

SELECTED PAPERS FROM THE 3RD EDITION OF THE INTERNATIONAL CONFERENCE
ON WASTES: SOLUTIONS, TREATMENTS AND OPPORTUNITIES, VIANA DO CASTELO,
PORTUGAL, 14–16 SEPTEMBER 2015

Wastes: Solutions, Treatments and Opportunities

Editors

Cândida Vilarinho & Fernando Castro

University of Minho, Guimarães, Portugal

Mário Russo

Polytechnic Institute of Viana do Castelo, Viana do Castelo, Portugal



CRC Press

Taylor & Francis Group

Boca Raton London New York Leiden

CRC Press is an imprint of the
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A BALKEMA BOOK

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© 2015 Taylor & Francis Group, London, UK

Typeset by MPS Limited, Chennai, India

Printed and bound in Great Britain by CPI Group (UK) Ltd, Croydon, CR0 4YY

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Published by: CRC Press/Balkema
P.O. Box 11320, 2301 EH Leiden, The Netherlands
e-mail: Pub.NL@taylorandfrancis.com
www.crcpress.com – www.taylorandfrancis.com

ISBN: 978-1-138-02882-1 (Hardback)

ISBN: 978-1-315-64900-9 (eBook PDF)

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Preface

Dear colleagues,

It is with great pleasure that we bring to you the book “Selected papers from the 3rd edition of the International Conference Wastes: Solutions, Treatments and Opportunities”.

The papers published in this book were submitted, revised and approved by the Scientific Committee in a full peer review process to be presented at Wastes 2015 that took place in the Polytechnic Institute of Viana do Castelo, between 14 and 16 of September.

The Wastes conferences, happening every two years, are a platform for the scientists and industries from the waste management and recycling sectors from around the world, to share experiences and knowledge with all who attend. Discussions regarding the balance between economic, environmental and social outcomes are carefully addressed. The development of innovative techniques, tools and strategies on how wastes can be transformed into good ideas, improving both the overall environmental performance and the understanding of the industry impact on the environment, as well as the options analysis for its improvement are key objectives of this conference.

With this publication we expect to take the scope of this event beyond the limits of its physical occurrence by providing both attendants and general public with an instrument that is the materialization of the main contributions to Wastes 2015.

The editors wish to thank all the reviewers that, taking part of the Scientific Committee of the Conference, gave a fundamental input to the process of reviewing the papers included in this book, namely:

Ana Luísa Fernando
Ana Maria Segadães
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António Brito
António Roque
Benilde Mendes
Carlos Nogueira
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Nuno Lapa
Rosa M. Quinta-Ferreira
Tiago Miranda

Fixed bed adsorption dynamics of CO₂/CH₄ mixtures in zeolite 13X for biogas upgrading

J.A.C. Silva

Escola Superior de Tecnologia e Gestão, Instituto Politécnico de Bragança, Bragança, Portugal

A.E. Rodrigues

Laboratory of Separation and Reaction Engineering, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Portugal

ABSTRACT: The separation performance of CO₂/CH₄ mixtures in binderless beads of zeolite 13X has been studied in a fixed bed adsorption system for biogas upgrading strategies to biomethane. Zeolite 13X proved to be very efficient for the separation leading to breakthrough curves that show a plateau of pure CH₄ of approximately 4 minutes depending of the operating conditions chosen. The separation performance for CO₂/CH₄ measured by the selectivities range from 37 at a low pressure of 0.1 MPa to approximately 5.0 at the high temperature of 423 K. A mathematical model for fixed bed adsorption studies was used and validated through the experimental data predicting with good accuracy the behavior of the transient breakthrough experiments being a valuable tool for the analysis and design of cyclic adsorption processes (PSA) for biogas upgrading strategies to biomethane and CO₂ capture using 13X zeolite.

1 INTRODUCTION

Biogas is a raw gaseous stream produced by the anaerobic decomposition of organic matter in units called digesters. It is mainly composed by CH₄ (50 to 70%) and CO₂ (30 to 40%) and to obtain a high energy content CO₂ needs to be separated from CH₄. Major sources of biogas production are landfills, waste-water treatment plants, manure fermentation, fermentation of energy crops and coal-bed methane. To increase the heating value of the biogas it's necessary to remove CO₂ and the upgraded biogas can be used as a vehicle fuel in cars and buses or injected in the natural gas grid of a city or power plant.

Two recent reviews discuss this matter with great detail concerning the use of adsorbents (porous solids) based technologies to handle CO₂ capture and CO₂/CH₄ separations (Férey et al., 2011; D'Alessandro et al., 2010). For this purpose many solid physical adsorbents have been considered including molecular sieve zeolites and a new class of adsorbents named Metal-Organic Frameworks (MOFs). Zeolite 13X is still one promising adsorbent to capture CO₂ because of the strong adsorbate-adsorbent interactions (D'Alessandro et al. 2010). One of the technologies for biogas upgrading to biomethane using adsorbents is called Pressure Swing Adsorption (PSA). With this technique, carbon dioxide is separated from the biogas by adsorption in a proper adsorbent under elevated pressure. The adsorbent material, is regenerated by a sequential decrease in pressure before the column is reloaded again, hence the name of the technique. A review about the use of PSA technology for biogas upgrading is described in detail by Grande, 2011.

The modelling of fixed bed adsorption dynamics is of fundamental importance for the design of industrial adsorbents due to the complexity of these systems, that involve several mechanisms for mass and heat transfer coupled with thermodynamic models that describe the equilibrium adsorption between gas and solid phases.

In this work, we present fixed bed adsorption transient experimental data with single and multicomponent mixtures of CO₂ and CH₄ on binderless beads of zeolite 13X at 313, 373 and 423 K

and pressures ranging from 0.1 to 0.5 MPa. A transient mathematical fixed bed adsorption model taking into account mass and energy conservation laws is used to capture the fixed bed adsorption experimental data, which could be used in the implementation (simulation) of cyclic adsorption processes (PSA, TSA) for the purification of biogas or CO₂ sequestration.

2 THEORETICAL

2.1 Mathematical model to study fixed bed adsorption dynamics

The modelling of fixed bed adsorption dynamics is very important to the design of cyclic adsorption processes to operate at industrial scale. The model should take into account the conservation laws of mass and energy in the fixed bed coupled with the thermodynamic (adsorption equilibrium isotherms) and kinetics (mass transfer rate of adsorbable species to solid adsorbent) of sorption characteristic of a certain system.

Let us consider that at time zero a mixture of known composition is introduced at the inlet of a fixed bed containing a suitable adsorbent for the separation of the mixture. If the following assumptions are made:

1. Ideal gas;
2. There is no pressure drop in the column;
3. The flow pattern is described by the axial dispersed plug flow model;
4. The mass transfer between bulk gas phase and adsorbent particle is accounted by a Linear-Driving-Force model (LDF);
5. The system is non-isothermal and non-adiabatic;
6. A resistance to heat transfer between solid adsorbent and bulk gas phase could exist in the external fluid film around the solid;
7. There is no temperature gradients inside the porous adsorbents (the temperature is homogeneous in the solid).

Silva (1998) according to these assumptions developed a mathematical model to simulate the fixed bed adsorption of gaseous mixtures and PSA cycles in adsorbent materials.

2.2 Thermodynamic adsorption model

Coupled with the mathematical fixed bed adsorption model we must have a suitable thermodynamic adsorption equilibrium description for the system since the transient response of the bed at the outlet will depend dramatically of the efficacy of such model. There are in literature several idealized adsorption isotherm models to describe the equilibrium distribution of guest molecules and host porous adsorbents. In a previous work it has been shown that an appropriate model to describe the binary sorption behavior of CO₂ and CH₄ on binderless zeolite 13X is the Fowler model (Silva et al., 2012) which is described by the following equations,

$$\frac{1}{p_1} \frac{\theta_1}{1-(\theta_1+\theta_2)} = b_1 \exp\left(-\frac{w_{11}\theta_1}{RT} - \frac{w_{12}\theta_2}{RT}\right) \quad (1)$$

$$\frac{1}{p_2} \frac{\theta_2}{1-(\theta_1+\theta_2)} = b_2 \exp\left(-\frac{w_{22}\theta_2}{RT} - \frac{w_{12}\theta_1}{RT}\right) \quad (2)$$

where $\theta = q/q_m$ is the degree of filling of sites, b is an equilibrium constant, p the pressure, q the amount adsorbed and q_m is the amount adsorbed at the saturation of the adsorbent, w is the extra energy when sorbate molecules occupy adjacent sites, R the ideal gas constant and T the temperature. The subscripts 1 and 2 refer to the adsorbable species (1) (CO₂) and 2(CH₄) along the manuscript. Table 1 show the adsorption equilibrium model parameters.

Table 1. Isotherm model parameters for single and binary sorption of CO₂ and CH₄ in binderless beads of 13X zeolite (data from Silva et al. 2012).

		CO ₂ (1)	CH ₄ (2)
q_m	(mol/kg _{ads})	7.4	7.4
ΔH	(kJ/mol)	-43.1	-8.9
w_{11}	(kJ/mol)	12.3	-
w_{22}		-	-
		313 K	
b	(atm ⁻¹)	21.3	0.0643
$-w_{12}/RT$	(-)		1.39
		373 K	
b	(atm ⁻¹)	1.49	0.0374
$-w_{12}/RT$	(-)		1.25
		423 K	
b	(atm ⁻¹)	0.286	0.0256
$-w_{12}/RT$	(-)		1.10

3 EXPERIMENTAL

3.1 Adsorbent and adsorbates

The powder of 13X from which the binderless beads were formed is from Chemiewerk Bas Kostritz GmbH (Germany) with a Si/Al ratio of 1.18. Metakaolin is used to manufacture the beads. The synthesis and characterization procedure is described in detail elsewhere (Schumann et al., 2012). Briefly, the beads formed consist in spherical particles with a diameter ranging from 1.2 to 2.0 mm. The size of the zeolite crystals are around 2 μ m.

The sorbate and inert gases were furnished by Air Liquid with the following purities: methane N35 (99.95%), carbon dioxide N48 (99.998%), and helium ALPHAGAZ 2 (99.9998%).

3.2 Single and multicomponent fixed bed experiments

To study of the adsorption of CO₂ and CH₄ in the fixed bed was performed in a stainless steel column of 4.6 mm i.d. with 80 mm length containing the zeolite 13X beads which were placed inside a chromatographic oven with automatic temperature control. A typical experiment consists in measuring continuously the transient concentration histories at the outlet of the column using a thermal conductivity detector (TCD) and a mass spectrometer (MS) after feeding the column with a single component or mixtures of CO₂ and CH₄ of known composition. When the saturation is reached, the column is regenerated being prepared for another run. Details of the apparatus and experimental procedure can be found in detail elsewhere (Bastin et al., 2008).

4 RESULTS AND DISCUSSION

Breakthrough curves or the transient response at the outlet of the bed to an input of a single component or mixture feed at inlet is the more realistic way to evaluate the performance of an adsorbent for a specific separation or encapsulation of compounds. In the present study, several breakthrough curves were performed by feeding a fixed bed column containing beads of zeolite 13X with CO₂ or CH₄ or a mixture of both to evaluate the separation performance of the fixed bed adsorption system.

4.1 Single component fixed bed adsorption experiments of CO₂ and CH₄

Figure 1 shows two typical experimental breakthrough experiments obtained for the sorption of CO₂ (Figure 1a) and CH₄ (Figure 1b) at 313 K and total pressure in the column of 0.1 MPa. The

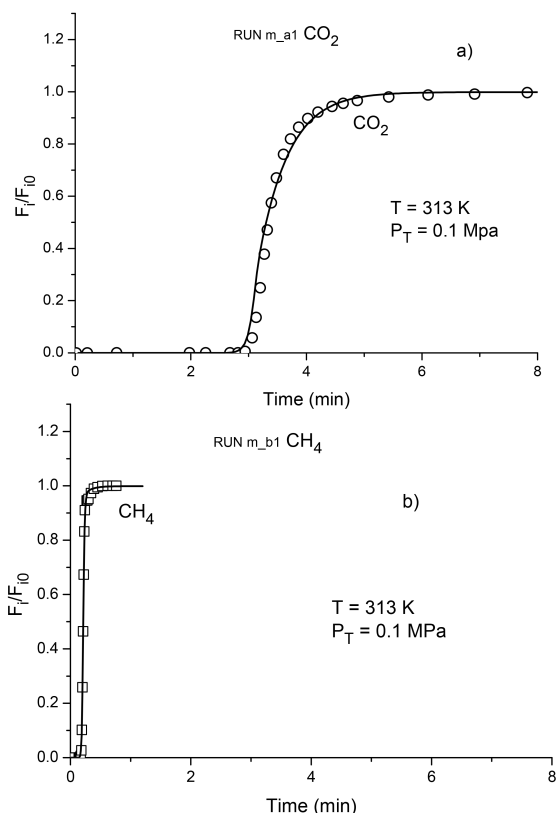


Figure 1. Single component experimental breakthrough curves (points) on binderless beads of 13X zeolite at 313 K and total pressure 0.1 MPa and comparison with the mathematical model (lines). (a) CO₂ feed at 21.7 Nml/min diluted in helium at 21.8 Nml/min. (b) CH₄ feed at 21.8 Nml/min diluted helium at 19.3 Nml/min. The simulation of the experimental runs with the mathematical model and respective parameters and correlations were adapted from the work of Silva (1998).

breakthrough time of CO₂ starts at 3 min spreading to the final input concentration at near 6 min. On the contrary, CH₄ (Figure 1b) breaks the column in much less than 1 min (practically with no adsorption) with a sharpening front. These results show that zeolite 13X has a strong affinity for CO₂ at 313 K being the sorption of CH₄ practically negligible. This means that we can predict that in mixture sorption zeolite 13X is able to separate with great efficiency CO₂ from binary mixtures of CO₂/CH₄ with a very high selectivity. At the same time, we can also conclude that the capacity of zeolite 13X to sequestrate CO₂ is very high being a good alternative to be used in systems where it is necessary to capture it. For the experiment reported in Figure 1a the amount adsorbed of CO₂ is around 3.8 mol/kg which can be considered a very high value at a total pressure in the column around 0.1 MPa. The lines in the figures represent model predictions and we can also conclude that the mathematical model capture with good accuracy the concentration profile of the transient breakthrough curves.

4.2 Binary CO₂/CH₄ fixed bed adsorption experiments

In strategies for biogas upgrading we wish to separate CO₂ from CH₄ by feeding the fixed bed column with mixtures of known composition and separate CH₄ from CO₂. When in contact with the adsorbent, the mixture is selectively adsorbed in the fixed bed due to differences in the adsorption strengths between the compounds, giving rise to the formation of different mass travelling waves

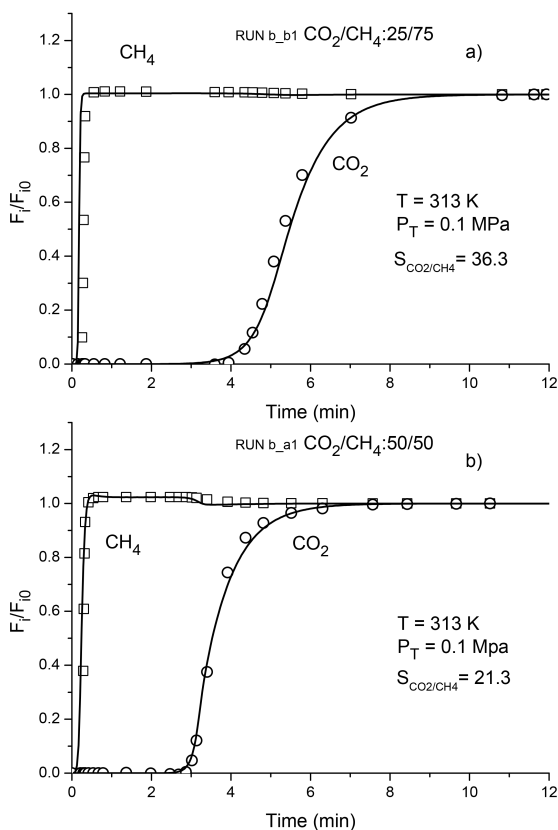


Figure 2. Binary CO₂/CH₄ experimental breakthrough curves (points) on binderless beads of 13X zeolite at 313 K and 0.1 MPa and comparison with the mathematical model (lines). (a) Binary mixture with 25(CO₂)/75(CH₄) feed at 9.2 Nml/min CO₂, 26.9 Nml/min CH₄ diluted in helium at 19.2 Nml/min. (b) Binary mixture with 50(CO₂)/50(CH₄) feed at 16.5 Nml/min CO₂, 16.5 Nml/min CH₄ diluted in helium at 16.5 Nml/min. The simulation of the experimental runs with the mathematical model and respective parameters and correlations were adapted from the work of Silva (1998).

along the bed, resulting in a transient breakthrough curve at the outlet with a different composition of the one at bed inlet until it is completely saturated. To demonstrate this, we present two typical binary breakthrough curves obtained after feeding the column with mixtures of CO₂/CH₄. Figure 2a shows an experimental breakthrough curve after feeding the column with a 50(CO₂)/50(CH₄) and Figure 2b with a 25(CO₂)/75(CH₄) mixture diluted with helium (inert) at the temperature of 313 K and total pressure in the column of 0.1 MPa. Figure 2a clearly shows a complete separation between CO₂ and CH₄ with a long plateau of pure CH₄ of almost 4 min for the 25/75 mixture ratio. The selectivity measured by the ratio of the amounts adsorbed of the two components is $S_{CO_2/CH_4} = 36.3$. Also interesting is the fact that Figure 2a,b shows that CH₄ breaks the column practically at the beginning of the experiment. Remarkable also is that the mass transfer zone for CH₄ is very sharp which very interesting for separation purposes. In Figure 2b for the 50/50 mixture ratio the selectivity decrease ($S_{CO_2/CH_4} = 21.3$) but it can be considered also very high. At the same time, the lines in the figures show that the mathematical model developed is also capable to capture with good accuracy the concentration profiles of both compounds as well as the plateaus of pure CH₄ observed experimentally in mixture sorption, being a valuable tool for the design of cyclic industrial processes (PSA).

Table 2. Selectivities as a function of temperature and total mixture pressure for several binary 50/50 and 25/75 binary, obtained from several breakthrough experiments.

Total Pressure (MPa)	50(CO ₂)/50(CH ₄)			25(CO ₂)/75(CH ₄)		
	313 K	373 K	423 K	313 K	373 K	423 K
0.5	10.4	6.4	5.4	14.4	8.7	6.8
0.3	11.3	7.9	5.5	19.7	10.8	7.1
0.1	21.3	16.6	7.4	36.3	19.8	10.3

4.3 Selectivities for several CO₂/CH₄ fixed bed experiments

Table 2 resumes the selectivities obtained for several 50/50 and 25/75 CO₂/CH₄ mixture breakthrough experiments as a function of total pressure. Table 2 shows that the selectivities are high at the low temperature of 313 K and total pressure 0.1 MPa being 36.3 (Experiment – Figure 2a) and 21.3 (Experiment – Figure 2b) for the 25/75 and 50/50 mixtures, respectively. As the pressure increases the selectivities decrease but the values are still considerable high at 313 K and total pressure of 0.5 MPa ranging from 14.4 to 10.4 for the 25/75 and 50/50 mixtures ratios, respectively. These results show that binderless beads of 13X zeolite can be considered an excellent separator of mixtures CO₂/CH₄ when appropriate operating conditions are chosen.

5 CONCLUSIONS

Through this work we show an experimental study of the sorption of single and binary mixtures of CO₂ and CH₄ in binderless beads of 13 X zeolite. The single component transient fixed bed adsorption experiments performed with CO₂ show that zeolite 13X is very efficient to encapsulate it. However, with CH₄ we see a complete different picture where the compound practically breaks the columns at beginning of the experiment practically with no adsorption. The efficiency of the separation of mixtures CO₂/CH₄ in the binderless beads of 13X zeolite starting from a fresh column is illustrated through two binary breakthrough curves where it is clearly seen the ability of zeolite 13X to separate CO₂ from CH₄. These results show that zeolite 13X is a good choice for strategies of upgrading biogas to biomethane. For other conditions, Table 2 resumes the selectivities obtained from several mixture breakthrough experiments with values ranging from 37 at the low pressure of 0.1 MPa and temperature of 313 K to approximately 5 at the high temperature of 423 K.

A mathematical fixed bed adsorption dynamic model coupled to the thermodynamic model of adsorption of Fowler was used and validated through the experimental data proving to be a valuable tool for the design of cyclic adsorption processes for biogas upgrading to biomethane (by PSA) and CO₂ capture.

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