, after the substitution of eq. (2), is a function of two 196 independent molar fractions (x_1, x_2) . Figure 2 shows an illustrative example of objective function surface. It 197 is convex and it has only a minimum whose coordinates are the equilibrium compositions. Because of the 198 absence of additional local minima, also in this case the objective function can be easily explored by 199 whatever local or global minimisation algorithm. A different representation of the problem is reported also in 200 Fig. 3, where the reduced spreading pressure difference curves are shown. The intersection point of the two 201 curves identifies the equilibrium compositions.



202

Figure 2: Objective function of eq. (7) (left) and reduced spreading pressure difference curves (π_1 - π_2) and (π_2 - π_3) (right) calculated using the Unilan isotherm for the ternary system Methane(1)/Nitrogen(2)/Carbon Dioxide(3) on activated carbon Norit R1 (Dreisbach et al. 1999) at 467kPa, 298K and compositions of the gaseous mixture (0.349; 0.403; 0.248).

200

The advantage of the presented procedure over the traditional one consists also in shorter computational times even if the FASTIAS method of solution remains the fastest solution. The computational speed assumes a fundamental importance when the IAST equations are applied to the dynamic modelling of adsorbent beds where the equilibrium calculations must be repeated for several time steps (Rubiera Landa et al. 2013; Santos et al. 2011).

As reported in Table 4 and Table 5, the calculation times are lower than the times required by the traditional solution approach, comparable to FASTIAS approach for binary mixtures adsorption and higher up to 4.2 times than the FASTIAS approach for ternary mixtures adsorption. However these times could be further reduced selecting more effective minimisation algorithms tailored on this specific problem.

217218 4. Conclusions

An alternative procedure for the solution of the IAST equations was proposed. The procedure is based on the minimisation of the iso-spreading pressure condition and leads to values close to the experimental equilibrium concentrations without any involvement of spreading pressure inversion and initial guess, which are the typical requirements of the presently adopted solution approaches.

- 223 The procedure was tested on binary and ternary systems adsorption using Dual Langmuir, Toth, Unilan and 224 O'Brien and Myers isotherms. A comparison with the most used existing solution procedures was presented
- in terms of calculation times which are fundamental in theoretical studies of adsorbent bed dynamics. 225
- In terms of calculation times, the proposed solution procedure is quicker than the traditional solution method 226 227 (Do, 1998; Myers and Valenzuela 1986; Valenzuela and Myers, 1989). Calculation times become comparable to the FASTIAS method (O'Brien and Myers, 1988) for binary systems adsorption. 228

229 230 **5** Acknowledgements

231 This work has received funding from the European Union's Seventh Programme for research, technological development and demonstration, under Marie Curie Career Integration Grant Agreement No PCIG14-GA-232 233 2013-630863 (Atmospheric Carbon CApture).

234 235 6. Nomenclature

- 236 Ρ Pressure [kPa]
- 237 Total pressure of the non-adsorbed mixture [kPa]
- $\begin{array}{c} P_{tot} \\ P_i^{\ 0} \end{array}$ 238 Surface pressure of the component i [kPa]
- 239 Molar fraction of the component i in the non-adsorbed mixture y_i
- 240 Molar fraction of the component i in the adsorbed mixture
- $\begin{array}{c}x_i\\q_i^0\\\pi_i^0\end{array}$ Specific amount adsorbed of component i in the adsorbent at equilibrium [mol/kg] 241
- 242 Spreading pressure of the component i at equilibrium [kPa m]
- 243 Specific surface area covered by the adsorbed mixture $[m^2/kg]$ А
- 244 Universal gas constant [kJ/(mol K)] R
- 245 Equilibrium temperature [K] Т
- 246 NC Number of components participating in the adsorption
- 247 Specific amount adsorbed of component i in the adsorbent [mol/kg] qi
- 248 Specific amount adsorbed of mixture [mol/kg] q_{tot}
- 249 Objective function in the case of binary mixture f_{binary}
- 250 Objective function in the case of ternary mixture f_{ternary} 251

252 7. References 253

254 Cessford NF, Seaton NA, Düren T. Evaluation of Ideal Adsorbed Solution Theory as a Tool for the Design 255 of Metal-Organic Framework Materials. Ind Eng Chem Res 2012;51:4911-4921. 256

- 257 Dawoud B, Hoefle P, Bornmann A, Chmielewski S, Marburger C. Vacuum sorption apparatus. patent 258 publication number: WO2012041265, 2012-04-05. 259
- 260 Do DD. Adsorption Analysis: Equilibria and Kinetics. London: Imperial College Press; 1998. 261
- 262 Dreisbach F, Staudt R, Keller JU. High Pressure Adsorption Data of Methane, Nitrogen, Carbon Dioxide and their Binary and Ternary Mixtures on Activated Carbon. Adsorption 1999;5:215-227. 263 264
- 265 Frey DD, Rodrigues AE. Explicit calculation of multicomponent equilibria for ideal adsorbed solutions. 266 AIChE J 1994;40:182-186. 267
- 268 Gritti F, Guiochon G. Band splitting in overloaded isocratic elution chromatography: II. New competitive adsorption isotherms. J Chromatogr A 2003;1008:23-41. 269 270
- 271 Gritti F, Guiochon G. New thermodynamically consistent competitive adsorption isotherm in RPLC. J Colloid Interface Sci 2003;264:43-59. 272 273
- 274 He Y, Yun JH, Seaton NA. Adsorption equilibrium of binary methane/ethane mixtures in BPL activated 275 carbon: isotherms and calorimetric heats of adsorption. Langmuir 2004;20:668-6678. 276
- 277 Ilic M, Flockerzi D, Seidel-Morgenstern A. A thermodinamically consistent explicit competitive adsorption 278 isotherm model based on second-order single component behaviour. J Chromatogr A 2010;1217:2132-2137.

279

282

285

288

291

293

296

298

307

316

319

322

325

329

- LeVan MD, Vermeulen T. Binary Langmuir-like and Freundlich isotherms for ideal adsorbed solutions. J.
 Phys Chem 1981;85:3247-3250.
- Liu Z, Grande CA, Li P, Yu J, Rodrigues AE. Multi-bed Vacuum Pressure Swing Adsorption for carbon
 dioxide capture from flue gas. Sep Purif Technol 2011;81:307-317.
- 286 Minceva M, Rodrigues AE. Two-level Optimization of an Existing SMB for p-Xylene Separation. Comput
 287 Chem Eng 2005;29:2215-.
- Mota JPB, Rodrigo AJS. Calculations of Multicomponent Adsorption-Column Dynamics Combining the
 Potential and Ideal Adsorbed Solution Theories. Ind Eng Chem Res 2000;39:2459-2467
- 292 Myers AL, Prausnitz JM. Thermodynamics of mixed-gas adsorption. AIChE J 1965;11:121-127.
- Myers AL, Valenzuela D. Computer Algorithm for Calculating Adsorption Equilibria of Gas Mixtures. J
 Chem Eng Jpn 1986;19:392-396.
- 297 Nelder JA, Mead R. A Simplex Method for Function Minimization. Comput J 1965;7:308-313.
- O'Brien JA, Myers AL. Rapid Calculations of Multicomponent Adsorption Equilibria from Pure Isotherm
 Data. Ind Eng Chem Process Des Dev 1985;24:1188-1191.
- O'Brien JA, Myers AL. A comprehensive technique for equilibrium calculations in adsorbed mixtures: the
 generalized FastIAS method. Ind Eng Chem Res 1988;27:2085-2092.
- Ramaswamy S, Huang HJ, Ramarao BV. Separation and Purification Technologies in Biorefineries. 1st ed.
 The Atrium, Southern Gate, Chichester: John Wiley & Sons; 2013.
- Rubiera Landa HO, Flockerzi D, Seidel-Morgenstern A. A method for efficiently solving the IAST equations
 with an application to adsorber dynamics. AIChE J 2013;59:1263-1277.
- Santori G, Frazzica A, Freni A, Galieni M, Bonaccorsi L, Polonara F, Restuccia G. Optimization and testing
 on an adsorption dishwasher. Energy 2013;50:170-176.
- Santori G, Santamaria S, Sapienza A, Brandani S, Freni A. A stand-alone solar adsorption refrigerator for
 humanitarian aid. Solar Energy 2014;100:172-178.
- Santos JC, Cheng Y, Dias MM, Rodrigues AE. Surface B-Splines fitting for Speeding Up the Simulation of
 Adsorption Processes with IAS Model. Comput Chem Eng 2011;35:1186-1191.
- Tarafder A, Mazzotti M. A Method for Deriving Explicit Binary Isotherms Obeying the Ideal Adsorbed
 Solution Theory. Chem Eng Technol 35 (2012) 102-108.
- Valenzuela DP, Myers AL. Adsorption Equilibrium Data Handbook. 4th ed. Englewood Cliffs: PrenticeHall; 1989.
- Yun JH, Düren T, Keil FJ, Seaton NA. Adsorption of methane, ethane, and their binary mixtures on MCM 41: an experimental evaluation of methods for the prediction of adsorption equilibrium. Langmuir
 2002;18:2693-2701.
- Yu N, Wang RZ, Wang LW. Sorption thermal storage for solar energy. Prog Energy Comb Sci 2013;39:489 514.