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# 1 Thermodynamics of thermally-driven adsorption compression

2 Giulio Santori<sup>a\*</sup>, Mauro Luberti<sup>a</sup>

3 \*corresponding author: Dr. Giulio Santori, g.santori@ed.ac.uk, tel: +4401316519043, fax: +4401316506551

4 <sup>a</sup> The University of Edinburgh, School of Engineering, Institute for Materials and Processes, Sanderson  
5 Building, The King's Buildings, Mayfield Road, EH9 3JL, Edinburgh, Scotland, UK

## 6 Abstract

7 Adsorption compressors are an emerging technology used to compress a gas stream with low grade heat  
8 which is of interest for the next long term extra-planetary bases. An analysis of thermodynamics of  
9 multicomponent gas/vapour mixtures compression with a thermally-driven adsorption bed is reported. In this  
10 unit a multicomponent stream is firstly adsorbed and secondly compressed by heating a bed at closed  
11 volume. The analysis is based on adsorbed solution theory applied to closed vessels where the composition  
12 and pressure of the bulk gas phase depends on temperature and volume of the whole system, leading to an  
13 isochoric-isothermal flash problem. Analysis of both an ideal and non-ideal adsorption compressor shows  
14 that the ideal approach is conservative, resulting in lower compression ratios at higher energy consumption.  
15

16  
17 Keywords: Isothermal flash; Isochoric flash; Adsorbed solution theory; Common tangent plane; Solid  
18 compressor; Adsorption compressor; Adsorption thermodynamics;

## 19 1. Introduction

20 The recent development of highly selective adsorption materials have enabled their integration in a number  
21 of traditional technologies, resulting in advanced processes demanding a sensibly lower energy consumption  
22 delivered at lower temperatures than their traditional counterparts [1-3]. A partial list of cases is included in  
23 Table 1. All these new technologies include a fundamental component that is the adsorption bed, which can  
24 be structured in numerous different shapes depending on the regeneration strategy [4-7].  
25  
26

Table 1: Emerging adsorption technologies

Sector	Traditional technology	Adsorptive technology	Ref.
Refrigeration & air conditioning	Electrically-driven vapour compression system	Adsorption refrigerators & heat pumps	[8-10]
Drying	Electrical dishwasher	Adsorption dishwasher	[11]
Desalination	Multi-effect distillation	Adsorption desalination	[12]
CO <sub>2</sub> removal	Absorption	Temperature and/or vacuum swing adsorption	[13-15]

27  
28 Adsorption beds are often operated as open systems where a single or multicomponent feed flows through  
29 the unit. However, some emerging technologies need to operate adsorption beds as closed systems. This is  
30 the case of the carbon dioxide removal and compression system, currently operating on the International  
31 Space Station and still under development to serve the next long term Mars or lunar bases [16-18].

32 Adsorption is the favourite method to produce a compressed gas in space applications because it does not  
33 have moving parts, requiring virtually no maintenance, and does not generate vibrations. The carbon dioxide  
34 removal system is the upstream process of the Sabatier reaction, which will be used in extra-terrestrial bases  
35 for the production of water. As demonstrated elsewhere [19, 20], the standard operating conditions to drive  
36 the Sabatier reaction towards higher CO<sub>2</sub> conversion are temperature ranging between 250-400°C and  
37 pressure of reagents greater than 130 kPa. So, compression of CO<sub>2</sub> from 20 kPa (Mars atmosphere) to 130  
38 kPa (Sabatier reaction pressure) is required, resulting in a minimum compression ratio of 6.5.

39 In this technology, compression is performed through a change in the bed temperature at closed volume. The  
40 operational steps of an adsorption compressor can be scheduled as:

41 1) Adsorption step: the adsorption bed is kept isothermal and is fed with the inlet stream at constant  
42 pressure and temperature.

43 2) Heating step: the bed is heated at constant volume. The new equilibrium state after heating results in  
44 a partition of the components between bulk gas phase and adsorbed phase at a bulk gas phase pressure higher  
45 than the initial pressure during the feeding. The pressure increase is mainly because of the release of material  
46 from the adsorbed phase to the bulk gas phase. The composition and the level of pressure in the bulk gas  
47 phase depend on the final temperature, volume available for the bulk gas phase, mass of adsorbent and total  
48 amount of moles in the enclosure.

49 3) Supply step: the outlet valve is open with a decrease in pressure and a variable flow of material is  
50 discharged.

51 Thus, adsorption compressors are thermally-driven compression systems adopting adsorption materials and  
52 operating according to temperature swing adsorption processes. An early thermodynamic analysis for  
53 adsorption of pure fluids has been presented in [21, 22] but no thermodynamic basis has been provided for  
54 the adsorption compression of a multicomponent mixture to date and some units such as the air revitalization  
55 module of the International Space Station (ISS) have been designed on the basis of simplifying assumptions,  
56 refining the performance in successive, trial and error steps. The air revitalization unit of the ISS uses  
57 zeolites 5A and 13X which adsorb significant amounts of carbon dioxide and nitrogen. This aspect has been  
58 addressed, at the design stage, by oversizing the mass of required material with a safety factor [22, 23]. The  
59 present work provides a tool for consistent thermodynamic investigation of adsorption compression of  
60 multicomponent gas mixtures.

61 The fundamental calculation for adsorption compression is the isochoric-isothermal flash (VT flash). VT  
62 flash in bulk gas/adsorbed phase equilibria has been already formulated by minimization of the Helmholtz  
63 energy of the system [24]. In this work we show that the well-known Rachford-Rice system of equations can  
64 be also applied to adsorption equilibrium after appropriate modifications.

65 For sake of clarity, at first an ideal ternary mixture in equilibrium with an ideal adsorbed solution [25] is  
66 evaluated. The aim is to provide the thermodynamic framework for the simple ideal case. Secondly, a non-  
67 ideal ternary mixture is considered using the Soave-Redlich-Kwong (SRK) equation of state for the  
68 description of the bulk gas phase and a Gibbs excess model for the adsorbed phase. This is aimed to show the  
69 differences between an ideal and non-ideal formulation.

70 Since no experimental multicomponent equilibrium data are presently available for this problem, the  
71 thermodynamic consistency of the results is validated through the common tangent plane approach for  
72 adsorption derived in [26]. The last section of this work is devoted to the performance analysis of ideal and  
73 non-ideal compressors.

74

## 75 2. Ideal isothermal-isochoric flash for adsorption

76 The ideal case includes an ideal bulk gas phase in equilibrium with an ideal adsorbed solution. The pressure  
77 and compositions in the new equilibrium state can be calculated considering the usual method based on the  
78 Rachford-Rice equations system [27], once a number of additional conditions arising from the adsorbed  
79 solution theory are provided [28]. The resulting system of equations for NC components is:

$$80 \sum_i^{NC} \frac{z_i (k_i - 1)}{1 + \frac{G}{F} (k_i - 1)} = 0 \quad (1)$$

$$81 x_i = \frac{z_i}{1 + \frac{G}{F} (k_i - 1)} \quad (2)$$

$$82 G = \frac{P_{bulk} V_{void}}{RT} \quad (3)$$

$$83 k_i = \frac{P_i^0}{P_{bulk}} \quad (4)$$

$$84 y_i P_{bulk} = P_i^0 x_i \quad (5)$$

$$85 \frac{m_{ads}}{N} = \sum_{i=1}^{NC} \left( \frac{x_i}{n_i} \right) \quad (6)$$

$$86 \psi_i = \int_0^{P_i^0} n_i d(\ln P_i) \quad i = 1, 2, \dots, NC \quad (7)$$

$$87 \psi_i = \psi_{eq} \quad i = 1, 2, \dots, NC \quad (8)$$

$$88 F - (G + N) = 0 \quad (9)$$

89 Eq. (1) is the original Rachford-Rice solving equation; eq. (3) is the ideal gas equation of state for the  
90 calculation of the amount of moles in the bulk gas phase. Eqns (4-8) follow the ideal adsorbed solution

91 theory [27, 28]. Eq. (9) is the overall mass balance. Assuming that the adsorbent occupies all the volume  
 92 available in the vessel, the gas mixture volume is calculated by:

$$93 \quad V_{void} = \frac{m_{ads}}{\rho_b} (\varepsilon_b + (1 - \varepsilon_b) \varepsilon_p) \quad (10)$$

94 Usually the parameters involved in eq. (10) are omitted in equilibrium measurements. This work assumes the  
 95 values reported in Table 2. Although the values of Table 2 do not perfectly correspond to the experimental  
 96 equilibrium data used for single isotherm parameters regression, they lay in the average range commonly  
 97 assumed for this kind of materials.

98 The system of eqns (1-9) can be reduced in a straightforward way to only two equations by substitution of  
 99 variables, holding the final variables  $P_{bulk}$  and reduced grand potential  $\psi_{eq}$ . The equivalent two equation  
 100 system includes eq. (1) and eq. (9).  
 101

Table 2: Adsorption materials and beds properties

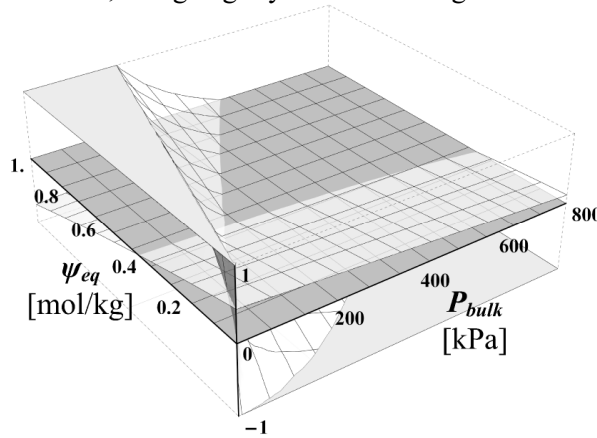
	$m_{ads}$ [kg]	$\varepsilon_b$	$\varepsilon_p$	$\rho_b$ [kg m <sup>-3</sup> ]	Ref
Zeolite 5A	1	0.39	0.50	687	[29]
Activated Carbon Norit R1 Extra	1	0.35	0.84	420	[30]
Zeolite 13X	1	0.37	0.60	641	[31]

102 Eqns (1-9) can be effectively solved by the Newton numerical method without any issue on the estimation of  
 103 the best initial guess. That is because the system has always only one solution in the physically meaningful  
 104 domain  $P_{bulk} > 0$  and  $\psi_{eq} > 0$ . In order to show this feature for the ideal problem, the Nitrogen/Oxygen/Argon  
 105 ternary system adsorption on zeolite 5A has been considered, using the Langmuir isotherm with parameters  
 106 reported in Table 3.  
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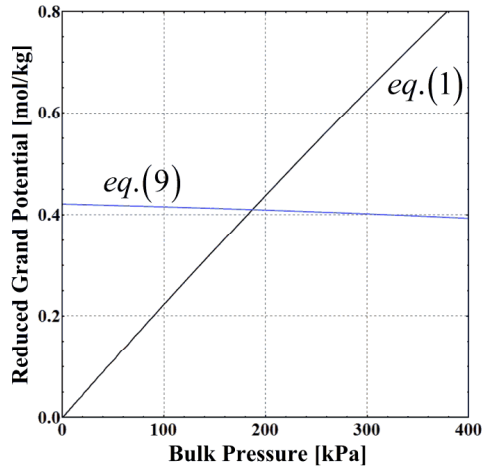
Table 3: Parameters of the Langmuir isotherm model for Nitrogen, Oxygen and Argon on zeolite 5A at 298.55 K. Equilibrium data are from [32].

	Pressure Range [kPa]	$q_s$ [mol kg <sup>-1</sup> ]	$b$ [kPa <sup>-1</sup> ]
N <sub>2</sub> (1)	34.1-442.9	2.114	0.001756
O <sub>2</sub> (2)	29.3-404.8	2.313	0.000524
Ar (3)	35.5-438.7	3.348	0.000314

109 Fig. 1 illustrates the solution of the system composed by eq. (1) and eq. (9). In the physically meaningful  
 110 region, the two functions intersect only in one point. The same equilibrium compositions are confirmed by  
 111 the common tangent plane of Gibbs energy of mixing (Fig. 2). The presence of a common tangent plane of  
 112 the Gibbs energy of mixing at the equilibrium point of Table 4 validates the thermodynamic consistency of  
 113 the solution. In Table 4 it can be noted that while the bulk gas phase composition is very different from the  
 114 feed, being enriched by oxygen and argon which are the less strongly adsorbed components, the adsorbed  
 115 phase composition is close to the feed, being slightly richer in nitrogen over the other components.  
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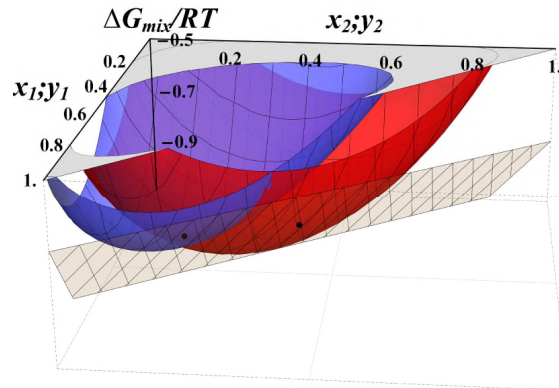
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Figure 1: Surfaces representing the left hand side functions of eq. (1) and eq. (9) (top). The horizontal plane passing through (0, 0, 0) defines the contour curves corresponding to eq. (1) and eq. (9) (bottom). eq. (1) and eq. (9) intersect in only one point, highlighting that the solution is necessary and sufficient.

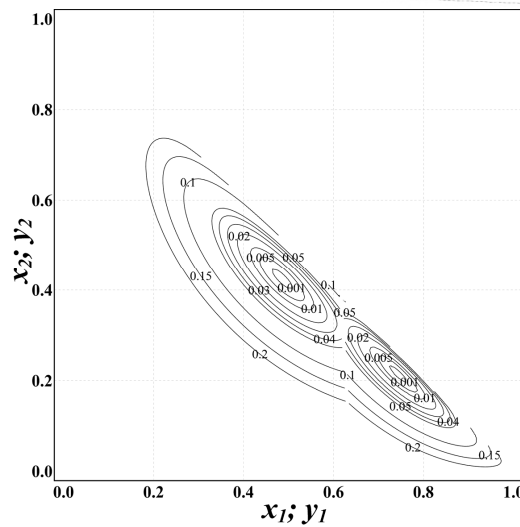
Table 4: Solution for the ideal VT flash calculation at the conditions:  $V_{\text{void}} = 1.021 \cdot 10^{-3} \text{ m}^3$ ;  $F = 0.45 \text{ moles}$ ;  $T = 298.55 \text{ K}$

Component	$z_i$	$P_{\text{bulk}}$ [kPa]	$\psi_{\text{eq}}$ [mol kg <sup>-1</sup> ]	$x_i$	$P_i^0$ [kPa]	$y_i$
N <sub>2</sub> (1)	0.70	186.80	0.410	0.744	122.03	0.486
O <sub>2</sub> (2)	0.25			0.214	370.54	0.425
Ar (3)	0.05			0.042	398.20	0.089

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Figure 2: Common tangent plane of the Gibbs energy of mixing at the equilibrium point of Table 4 (top). Contour plot of the distance function between Gibbs energy of mixing and common tangent plane at the equilibrium point of Table 4 (bottom).

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### 3. The non-ideal isothermal-isochoric flash

In the non-ideal formulation fugacity and activity coefficients respectively for the bulk gas phase and the adsorbed phase are considered [33]. Based on the experimental measurement reported in [34], the ternary mixture Methane/Nitrogen/Carbon Dioxide on activated carbon Norit R1 Extra at 298 K and high pressure is analysed. Single component adsorption experimental data were fitted using the Unilan isotherms, considering the absolute adsorbed amount versus fugacity, resulting in the parameters of Table 5.

Table 5: Parameters of the Unilan isotherm model for Methane, Nitrogen and Carbon Dioxide on activated carbon Norit R1 Extra at 298 K. Experimental data are from [34].

	Pressure Range [kPa]	Fugacity Range [kPa]	$q_s$ [mol kg <sup>-1</sup> ]	$b$ [kPa <sup>-1</sup> ]	$s$
CH <sub>4</sub> (1)	0-5753	0-5219	24.537	2.873 10 <sup>-5</sup>	5.220
N <sub>2</sub> (2)	0-5958	0-5934	21.187	1.403 10 <sup>-5</sup>	4.759
CO <sub>2</sub> (3)	0-6000	0-4239	34.824	5.833 10 <sup>-5</sup>	5.086

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#### 3.1 Bulk gas phase model

The eqns (3-7) must be modified introducing fugacity for the description of the bulk gas phase and activity coefficients for the adsorbed phase. The SRK [35, 36] equation of state has been used for the evaluation of the fugacity coefficients.

$$Z^3 - Z^2 + Z(A - B - B^2) - AB = 0 \quad (11)$$

$$\ln(\varphi_{i,bulk}) = \frac{b_i}{b}(Z - 1) - \ln(Z - B) - \frac{A}{B} \left( 2 \frac{a_i^{1/2}}{a^{1/2}} - \frac{b_i}{b} \right) \ln \left( 1 + \frac{B}{Z} \right) \quad (12)$$

Eq. (11) is the fugacity coefficient of component  $i$  in the bulk gas phase from SRK equation of state. The correlations for the calculation of the parameters of eq. (11) and (12) are reported elsewhere [37]. The interaction parameters are neglected in all of the following calculations and the number of total moles of the mixture in the bulk phase (G) is derived by the compressibility factor  $Z$  as follows:

$$G = Z \frac{P_{bulk} V_{void}}{RT} \quad (13)$$

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#### 3.2 Excess Gibbs energy model for the adsorbed phase

The adopted activity coefficient model is the ABC equation [38]. At constant temperature, it proposes the following expression for the excess Gibbs energy:

$$g_{ex} = \sum_{i=1}^{NC} \sum_{j=1}^{NC} A_{0,ij} x_i x_j (1 - e^{-C_{ij} \psi}) \quad (14)$$

Its application requires the preliminary regression on the experimental data of binary systems of the binary interaction parameters  $A_{0,ij}$  and  $C_{ij}$  at constant temperature. The results of the regression on the binary experimental data in [34] are reported in Table 6.

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Table 6: Parameters of the ABC equation for Methane, Nitrogen and Carbon Dioxide binary systems on activated carbon Norit R1 Extra at 298 K. Experimental data are from [34].

Components (i/j)	Fugacity range [kPa]	$A_{0,ij}$ [kJ mol <sup>-1</sup> ]	$C_{ij}$ [kg mol <sup>-1</sup> ]
CH <sub>4</sub> /N <sub>2</sub> (1/2)	150.9-5578.7	-1.726	10.060
CH <sub>4</sub> /CO <sub>2</sub> (1/3)	97.7-5342.1	0.474	0.0162
N <sub>2</sub> /CO <sub>2</sub> (2/3)	107.9-4459.2	1.017	14.699

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The activity coefficients are defined as:

$$RT \ln(\gamma_i) = \left. \frac{\partial(Ng_{ex})}{\partial n_i} \right|_{T, \psi, n_j} \quad (15)$$

where  $N$  is the total amount of moles adsorbed. According to the definition of eq. (15), for a ternary system, the activity coefficients result in:

162

$$163 \quad \ln(\gamma_1) = \frac{e^{-(C_{12}+C_{13}+C_{23})\psi}}{RT(x_1+x_2+x_3)^2} \left( \begin{aligned} &A_{0,12}e^{(C_{13}+C_{23})\psi} (e^{C_{12}\psi} - 1)x_2(x_2+x_3) + \\ &+ A_{0,23} (e^{(C_{12}+C_{13})\psi} - e^{(C_{12}+C_{13}+C_{23})\psi})x_2x_3 + \\ &+ A_{0,13}e^{(C_{12}+C_{23})\psi} (e^{C_{13}\psi} - 1)(x_2+x_3)x_3 \end{aligned} \right) \quad (16)$$

$$164 \quad \ln(\gamma_2) = \frac{e^{-(C_{12}+C_{13}+C_{23})\psi}}{RT(x_1+x_2+x_3)^2} \left( \begin{aligned} &A_{0,12}e^{(C_{13}+C_{23})\psi} (e^{C_{12}\psi} - 1)x_1(x_1+x_3) + \\ &+ A_{0,13} (e^{(C_{12}+C_{23})\psi} - e^{(C_{12}+C_{13}+C_{23})\psi})x_1x_3 + \\ &+ A_{0,23}e^{(C_{12}+C_{23})\psi} (e^{C_{23}\psi} - 1)(x_1+x_3)x_3 \end{aligned} \right) \quad (17)$$

$$165 \quad \ln(\gamma_3) = \frac{e^{-(C_{12}+C_{13}+C_{23})\psi}}{RT(x_1+x_2+x_3)^2} \left( \begin{aligned} &A_{0,13}e^{(C_{13}+C_{23})\psi} (e^{C_{13}\psi} - 1)x_1(x_1+x_2) + \\ &+ A_{0,12} (e^{(C_{13}+C_{23})\psi} - e^{(C_{12}+C_{13}+C_{23})\psi})x_1x_2 + \\ &+ A_{0,23}e^{(C_{12}+C_{13})\psi} (e^{C_{23}\psi} - 1)(x_1+x_2)x_2 \end{aligned} \right) \quad (18)$$

166 To take into account the non-idealities both in adsorbed and bulk gas phase, eqns. (6) and (7) are now  
167 replaced by eqns (19) and (20):

$$168 \quad \psi_i = \int_0^{f_{i,ads}} n_i d(\ln f_i) \quad i = 1, 2, \dots, NC \quad (19)$$

169 Eq. (19) is an integral function of each single isotherm. In the ideal case it is fitted directly on the  
170 experimental pressures, in the non-ideal the isotherms have to be fitted on the fugacity, modifying the  
171 experimental pressure with an equation of state (in this case SRK).

$$172 \quad \frac{m_{ads}}{N} = ex + \sum_{i=1}^{NC} \frac{x_i}{n_i} \quad (20)$$

173 where the excess contribution to the total number of adsorbed moles  $ex$  is given by:

$$174 \quad ex = \left. \frac{\partial(g_{ex} / RT)}{\partial \psi} \right|_{T,x} = \sum_{i=1}^{NC} \sum_{j=1}^{NC} \left( \frac{A_{0,ij} C_{ij}}{RT} x_i x_j e^{-C_{ij}\psi} \right) \quad (21)$$

175 The two contributions on the right hand side of eq. (20) are respectively the contribution of the non-idealities  
176 in the adsorbed phase according to the ABC equation and the contribution considering ideal adsorption of a  
177 non-ideal gas mixture. In fact, in eq. (20),  $n_i$  is the adsorption isotherm of the pure component  $i$  with  
178 parameters regressed on fugacities instead of pressures [28].  
179

### 180 3.3. Non-ideal flash calculation

181 The  $k_i$  factors for the non-ideal case are no longer only function of pressures but also of the compositions  
182 because of the presence of the fugacity coefficient in the bulk gas phase ( $\varphi_{i,bulk}$ ), the activity coefficient of the  
183 adsorbed phase ( $\gamma_i$ ) and the fugacity of the pure component  $i$  in adsorbed phase ( $f_{i,ads}$ ). Therefore  $k_i$  factors  
184 become:

$$185 \quad \frac{y_i}{x_i} = \frac{f_{i,ads} \gamma_i}{\varphi_{i,bulk} P_{bulk}} \quad (22)$$

186 This feature makes the system of equations larger and more nonlinear than the ideal case. Furthermore, in  
187 order to have consistency between the number of equations and the number of variables, for a three  
188 components mixture, three isofugacity condition equations and conservation of moles equation for one of the  
189 components must be included.

190 The Newton method can again effectively solve this problem, providing an initial guess reasonably close to  
191 the actual solution, e.g. assuming a value of 1 for fugacity and activity coefficients. After some sensitivity  
192 analysis, it has been noticed that the convergence to a feasible solution is affected by the initial value of  $P_{bulk}$   
193 more than the initial value of the other variables.

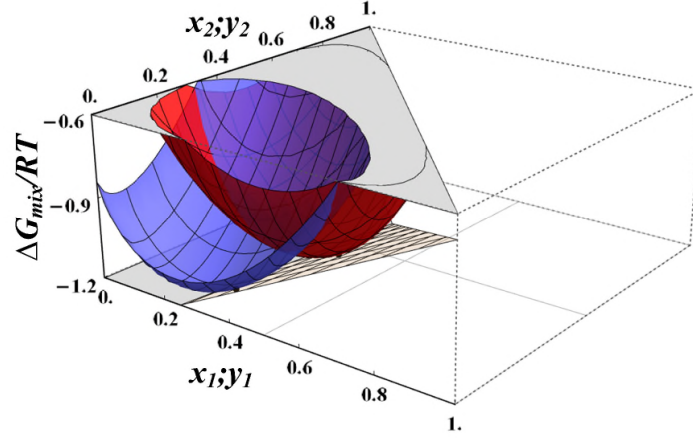
194 Assuming the parameters of Tables 5 and 6, the results of the calculation for the non-ideal high pressure case  
195 are reported in Table 7. Carbon dioxide, being the most strongly adsorbed component, exhibits a higher

196 concentration in the adsorbed phase compared to the feed; an opposite trend can be seen for methane and  
 197 nitrogen components. The result is again validated testing the presence of the common tangent plane of the  
 198 Gibbs energy of mixing surface at the equilibrium (Fig. 3).  
 199

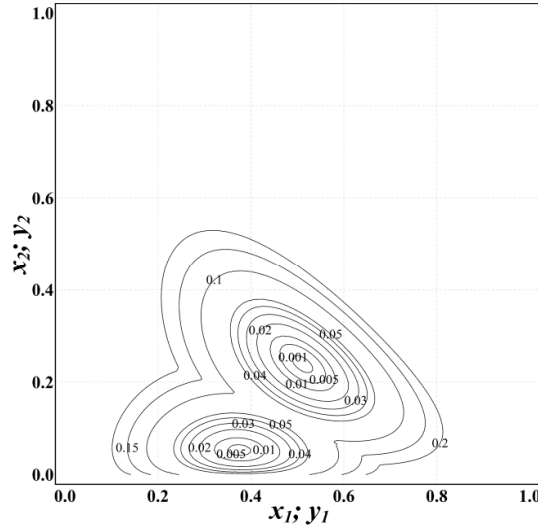
Table 7: Solution for the non-ideal VT flash calculation at the conditions:  $V_{\text{void}} = 2.133 \cdot 10^{-3} \text{ m}^3$ ;  $F = 10 \text{ moles}$ ;  $T = 298 \text{ K}$

Component	$z_i$	$P_{\text{bulk}}$ [kPa]	$\psi_{\text{eq}}$ [kg/mol]	$x_i$	$\gamma_i$	$f_{i,\text{ads}}$ [kPa]	$y_i$	$\Phi_{i,\text{bulk}}$
CH <sub>4</sub> (1)	0.4	2837.29	14.336	0.373	0.980	3784.88	0.511	0.511
N <sub>2</sub> (2)	0.1			0.052	0.970	13724.31	0.239	0.239
CO <sub>2</sub> (3)	0.5			0.575	1.029	1055.05	0.250	0.250

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#### 4. Enthalpy of adsorption

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The thermal energy required for compression includes both enthalpy of desorption and sensible heat. In case of multicomponent mixture, the enthalpy of desorption  $\Delta H_{\text{ads}}$  [kJ] can be calculated following the derivation described in [38]:

211

$$\Delta H_{\text{ads}} = m_{\text{ads}} \sum_{i=1}^{NC} \left( \int_0^{n_i^o} \Delta \bar{h}_i dn_i \right) \quad (23)$$

212

213

where  $\Delta \bar{h}_i$  is the differential enthalpy of adsorption [kJ mol<sup>-1</sup>] of the  $i^{\text{th}}$  component of the mixture. For non-ideal adsorbed solutions and non-ideal bulk gases, the differential enthalpy is:



$$\Delta \bar{h}_i = \Delta h_i^o + RT^2 \left( \frac{\partial \ln \gamma_i}{\partial T} \right)_{\psi, x} + \left[ \frac{1}{n_i^o} + \left( \frac{\partial \ln \gamma_i}{\partial \psi} \right)_{T, x} \right] \times \left[ \frac{\sum_j x_j G_j^o n_j^o (\Delta \bar{h}_j^o - \Delta h_j^o) + RT^2 \left( \frac{\partial (ex)}{\partial T} \right)_{\psi, x}}{\sum_j x_j G_j^o - \left( \frac{\partial (ex)}{\partial T} \right)_{T, x}} \right] \quad i=1,2,\dots,NC \quad (24)$$

which, for an ideal gas adsorbed ideally, becomes:

$$\Delta \bar{h}_i = \Delta h_i^o + \frac{1}{n_i^o} \left( \frac{\sum_j x_j G_j^o n_j^o (\Delta \bar{h}_j^o - \Delta h_j^o)}{\sum_j x_j G_j^o} \right) \quad i=1,2,\dots,NC \quad (25)$$

The terms composing eq. (24) are:

$$G_i^o = \frac{1}{(n_i^o)^2} \left( \frac{\partial \ln n_i^o}{\partial \ln f_i} \right)_T \quad i=1,2,\dots,NC \quad (26)$$

Eq. (24) is a function of the pure component molar integral enthalpy of adsorption [kJ mol<sup>-1</sup>], which neglecting the Poynting term, becomes:

$$\Delta h_i^o = \frac{1}{n_i^o} T^2 \frac{\partial}{\partial T} \left( \frac{\Omega_i}{T} \right)_{f_i} \quad (27)$$

where  $\Omega$  [kJ kg<sup>-1</sup>] is the grand potential of adsorption. The other variable in eq. (24) is the pure component differential enthalpy [kJ mol<sup>-1</sup>]:

$$\Delta \bar{h}_i^o = RT^2 \left( \frac{\partial \ln f_i}{\partial T} \right)_{n_i} \quad (28)$$

Assuming that the specific heats of the gases are constant in the operating range of temperatures and the specific heats in adsorbed and bulk gas phase are identical [39], the sensible heat can be derived as follows:

$$\Delta H_{sens} = \left[ m_{ads} c_{p,ads} + \sum_i^{NC} (n_{i,bulk} + n_{i,ads}) c_{p,i} \right] (T_{heating} - T_{ads}) \quad (29)$$

where  $c_{p,ads}$  is the specific heat capacity of the adsorbent assumed 0.858 kJ kg<sup>-1</sup> K<sup>-1</sup> [11],  $c_{p,i}$  is the bulk gas phase specific heat capacity of the i<sup>th</sup> component of the mixture [kJ mol<sup>-1</sup> K<sup>-1</sup>] as reported in [40].  $n_{i,bulk}$  is the number of moles of component i in the bulk gas phase [mol] and  $n_{i,ads}$  is the number of moles of component i in the adsorbed phase [mol],  $T_{ads}$  is the adsorption temperature which is kept at 298 K and  $T_{heating}$  is the heating temperature.

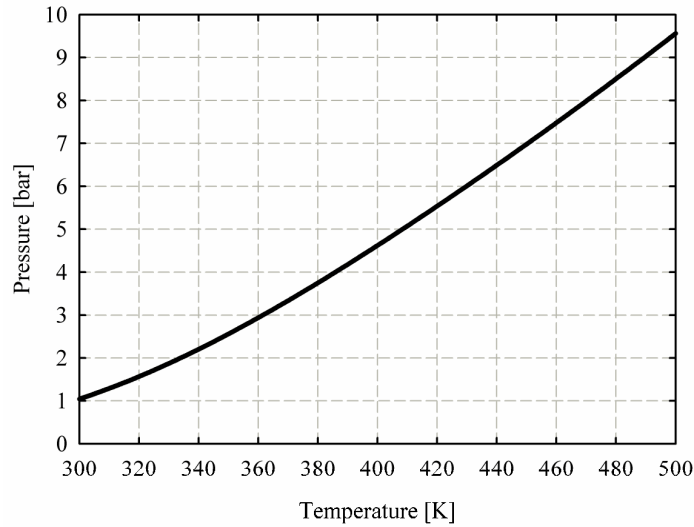
## 5. Ideal adsorption compression

The case of a solid compressor is presented where 1 kg of zeolite 13X adsorbs from a three components feed mixture of Nitrogen, Oxygen, Carbon Dioxide with composition (0.7897,0.2099,0.0004) mole fraction at 101.325 kPa, 298 K in accordance to the ideal adsorbed solution theory, with adsorption isotherms parameters reported in Table 8.

Table 8: Langmuir, Dual Site Langmuir and Toth isotherm parameters of the ideal and non-ideal adsorption zeolite 13X compressor

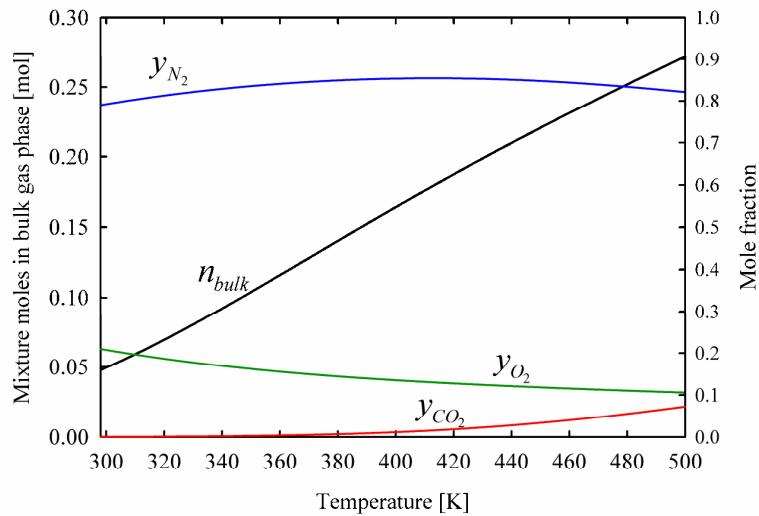
	Isotherm	q <sub>s1</sub> [mol/kg]	b <sub>01</sub> [kPa <sup>-1</sup> ]	ΔH <sub>1</sub> [kJ mol <sup>-1</sup> ]	q <sub>s2</sub> [mol kg <sup>-1</sup> ]	b <sub>02</sub> [kPa <sup>-1</sup> ]	ΔH <sub>2</sub> [kJ mol <sup>-1</sup> ]	t	Ref
	N <sub>2</sub> Langmuir	4.725	3.616 10 <sup>-7</sup>	-19.59	--	--	--	--	[41]
	O <sub>2</sub> Langmuir	4.650	1.452 10 <sup>-5</sup>	-7.80	--	--	--	--	[41]
	CO <sub>2</sub> Dual site Langmuir	3.573	1.681 10 <sup>-8</sup>	-35.00	1.789	3.812 10 <sup>-9</sup>	-49.26	--	[42]
	C <sub>2</sub> H <sub>4</sub> Toth	2.21	5.22 10 <sup>-6</sup>	-21.4	--	--	--	1.75	[43]
	C <sub>2</sub> H <sub>6</sub> Toth	2.72	1.13 10 <sup>-7</sup>	-36.3	--	--	--	0.97	[43]

241 After adsorption, the bed is heated up at closed volume. The significant amount of material moving from the  
 242 adsorbed phase to the bulk gas phase causes a pressure increase with a magnitude depending on the heating  
 243 temperature (Fig. 4).



244  
 245 Figure 4: Evolution of the bulk gas phase pressure heating the bed at different temperature levels for 1 kg of  
 246 zeolite 13X compressing a stream of Nitrogen, Oxygen, Carbon Dioxide adsorbed at 101.325 kPa, 298 K and  
 247 composition (0.7897, 0.2099, 0.0004) mole fraction.  
 248

249 The composition of the compressed stream is variable because of the changed temperatures and bulk gas  
 250 phase pressures. Fig. 5 highlights the change in bulk gas phase composition along with the increase in the  
 251 amount of gas mixture  $n_{bulk}$  when the adsorption bed is heated.



252  
 253 Figure 5: Evolution of the gas mixture moles (left) and component mole fraction (right) at different heating  
 254 temperatures for 1 kg of zeolite 13X compressing a stream of Nitrogen, Oxygen, Carbon Dioxide adsorbed at  
 255 101.325 kPa, 298 K and composition (0.7897, 0.2099, 0.0004) mole fraction.  
 256

257 Fig. 6 shows that the dominant part in the total energy required for compression is the sensible heat,  
 258 accounting, in this particular case, for an average of 91% of the total energy.

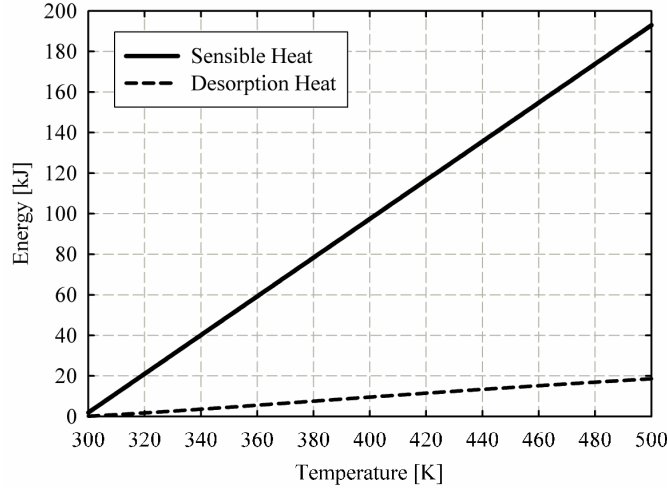


Figure 6: Evolution of sensible and desorption heat at different heating temperatures for 1 kg of zeolite 13X compressing a stream of Nitrogen, Oxygen, Carbon Dioxide adsorbed at 101.325 kPa, 298 K and composition (0.7897, 0.2099, 0.0004) mole fraction

## 6. Non-ideal adsorption compression

When adsorption cannot be described as ideal, ideal and non-ideal interpretations can result in significant performance discrepancies. In this section a gas mixture of Carbon Dioxide/Ethylene/Ethane adsorbed on zeolite 13X is considered. This gas mixture shows non-ideal behaviour in gas phase already at moderate pressure and ambient temperature and non-idealities in adsorbed phase on zeolite 13X. As measured in [30 38], ABC equation excess model can describe correctly the equilibrium of a non-ideal adsorbed phase of Carbon Dioxide/Ethylene/Ethane on zeolite 13X with the binary interaction parameters of Table 9. The bulk gas phase, especially for Ethane and Ethylene, require the specification of an equation of state for the calculation of fugacity coefficient in the range of operating conditions. Accordingly SRK equation of state is used to describe the thermodynamic behaviour of the bulk gas phase.

Table 9: Parameters of the ABC equation for Carbon Dioxide, Ethylene and Ethane binary systems on zeolite 13X. Experimental data are from [38].

Components (i/j)	$A_{ij}$ [kJ mol <sup>-1</sup> ]	$B_{ij}$ [kJ mol <sup>-1</sup> K <sup>-1</sup> ]	$C_{ij}$ [kg mol <sup>-1</sup> ]
CO <sub>2</sub> /C <sub>2</sub> H <sub>6</sub> (1/3)	-10.0	0.01917	0.110
CO <sub>2</sub> /C <sub>2</sub> H <sub>4</sub> (1/2)	-6.5	0.01450	0.030
C <sub>2</sub> H <sub>4</sub> /C <sub>2</sub> H <sub>6</sub> (2/3)	-4.5	0.00437	0.067

Note: temperature dependent interaction parameters are considered according to

$$A_{0,ij} = A_{ij} + T B_{ij}$$

In the first operational step, the adsorption compressor is loaded at 101.325 kPa and 298 K with a multicomponent gas mixture having composition (0.05, 0.15, 0.8) mole fraction. Table 10 reports the distribution of the components in bulk gas phase and adsorbed phase at this initial adsorption step. The non-ideal approach predicts more amount of initial gas in the vessel than the ideal approach. The main difference is in the carbon dioxide adsorbed. This is because both the binary interaction parameters of carbon dioxide, which is the most strongly adsorbed compound, are higher in magnitude than the interaction parameters of ethane/ethylene, making carbon dioxide equilibrium more sensible to the non-ideal approach. However, total amount of moles in the vessel does not change significantly because carbon dioxide is present in small amount in the feeding mixture.

Table 10: comparison of the amount of moles between ideal and non-ideal compressor after adsorption at 101.325 kPa and 298 K for 1 kg of zeolite 13X.

	Carbon Dioxide	Ethylene	Ethane	Total
Ideal case				
Bulk gas phase	0.002	0.007	0.038	0.048
Adsorbed phase	0.459	0.041	2.183	2.683
Total	0.461	0.048	2.221	2.731
Non-ideal case				
Bulk gas phase	0.002	0.007	0.038	0.047
Adsorbed phase	0.756	0.045	2.079	2.880
Total	0.758	0.052	2.117	2.927

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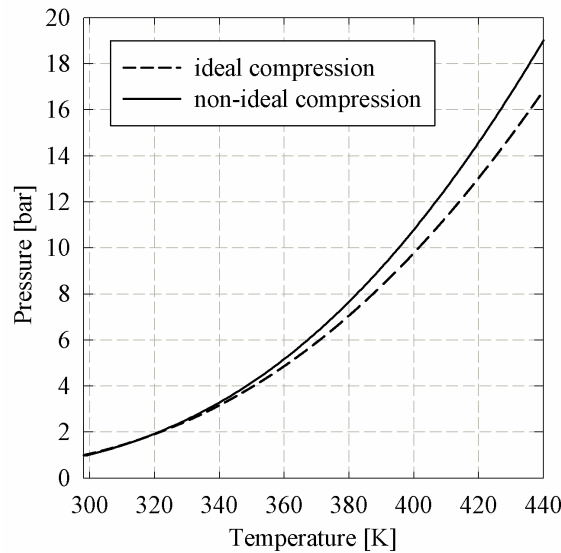
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The excess part of the total adsorbed amount (eq. (20)) makes the compressor performance also dependent of the excess thermodynamic potentials which are inverse functions of temperature. This results in a decrease of the excess adsorbed amount with increasing temperatures. Thus, the non-ideal approach introduces a higher sensitivity of equilibrium with temperature. This is illustrated in Fig. 7, where in the non-ideal compressor the release of gas from the adsorbed phase to the bulk gas phase is larger than the ideal compressor, resulting eventually in higher equilibrium pressures.



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Figure 7: Compression of a gas mixture of Carbon Dioxide/Ethylene/Ethane with 1 kg of zeolite 13X and (0.05,0.15,0.80) feed composition, adsorbed at 101.325 kPa, 298 K. Pressure profile against heating temperature in the ideal (dashed line) and non-ideal (solid line) cases.

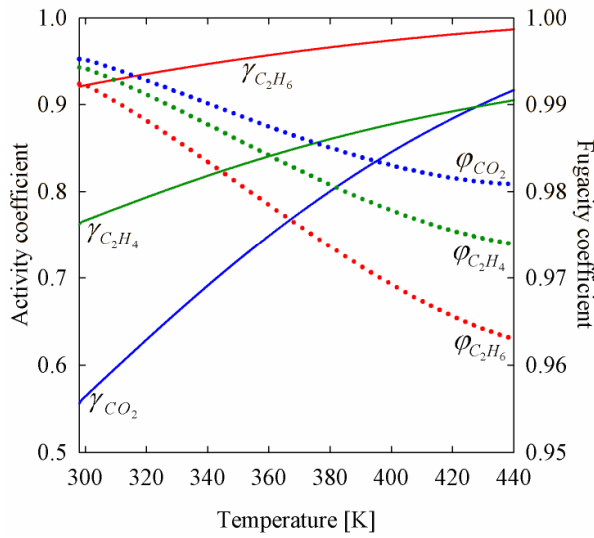
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In Fig.8, the change in the activity coefficients over temperature promotes increasingly higher pressures. Among the three components, carbon dioxide shows the steepest trend, spanning from 0.55 at 298 K to 0.92 at 440 K. Fugacity coefficients vary in smaller proportion. In this case ethane has the larger variation ranging between 0.992 at 298 K and 0.96 at 340 K.

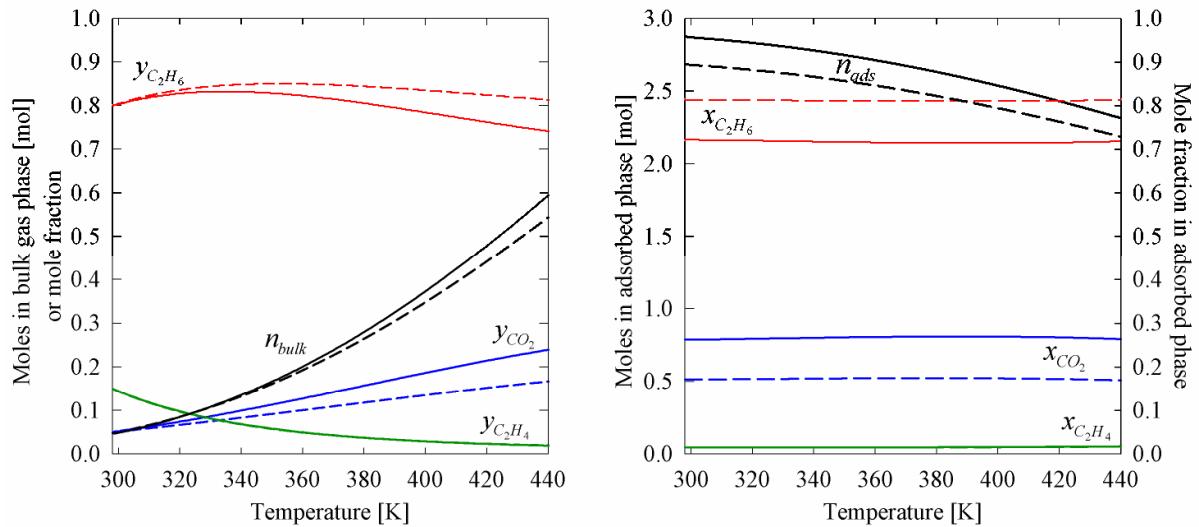


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Figure 8: Compression of a gas mixture of Carbon Dioxide/Ethylene/Ethane with 1 kg of zeolite 13X and (0.05, 0.15, 0.80) feed composition, adsorbed at 101.325 kPa, 298 K. Activity and fugacity coefficients profiles against heating temperature.

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Compositions in bulk gas phase and adsorbed phase are illustrated in Fig. 9, where adsorbed phase compositions keep essentially constant throughout the heating range, while bulk gas phase compositions visibly change. Also a significant difference is observed in the adsorbed phase compositions of carbon dioxide and ethane between ideal and non-ideal approach already in the adsorption step. The feature of the non-ideal approach of predicting higher pressures depends also on this initial difference.



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Figure 9: Compression of a gas mixture of Carbon Dioxide/Ethylene/Ethane with 1 kg of zeolite 13X and (0.05,0.15,0.80) feed composition, adsorbed at 101.325 kPa, 298 K. Comparison between compositions, bulk gas phase amount and adsorbed amount against heating temperature in the ideal (dashed line) and non-ideal (solid line) cases.

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Fig. 9 shows also that in the bulk gas phase, at temperatures <320 K (<2 bar), the ideal and non-ideal approaches provide the same results, while in the adsorbed phase the two approaches result in significant discrepancies already at low pressure. This is due to non-idealities in the adsorbed phase. Energy consumption for the two cases is depicted in Fig. 10, where the difference in sensible energy is negligible because it is dominated by the adsorption material heat capacity more than by the adsorbed amount. A difference between ideal and non-ideal desorption heat can be observed already at temperatures >320 K. This difference increases up to 10.5 kJ at 440 K. This results in a lower total energy consumption for the non-ideal compression than ideal compression.

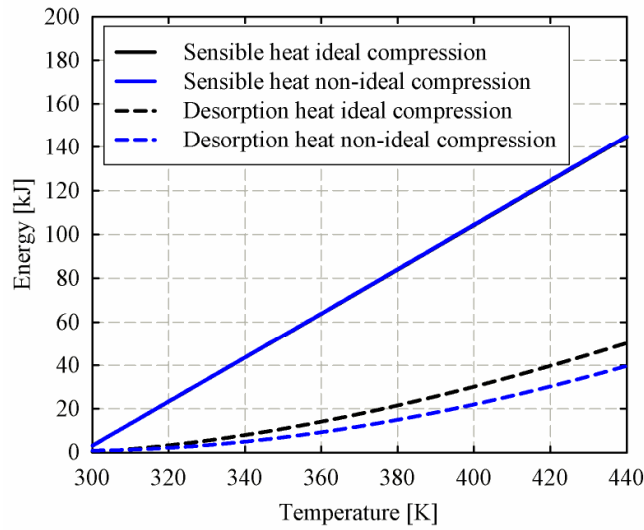


Figure 10: Evolution of sensible and desorption heat at different heating temperatures for 1 kg of zeolite 13X compressing a stream of Nitrogen, Oxygen, Carbon Dioxide. Comparison between ideal and non-ideal compression.

Desorption heat is dominated by the pure component molar integral enthalpies ( $\Delta h_i^0$ ) which are similar for the ideal and non-ideal approaches. The second major contribution to the desorption heat consists of the term  $RT^2 (\partial \ln \gamma_i / \partial T)_{\psi, x}$  which is negligible for all gases except that ethane. This builds the difference between ideal compressor and non-ideal compressor in terms of energy consumption. These results show that considerations based on ideal adsorbed solution theory lead to conservative assessment of the compressor performance, with lower pressure generated at higher energy consumption.

## 5. Conclusion and outlook

Adsorption compressor is an emerging technology which is currently under development for the next long term Mars and lunar missions. Thermodynamics of this system is based on the solution of the isochoric-isothermal flash problem for bulk gas/adsorbed phases. A system composed by Rachford-Rice equation and additional equations embedding the iso-reduced grand potential condition enables the determination of the compressed state. The flash problem has been solved in both cases respectively for two ternary mixtures and validated through its thermodynamic consistency testing the presence of the common tangent plane to the Gibbs energy of mixing at the equilibrium compositions. In this way the applicability of the Rachford-Rice equation is extended to the adsorbed solution theory. This procedure has been applied for the characterisation of one zeolite 13X compressor working ideally with a Nitrogen/Oxygen/Carbon Dioxide gas mixture and non-ideally with a Carbon Dioxide/Ethylene/Ethane mixture. In the latter non-ideal mixture, calculations based on ideal approach proved to be more conservative compared to the non-ideal compressor performance. The application of the proposed thermodynamic framework is at the basis of adsorption compressor performance calculation. The precise design of the single unit and of multi-compressor systems [44] can be reached by embedding the described approach of the equilibrium in the wider dynamic description of the compressor. This impacts directly on the development of sustainable systems that capture, compress and concentrate gases in extremely dilute conditions such as planetary and extra-planetary systems for greenhouse gases removal and compression [45, 46].

## Acknowledgements

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## Nomenclature

$c_{p,ads}$	Specific heat capacity of the adsorbent material [ $\text{kJ kg}^{-1} \text{K}^{-1}$ ]
$c_{p,i}$	Specific heat capacity of component $i$ [ $\text{kJ mol}^{-1} \text{K}^{-1}$ ]
ex	Excess contribution to the total number of adsorbed moles [ $\text{kg mol}^{-1}$ ]
F	Total number of moles in the feed [mol]

373	$f_{i,ads}$	Fugacity of pure component $i$ at the system temperature and pressure [kPa]
374	$G$	Total number of moles in the bulk gas phase [mol]
375	$g_{ex}$	Excess Gibbs energy [kJ mol <sup>-1</sup> ]
376	$k_i$	Equilibrium constant of component $i$
377	$m_{ads}$	Mass of adsorbent [kg]
378	$N$	Total number of moles in the adsorbed phase [mol]
379	$NC$	Number of components participating in the adsorption
380	$n_i$	Specific amount adsorbed of component $i$ [mol kg <sup>-1</sup> ]. It is calculated directly from adsorption
381	isotherm using either $P_i^0$	(ideal adsorbed phase) or adsorbed phase fugacity $f_{i,ads}$ (non-ideal adsorbed phase).
382	$n_{i,ads}$	Amount of adsorbed moles of component $i$ [mol] in adsorbed phase phase;
383	$n_{i,bulk}$	Amount of adsorbed moles of component $i$ [mol] in bulk gas phase;
384	$P_{bulk}$	Pressure of the mixture in the bulk gas phase [kPa]
385	$P_i^0$	Bulk pressure of the component $i$ at a given reduced grand potential $\psi_i$ [kPa]
386	$R$	Universal gas constant [kJ mol <sup>-1</sup> K <sup>-1</sup> ]
387	$T$	Equilibrium temperature [K]
388	$T_{ads}$	Temperature of the adsorption bed during adsorption [K]
389	$T_{heating}$	Temperature of the bed after heating [K]
390	$V_{void}$	Volume occupied by the bulk gas phase (dead volume) [m <sup>3</sup> ]
391	$x_i$	Molar fraction of the component $i$ in the adsorbed phase
392	$y_i$	Molar fraction of the component $i$ in the bulk gas phase
393	$z_i$	Molar fraction of the component $i$ in the feed
394	$Z$	Compressibility factor
395	$\Delta H_{ads}$	Enthalpy for adsorption or desorption [kJ];
396	$\Delta H_{sens}$	Sensible thermal energy and its bulk gas and adsorbed phases [kJ] ;
397	$\Delta \bar{h}_i$	Differential enthalpy of adsorption [kJ mol <sup>-1</sup> ] for component $i$ in the mixture;
398	$\Delta \bar{h}_i^0$	Differential enthalpy of adsorption [kJ mol <sup>-1</sup> ] for pure component $i$ ;
399	$\Delta h_i^0$	Integral enthalpy of adsorption [kJ mol <sup>-1</sup> ] for pure component $i$ ;
400		
401	<b>Greek letters</b>	
402	$\gamma_i$	Activity coefficient of component $i$
403	$\varepsilon_b$	Bed porosity
404	$\varepsilon_p$	Particle porosity
405	$\rho_b$	Bed bulk density [kg m <sup>-3</sup> ]
406	$\Phi_{i,bulk}$	Fugacity coefficient of component $i$ in the bulk gas phase
407	$\Psi_{eq}$	Reduced grand potential at equilibrium [mol kg <sup>-1</sup> ]
408	$\psi_i$	Reduced grand potential of component $i$ [mol kg <sup>-1</sup> ]
409	$\Omega$	Grand potential for adsorption [J kg <sup>-1</sup> ]

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