# 25 Abril 1974 - 50 years

## The democratization of higher education and scientific research in Portugal

## My adsorption journey

**Alírio E. Rodrigues**
**Emeritus Professor, University of Porto**


**43ª Reunião Ibérica de Adsorção (RIA)**
**September 1, 2024, Porto, Portugal**

SRE CM ASSOCIATE LABORATORY
LABORATORY OF SEPARATION AND REACTION ENGINEERING
LABORATORY OF CATALYSIS AND MATERIALS

U.PORTO
FEUP FACULDADE DE ENGENHARIA
UNIVERSIDADE DO PORTO

**Born 1943 in Madeira island**

**WW2…no memory…**

**.. heard from grandmother about food shortages…and visited concentration camp near Lublin …**


1961

2011

**De Vault eq**., JACS (1943)

Dona Sofia taught me **perseverance** is needed in life! ~9 years old

Physics teacher Atouguia gave me a lesson by simply saying “I appreciate your memory”

~15 years old

# 1961- University of Porto; colonial war; hippies generation; May 68- students revolution in France

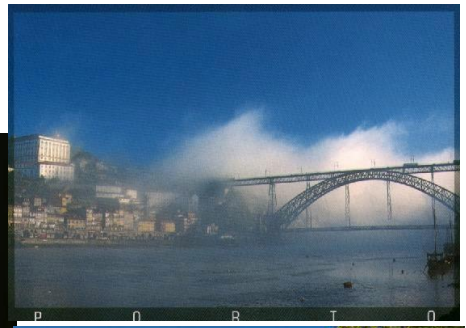

Rectorat of U.Porto-In the 60's it was the Faculty of Sciences where I studied

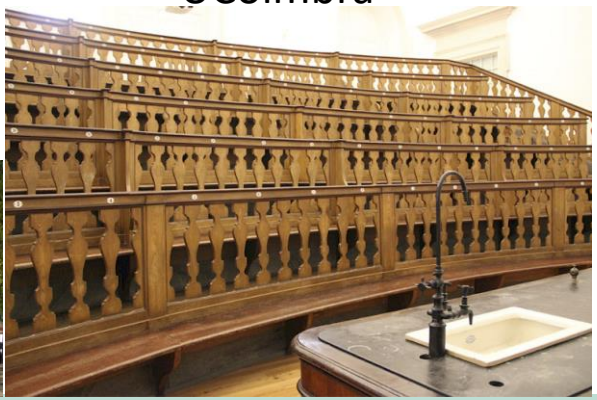
**Qualitative Analytical Chemistry**
**Find cations in a liquid mixture: external contamination!**

Chemistry Lab Prof. Ferreira da Silva

UCoimbra

Old and New FEUP





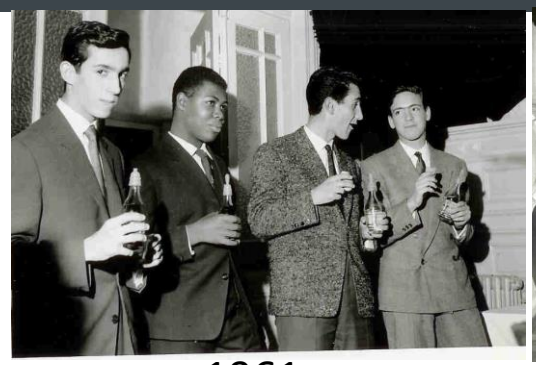
# U. Porto, training in industry, Angola…change in life (Research & Academia)

**José Saramago-**
**"The wisest man I ever knew in my whole life could not read or write"**
I was the second in my family to study in the University

**Training in a nitric acid plant (Alverca) and Hoescht textile dyeing lab (Porto)**

1966-Nitratos de Portugal

1967- Hoescht



1961

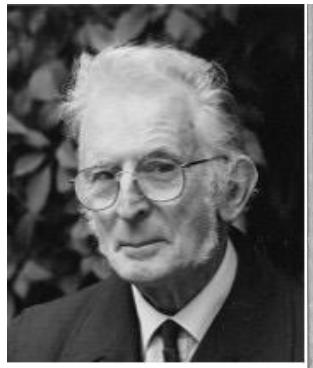
1962

1966

Luanda , Angola, October 1968-August 1970

Cuca brewery; lab of PetroFina oil refinery; U. Luanda

**Books**: **BSL** and C. **Mantell** , Adsorption, McGraw Hill, 1945


1970-September 1973 CCPC-CNRS, Dr Ing U. Nancy I

2024

Library: saturdays afternoon…

ENSIC

# São João no Porto, 1974

**Concurso  Jornal de Notícias**

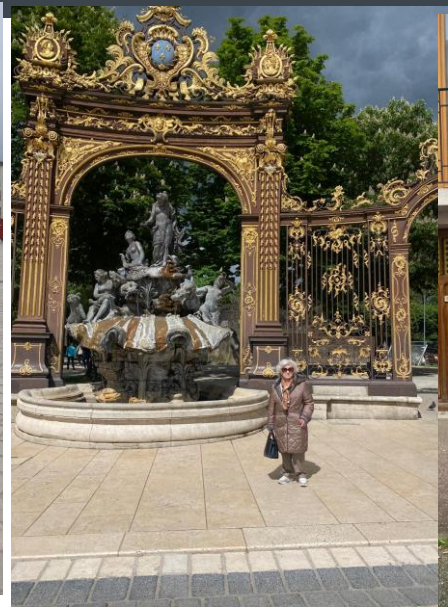
Agora também sou rico,
Ó meu rico São João
Tenho além do manjerico
Um cravo, que cheira a pão…

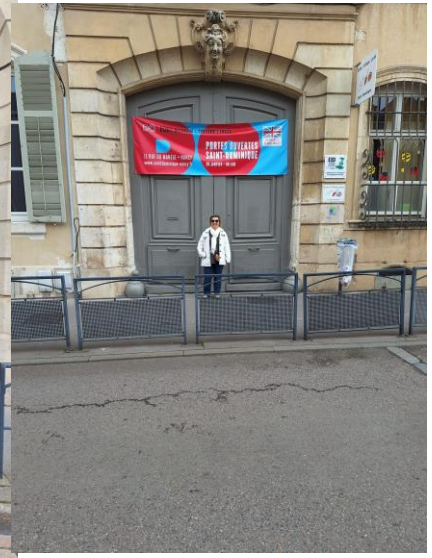
Ahora yo también soy rico
Oh mi rico San Juan
tengo ademas la albahaca
Un clavo, que huele a pan…

Google translator

**Eduardo Beira**
25 A+ 50
Uma série de fotografias sobre os “tempos de Abril”, cinquenta anos depois

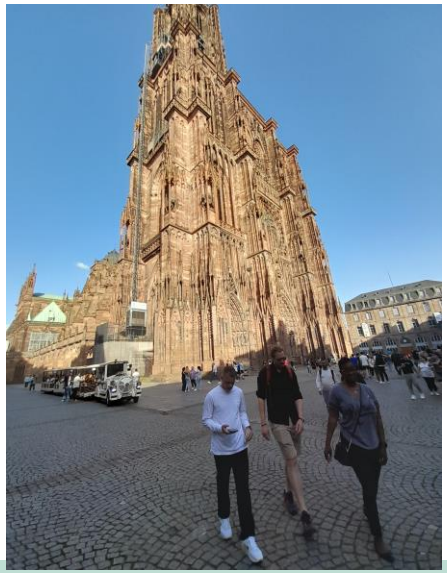
# 51 years later…Place Stanislas, 52 Rue Pierre et Marie Curie, 6 rue du Manège



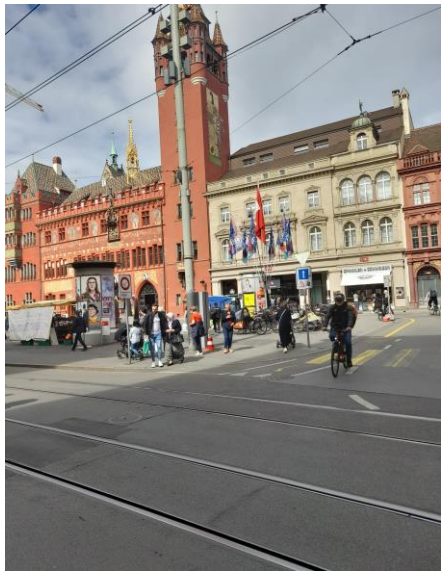



Colmar

Strasbourg



Basle



# 1970- Visit of Veiga Simão to the U. of Luanda in his travel to Lisbon to be Minister of Education

Rector of “Estudos Gerais Universitários de Mozambique”

**Minister of Education: 1970- 25/4/1974**

Curso de Engenharia Química na Univ. de Coimbra **1972**

**Created in 1973**:

Universidade Nova de Lisboa.
Universidade do Minho,
Universidade de Aveiro e
Instituto Universitário de Évora
Insituto Politécnico da Covilhã (later UBI)
IPVR, later UTAD

Ambassator of Portugal at ONU 1974-75

President of LNETI : 1978-1983

Minister of Industry and Energy 1983-85

IX Governo Constitucional

Full Professor at UBI ( 1985-1992)

**…mas também meteu “gorilas” nas Universidades em 1972**

# Back to Luanda, 25April 1974 revolution, army at the age of 30, back to Portugal

Back to U.Luanda
Nov 1973-Oct 1975
Military service at the age of 30

## April 25, 1974 Revolution

**July 1974-October 1975**
**Angola independent**
**11 November 1975**

**Back to Portugal: U. Évora Jan1976-August 76**


"Agregação" IST, Lisbon
July 1976

**Back to FEUP**
**Sept 1976**

**Creation of LSRE**
**Director of FEUP**
**1978/79**
**1984/1990**

**LSRE-LCM**
**Assoc. Lab, Dec 2004**



**Left LSRE-LCM direction end 2012**
**Retired July 2013**
**Since then Emeritus Professor**


**MMM+K**

## How to build a research group or lab

i) All projects are dreams at the beginning; if you don't wish something you don't get it!

ii) Keep eyes open to the links with other areas (cross-fertilization)

iii) In research we do what we really want to do; it can take longer than we would like because of…

*iv) Accountability*: publish research results

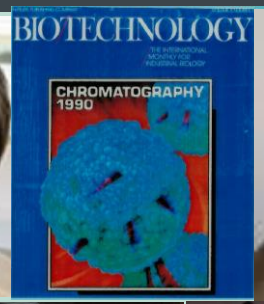
v) Each researcher has to put his fingerprint in the lab by making his own equipment*

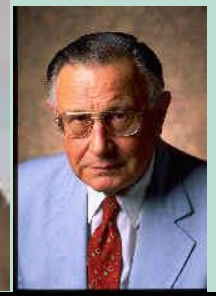
vi) Research can not be done with absent people

*this one was reinforced after listening to a lecture in a CYTED conference in Buenos Aires by Nobel Prize Richard Ernst from ETH…



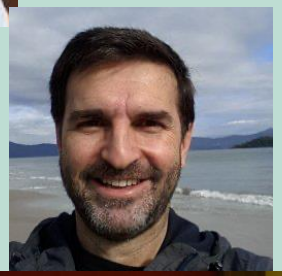


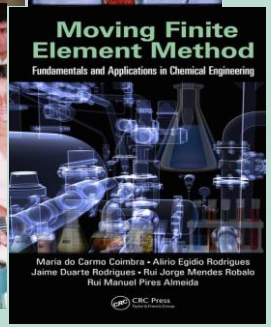



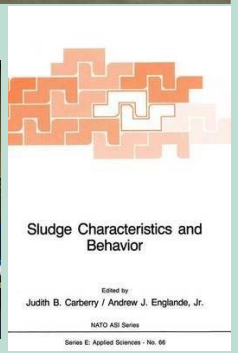
1979 Delaware











# Transition to democracy…meetings in Hungary, Checoslovakia, Poland

A.E. Rodrigues, “Ion exchange in agitated beds”, Third Symposium on Ion Exchange, Balaton Lake, May 28-31 (1974)

Letter received from the organization---saying more or less : if you are from Angola you are wellcome; if you are a colonialist don’t come…Unfortunately when coming to the new FEUP I put that letter in the garbage. I regret…
Arrival at Hotel Gloria….badge already prepared Rodriguez, France!

A.E. Rodrigues and C.Costa,”Sorption in fixed beds: Equilibrium model for sigmoid isotherms”, 6th CHISA Congress, Prague (1978)

Arriving in Prague without visa….go to the other line…but could enter the country and get a visa in the Central Police

A.E.Rodrigues, “Modeling of percolation processes” in Mathematical modeling in Chemical Engineering, Alsovice, Checoslovakia (1979)

I had a visa…but expiring the day before my flight back to Portugal….I could not get an hotel in Prague to stay the last night
After 3 trials…I stayed at the house of Vladimir Hlavacek…if police asked me where did I stay I had to answer …in the garden…

F. Almeida, C.Costa, A.E. Rodrigues and G. Grevillot, “Removal of Phenol from Wastewaters by Recuperative Mode Parametric Pumping”, 3rd International Conference “Physicochemical methods for water and wastewater treatment”, Lublin (Poland), 14-19 September 1981, in Physico-Chemical Methods for Water and Wastewater Treatment, L. Pawlowski (ed.), Studies in Environmental Sciences 19, pp 169-178, Elsevier, 1982.

An adventure arriving in Warsaw with Grevillot…without hotel room. We stayed in the house of a polish engineer (Alojamento Local). It was the time of Jaruzelvski and union movement Solidarity of Lech Walesa…To get dinner there was a queue like a canteen. In the meeting in Lublin we got at breakfast a red soup (it seems it was beet)…dinner at the house of Jaroniec and I was forgetting my passport when leaving the residence to get a train to Warsaw…

# Funding agencies…

**IAC** – Instituto de Alta Cultura, 1952-1976 ; after 1976 it became Instituto da Cultura Portuguesa ----and Research under…

**INIC Instituto Nacional Investigação Científica** : 1976-1992 extinction

**Centro de Engenharia Química (FEUP)- Linha 5: Processos de separação e reação em meios porosos e dispersos**

**JNICT Junta Nacional Investigação Cientifica e Tecnológica**: 1967-1997

Extinto em 1996 planear…coordenação e financiamento da investigação cientifica;

**Since 1997**

**FCT – Fundação para a Ciência e Tecnologia** : evaluation and funding of science and technology

**ICCTI** – internacional Cooperation

**OCT** Observatory of Science and Technology

In1991 **Mariano Gago** was the coordinator of the scientific program of Europalia, show of Portuguese art and culture which took place in Belgium.
**O estado das ciências em Portugal / coord. José Mariano Gago; ed. lit. Comissariado para a Europália 91-Portugal,** Dom Quixote, 1992 (Lisboa)

# R&D+I structure in Portugal

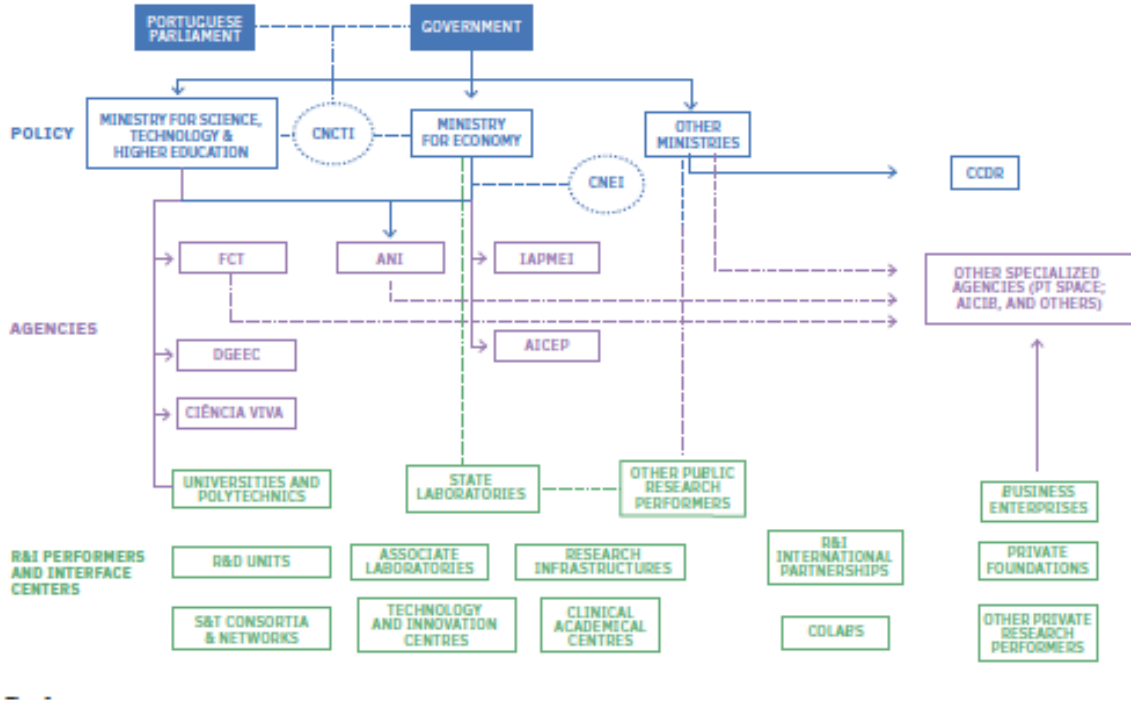

Associate Laboratory in Chemical Engineering

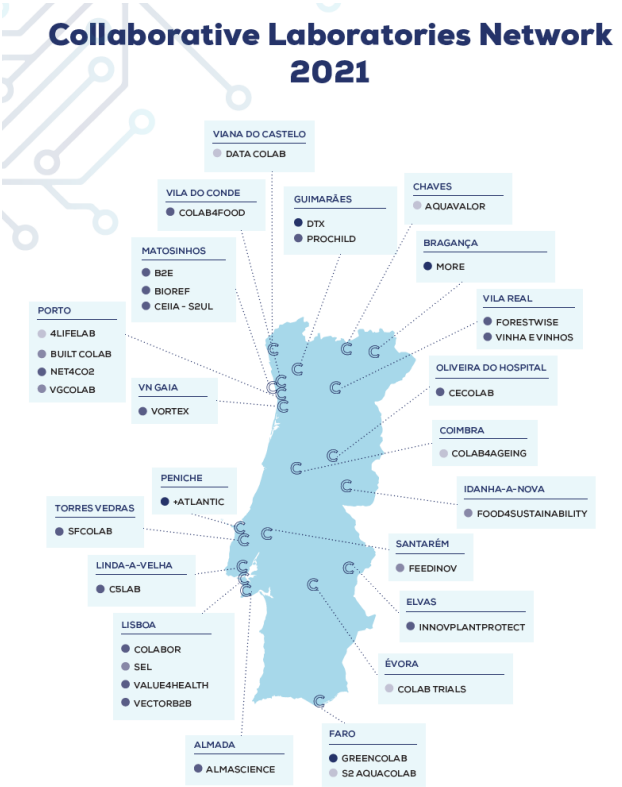
ALiCE

ALiCE

40 Laboratórios Associados (LA)
2000, Mariano Gago MCT 1995-2002 ; 2005-2011

41 Collaborative Laboratories
CoLabs (2016, Manuel Heitor MCTES 2015-2022)
336 Research Units



Ciência 2004

2002

Pedro LynceMCES 2002-2003

FCT projetos 2008

Maria da Graça Carvalho
MCES 2003-04 ; MCIES 2004-2005


LA 2004 December

# Alguns números e datas…

**1979**
**Criação do Ensino Superior Politécnico**

**1988**
**Autonomia das Universidades**

**1999**
**Avaliação das Instituições CNA**

**PhDs**

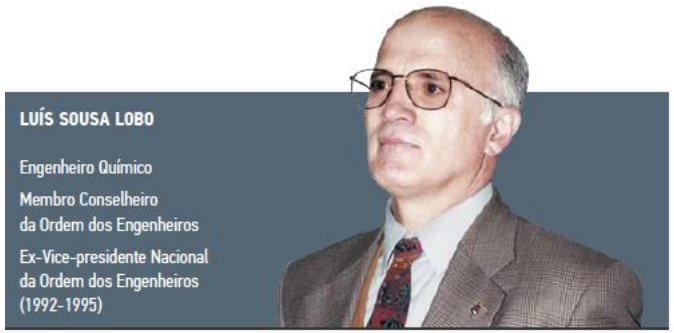
| | | |
|---|---|---|
| **1990** | **232** | |
| **2021** | **2310** | **x10** |

**Novos Alunos no Ensino Superior**

| | |
|---|---|
| 1995/96 | 81083 |
| 2022/23 | 155082 (licenciaturas 54.7%+ mestrados) |
| | (31.5% Politécnico; 49.1% Universidade) |

**Ordem do Engenheiros**
**Bastonário João Vaz Guedes 1992-95**

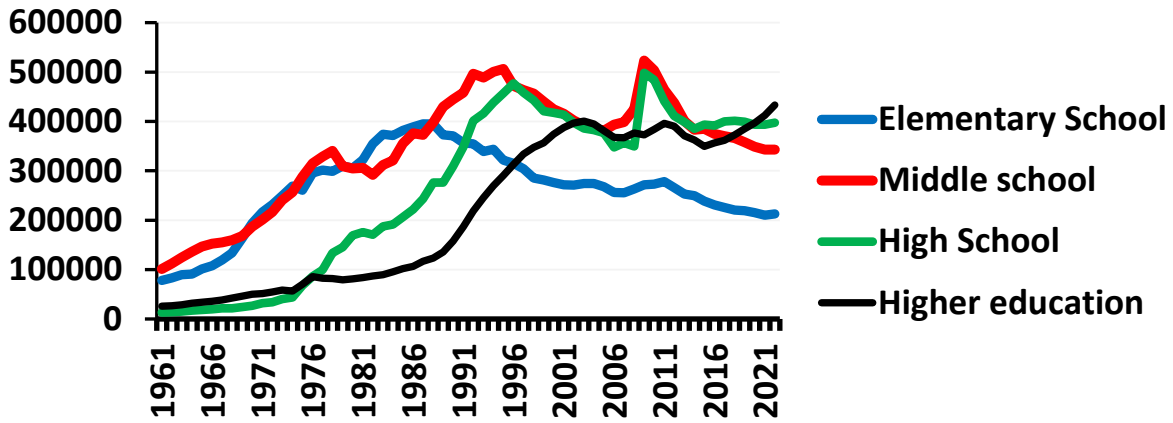
**Vice-Presidente Nacional da OE**
**Luís Sousa Lobo 1992-95**



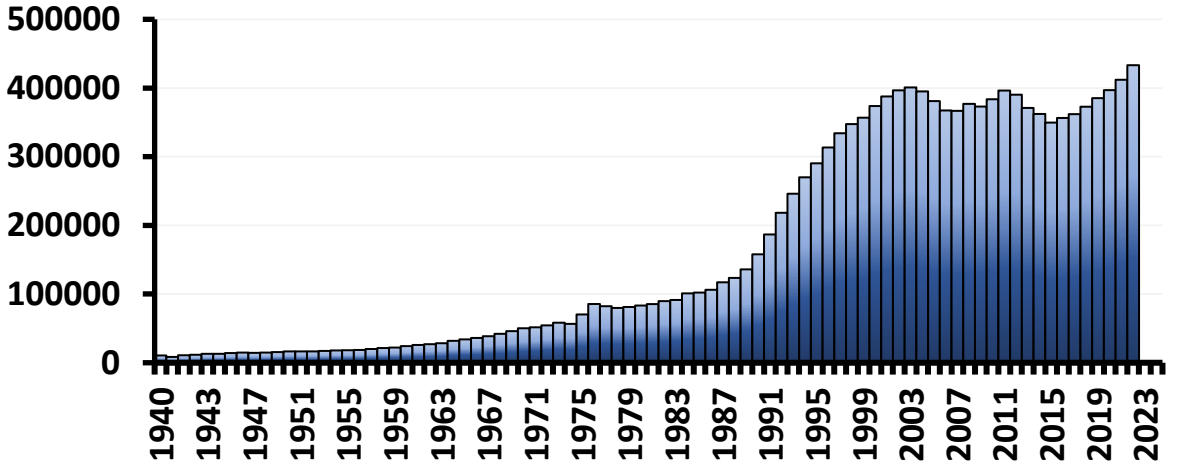

**Criação Colégios (Presidente Colégio Engenharia Química- AER)**
**Sistema de Acreditação dos Cursos Superiores de Engenharia**

# From elementary school to PhD

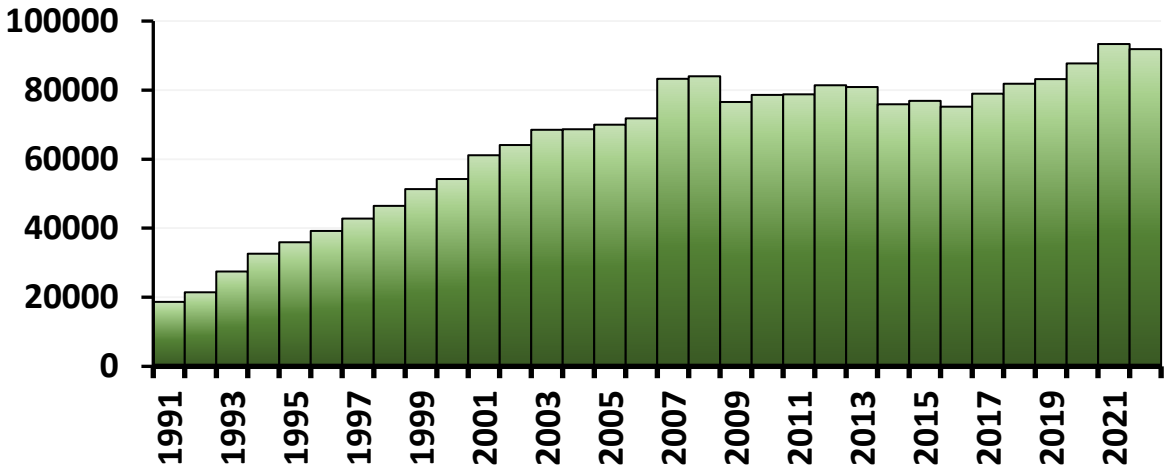
**Students enrolled : from elementary school to higher education**



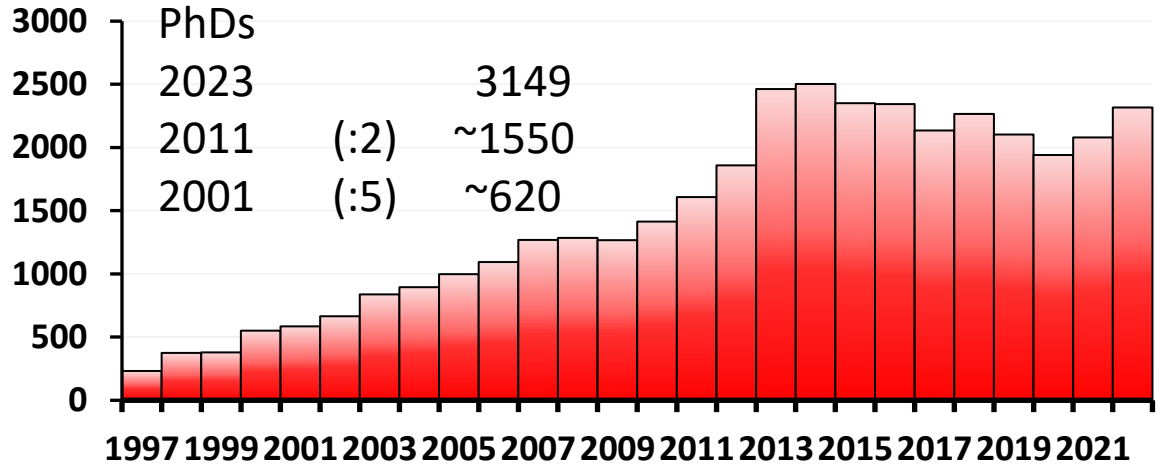

**Students enrolled in Higher Education**




**Students who completed Higher Education**



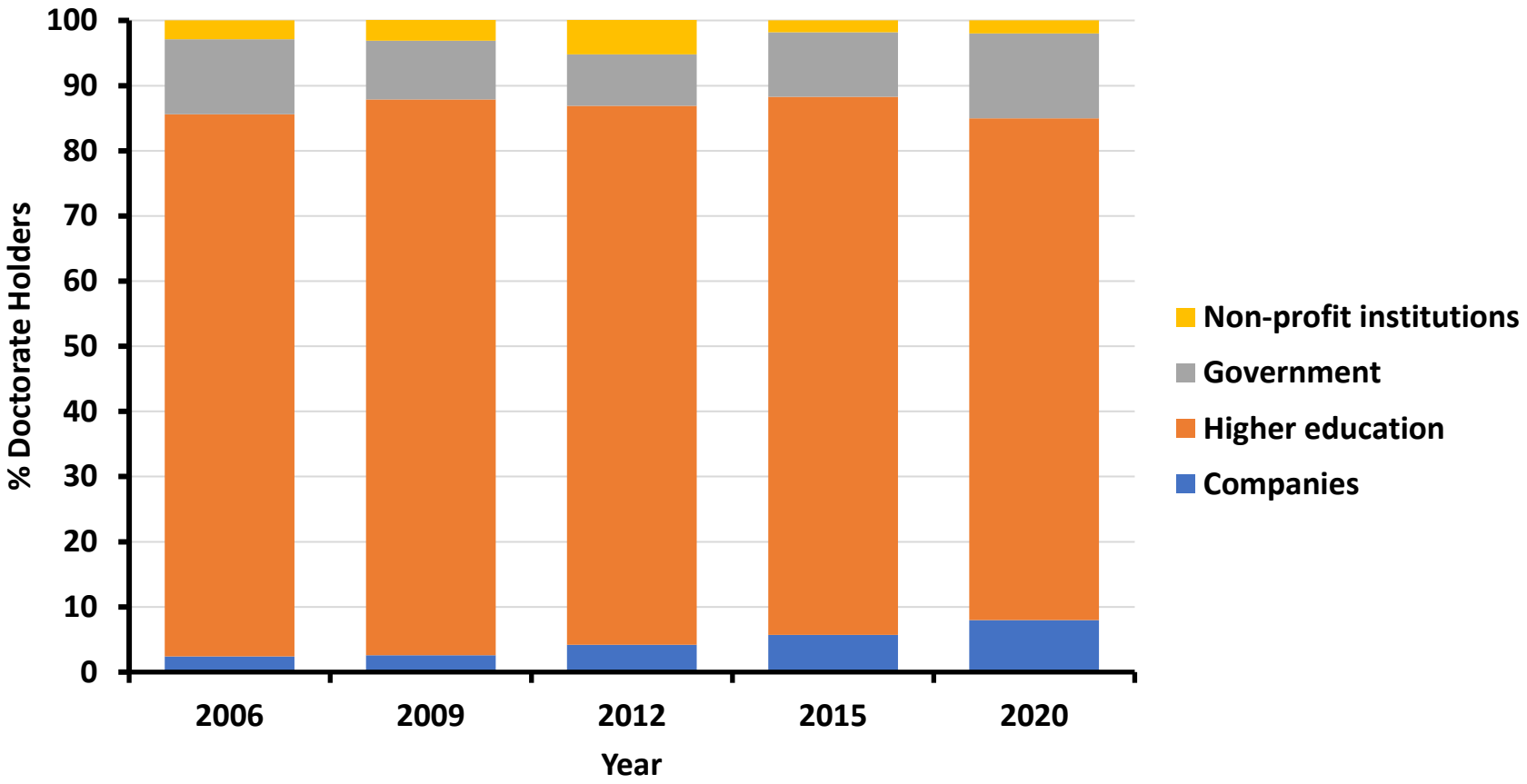

**Students who completed their PhD**






Source: Pordata (data and graphs collected by Rute Seabra and Alexandre Ferreira)

# Jobs for PhDs




11 inv/1000 hab (em linha com OCDE); 43000 PhDs in Portugal 2023
40% dos investigadores nas empresas Há 25 anos menos de 10%
despesa em I&D 1.73% PIB

Source: Pordata

Maria Manuela Leitão Marques , "A Ciência não ocupa lugar", DN 12-04-2024

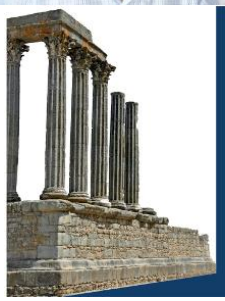
# Participation in RIA…

Oviedo III RIA (Madalena Dias) 1978
Sevilha, IV RIA, 1979
Porto, X RIA, Casa do Infante, 1985
Leon, XXVII RIA, 2002 (Carlos Grande)
Porto , XXIX RIA, 2004
Madrid, XXXIII Universidad Rey Juan Carlos I, 2008
Sevilha, XXXVII Univ Pablo de Olavide, 2012
Santander, XXXVIII RIA, 2013
Baeza, XXXIX RIA, 2014
Evora, XV RIA, 2016
Gijon, XVI RIA & IBA 3, 2018
Valencia, XVII RIA, 2022
Porto, XVIII RIA, 2024

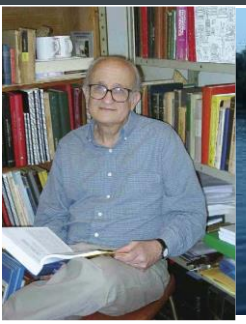

Universidad de Oviedo


2008

EBA/IBA1 -2012

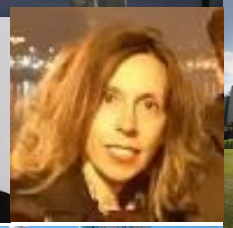
# Cooperation

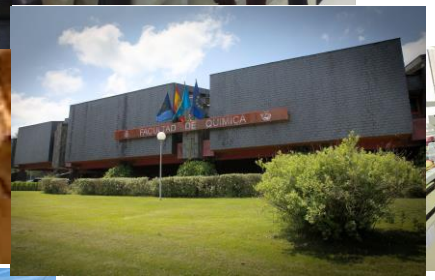


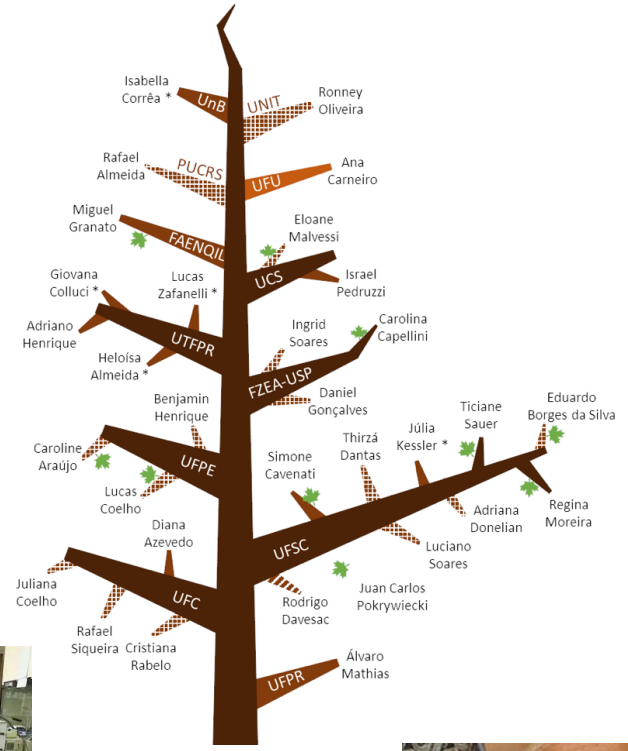
1978

1988










MsC

MsC + PhD

PhD

PhD Sandwich

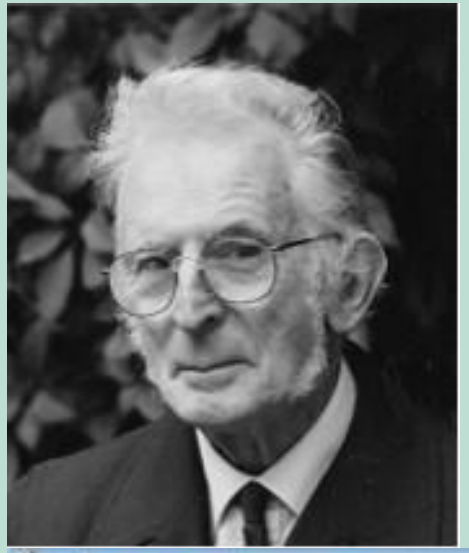
Pos

* Ongoing

# UFC, ATOMS UFRJ and UFPE



Pierre Le Goff



# Modelling

a) conservation equations (mass, energy, momentum, electric charge)

b) equilibrium laws at the interface(s)

c) constitutive laws

d) kinetic laws of heat/mass transfer and reaction

e) initial and boundary conditions

f) optimization criterion

“Se você não consegue explicar algo de forma simples, você não entendeu suficientemente bem.“
"If you can't explain something simply, you don't understand it well enough"
Le Goff told me that in Nancy; it seems the “quote” is from Einstein

# Mathematical modeling

## Mathematical model

“Any complete and consistent set of mathematical equations which is sought to correspond to some other entity, its prototype. The prototype may be a physical, biological, social, psychological or conceptual entity, perhaps even another mathematical model, though in detailed examples we shall be concerned with a few physico-chemical systems.”

Rutherford Aris

**Mathematical modelling techniques,** Pitman, **1978**

“A mathematical model is a representation, in mathematical terms, of certain aspects of a nonmathematical system. The arts and crafts of mathematical modeling are exhibited in the construction of models that not only are consistent in themselves and mirror the behavior of their prototype, but also serve some exterior purpose”.

Rutherford Aris

**Mathematical modeling. A chemical engineer´s perspective**

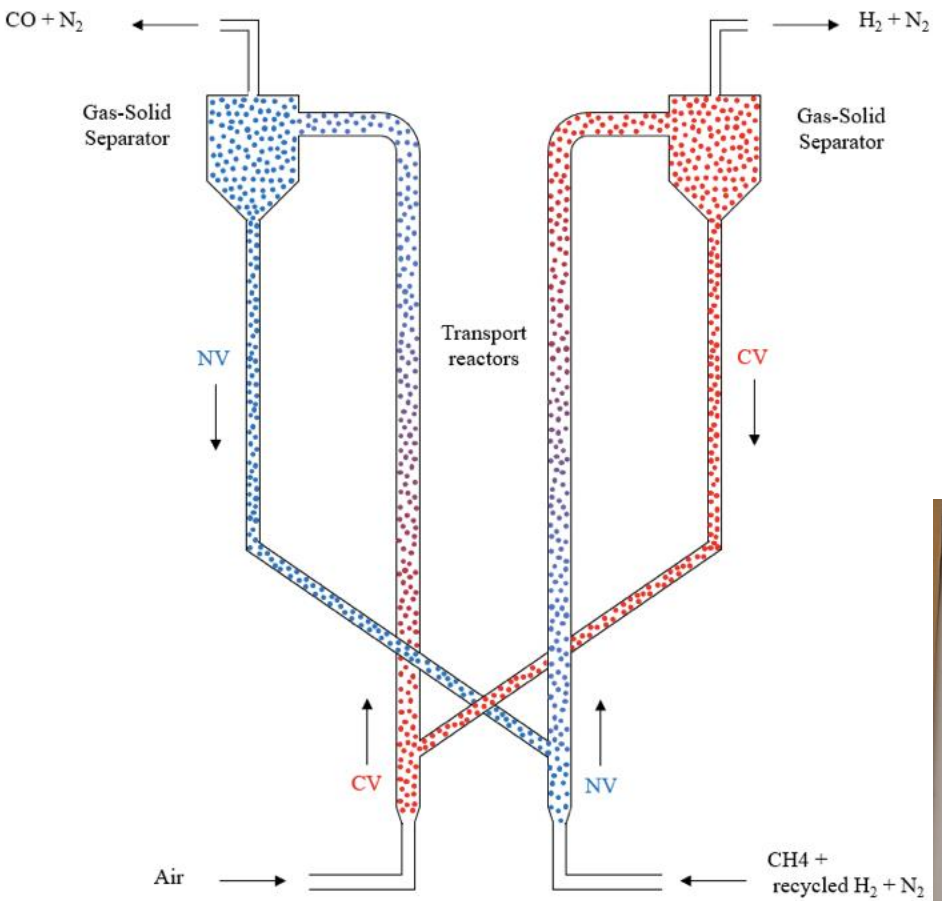
Process Systems Engineering Series Vol. 1, Academic Press, **1999**

“A mathematical model of a process is a system of equations whose solution, given specified input data, is representative of the response of the process to a corresponding set of inputs”.

Morton M. Denn

**Process Modeling**, Longman Scientific & Technical, **1986**

# Remembering DEA research

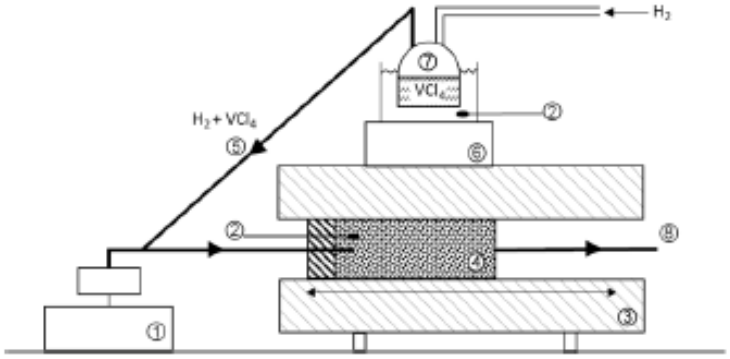



$2\ CH_4 + 2\ NV = 2\ CV + N_2 + 4\ H_2$

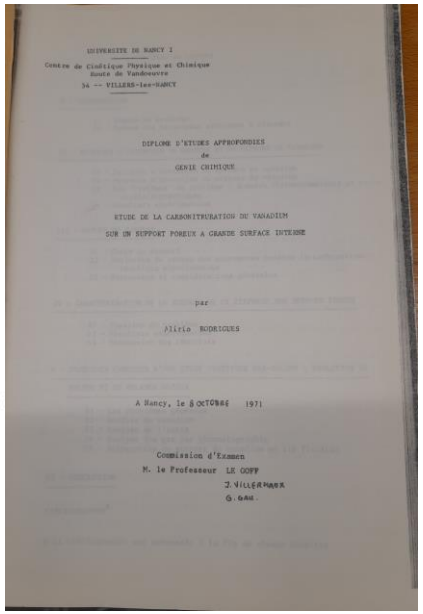
$2\ CV + N_2 + O_2 = 2\ NV + 2\ CO$

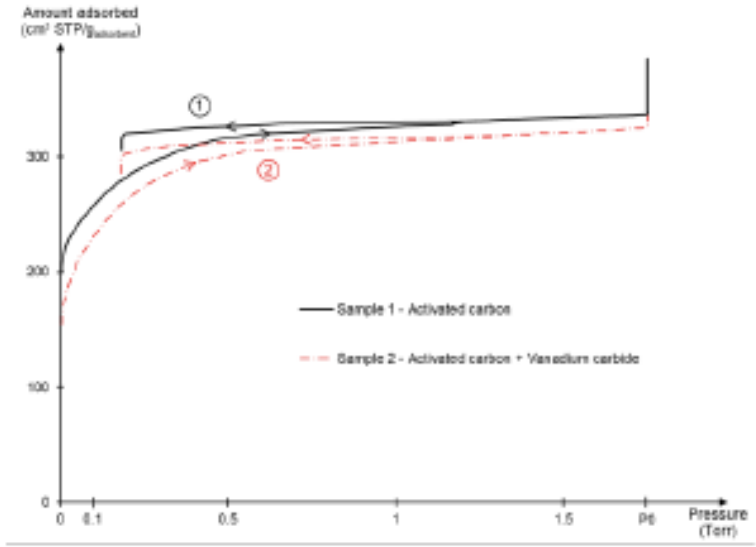
Preparing Vanadium Carbide (CVD)

$VCl_4 + 2H_2 + C = CV + 4\ HCl$




1 – Motor
2 – Thermocouples
3 – Oven
4 – Reactor with activated carbon particles ($d_p$ = 1.5mm)
5 – Tube Voltalef
6 – Heating magnetic stirrer
7 – $VCl_4$ vessel
8 – Exit to exhaust

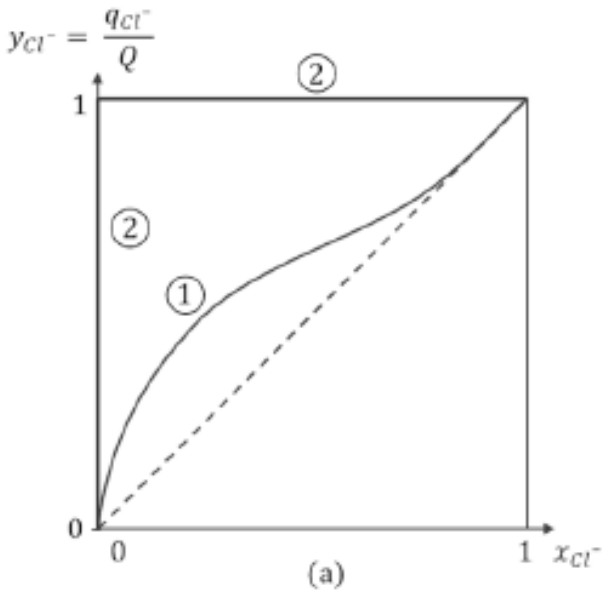





Kr, 77K

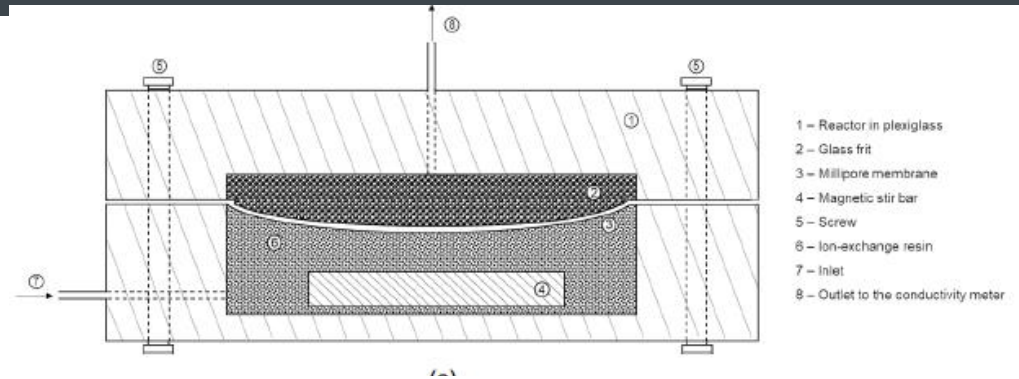
# Reaction-enhanced ion exchange

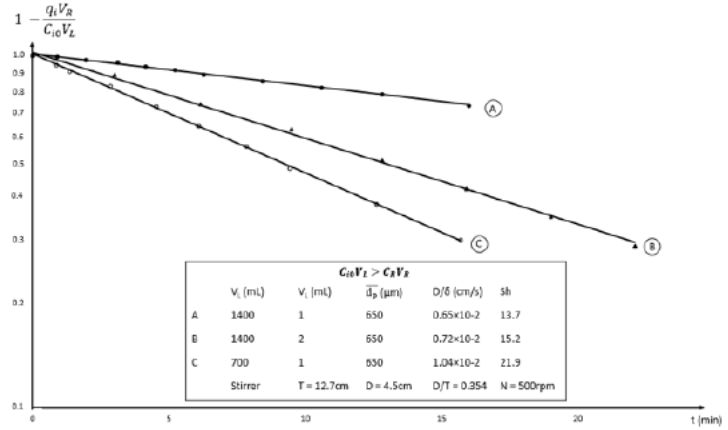
**Ion exchange with neutralization**
Anionic step of water demineralization



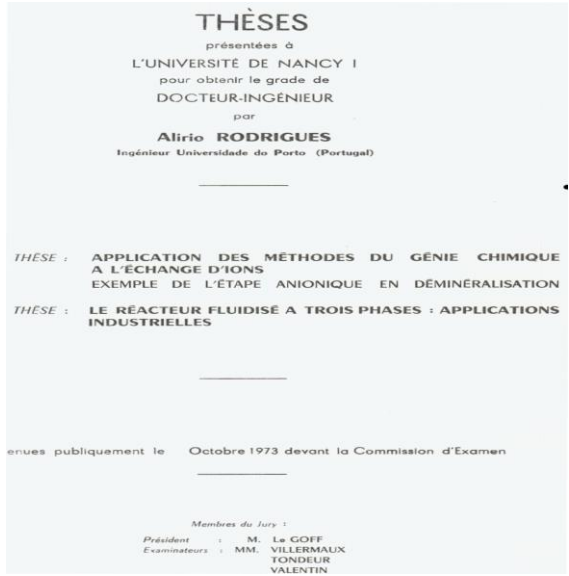

1- Ion exchange isotherms $Cl^-/OH^-$

**Reaction-enhanced ion exchange!**




Batch System

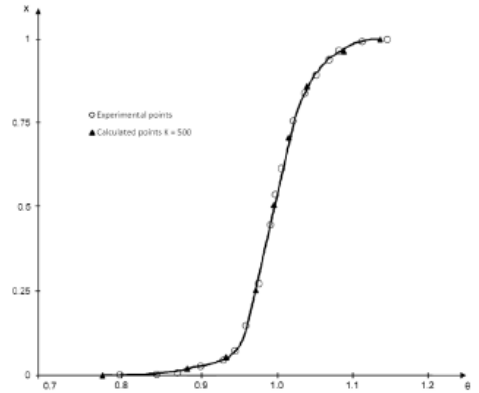

THÈSES
présentées à
L'UNIVERSITÉ DE NANCY I
pour obtenir le grade de
DOCTEUR-INGÉNIEUR
par
Alirio RODRIGUES
Ingénieur Universidade do Porto (Portugal)

THÈSE : APPLICATION DES MÉTHODES DU GÉNIE CHIMIQUE A L'ÉCHANGE D'IONS
EXEMPLE DE L'ÉTAPE ANIONIQUE EN DÉMINÉRALISATION

THÈSE : LE RÉACTEUR FLUIDISÉ A TROIS PHASES : APPLICATIONS INDUSTRIELLES

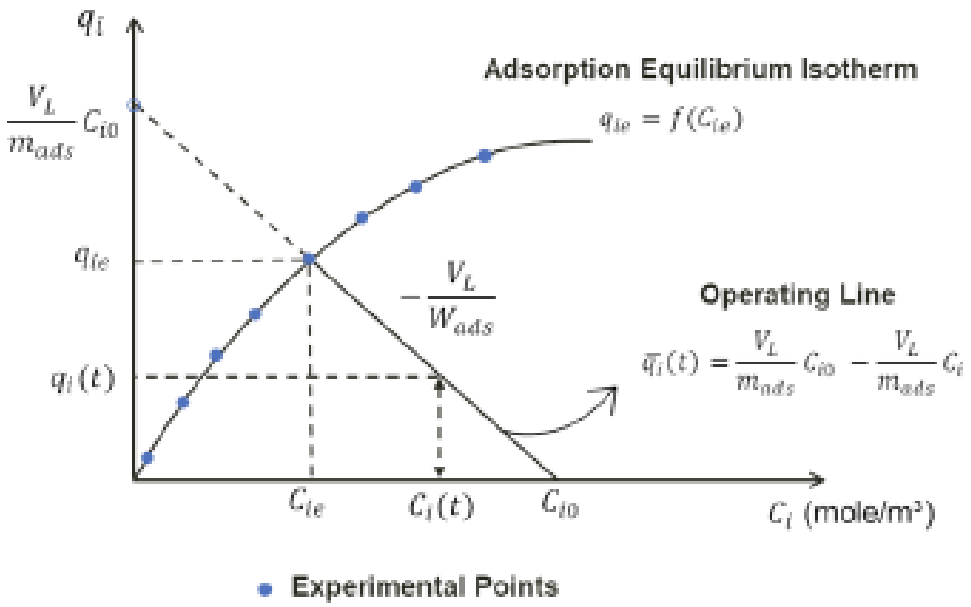
enues publiquement le Octobre 1973 devant la Commission d'Examen

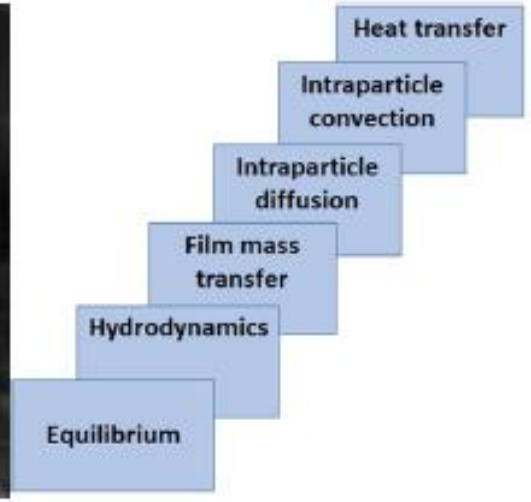
Membres du Jury :
Président : M. Le GOFF
Examinateurs : MM. VILLERMAUX
TONDEUR
VALENTIN




Open system- CSTR

# From batch adsorption to continuous column process




**First order factors**
**Langmuir…**

**Second order factors**
**Glueckauf**

## All we need: equilibrium and operating lines

**Adsorption equilibrium isotherm first.. at various temperatures…get heat of adsorption**
**Accounting: mass balance**

# Knowing and being. Essays by Michael Polanyi (edited byMarjorie Grene) University of Chicago Press, 1969

1891-1976

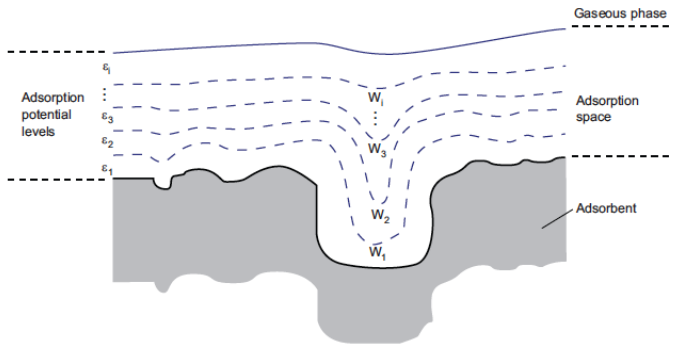


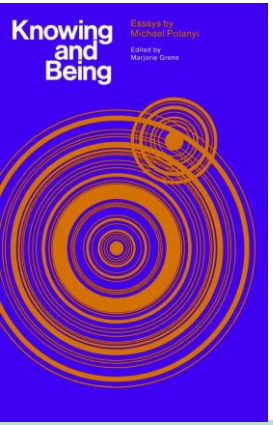

Figure 1. Schematic representation of the adsorption space corresponding to different potential levels ($\varepsilon_i$) (Brunauer 1943); the dashed lines outline the adsorbate volume, $W_i$, ascribed to each $\varepsilon_i$ value.

**The Potential Theory of Adsorption**

Authority in science has its uses and its dangers.

Michael Polanyi

Science, 141,1010 (1963)




6

## The Potential Theory of Adsorption

1963

Since 1948, when I retired from the professional pursuit of science to take up philosophy, occasional reports have reached me that my theory of adsorption, which hitherto had been rejected, was gradually gaining acceptance. Assuming that this outcome is no longer in doubt,[1] I think it worthwhile to look back on the reasons why this fairly simple matter has so long been left undecided. The story also throws light on an interesting aspect of the scientific method.

I wrote my first paper on adsorption over fifty years ago; it was published in 1914. In it I assumed (i) that the adsorption of gases on solids is due to an attraction that derives from a potential which is uniquely determined by the spatial position of the gas molecule and therefore independent of the presence of any other molecules in the field of the adsorption potential; and (ii) that, when subject to the field of adsorption, the gas behaves in accordance with its normal equation of state. When compressed to its normal vapour density, it condenses to a liquid.

These principles were first fully developed in a paper published in 1916, which also supplied a wide range of experimental verification, as follows. From a complete adsorption isotherm of a vapour, a distribution of the adsorption potential was derived, in the form $\varepsilon = f(\phi)$, $\varepsilon$ being the adsorption potential and $\phi$ the space enclosed by the level having this potential, and from this adsorption-potential curve all other measured isotherms were computed and found to agree with the theory. This result was confirmed later in a number of papers by my pupils and by other authors.[2]

Mary Jo Nye

Michael Polanyi's theory of surface adsorption: how premature?

Ernest B. Hook (Ed.), Prematurity in Science Discovery, University of California Press (2002), pp. 151-163

# The potential theory of adsorption (Michael Polanyi )

The weight of these theoretical objections was greatly increased by three experimental claims put forward by Irving Langmuir in the years 1916 to 1918. (i) Langmuir reported that the adsorption of gases on mica surfaces reached saturation with the formation of an adsorbed layer of less than monomolecular strength. (ii) He claimed that isotherms could be accounted for by an equation that has since been known as 'Langmuir's isotherm'—an equation in which it is presupposed that molecules are adsorbed at scattered centres by forces that render attraction between adsorbed molecules negligible. (iii) Langmuir proved by beautiful experiments that surface layers on water are monomolecular and that their structure is determined by electrostatic interaction with the underlying water. For this work he was awarded the Nobel prize.

All this evidence seemed to bear out the picture of short-range electrical forces, or valences, originating at discrete points of the atomic lattice forming the wall—a picture which would render my theory of adsorption untenable.

The turning point came when I was invited by Fritz Haber to give a full account of my theory in the Kaiser Wilhelm Institute for Physical Chemistry, in Berlin. Einstein was specially invited to attend my lecture. Some scientists present who had not yet fully accepted the electrical concept of interatomic forces congratulated me on the 'flood of light' I had thrown on the subject, but Einstein and Haber decided I had displayed a total disregard for the scientifically established structure of matter. Professionally, I survived the occasion only by the skin of my teeth.

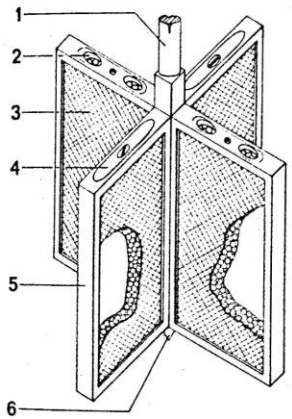
Even as professor of physical chemistry at the Victoria University of Manchester, I was unable to teach my theory. Undergraduates would have expected to be examined on it. But examinations were set and marked by a committee that included an external examiner and members of the teaching staff junior to myself. I could not undertake to force on them views totally opposed to generally accepted opinion. A system of collegiate examinations severely curtails the teaching of views that conflict with currently dominant scientific opinion.

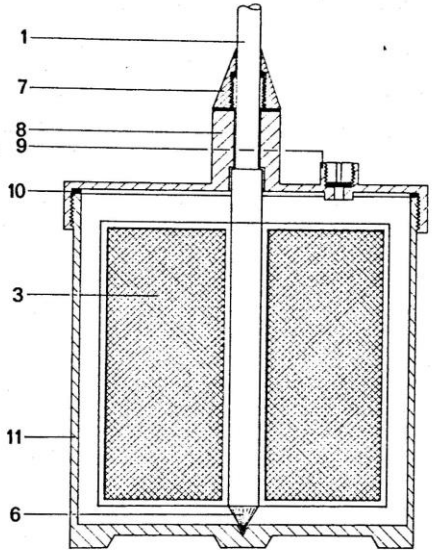
And yet deliverance was approaching. In 1930, F. London put forward a new theory of cohesive forces, based on quantum mechanical resonance between the polarization of electronic systems. I immediately fired the following question at London: 'Are these forces subject to screening by intervening molecules? Would a solid acting by these forces possess a spatially fixed adsorption potential?' London carried out the computation, and we published the result jointly (in 1930): adsorptive forces behave exactly in accordance with the assumptions of my theory. Having found this, we inferred that the adsorption potential of a solid wall decreases with the third power of the distance from the wall. (I refer to this inference hereafter as the 'inverse third power law'.)

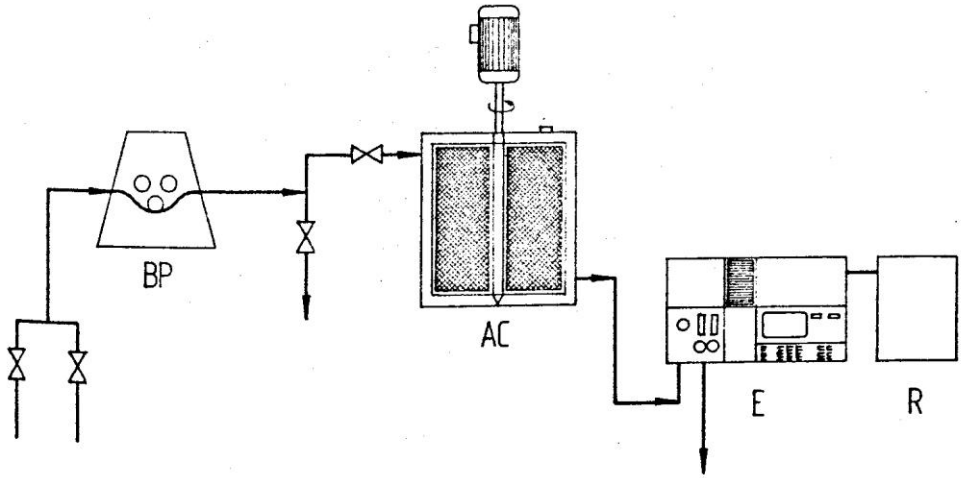
The following year I was invited to give an introductory lecture before the Faraday Society on the subject of adsorption. In this lecture I showed that application of the inverse third power law to determine adsorption potential for a wedge-shaped crevice yields $\varepsilon = f(\phi)$ curves of the characteristic type observed for charcoal.

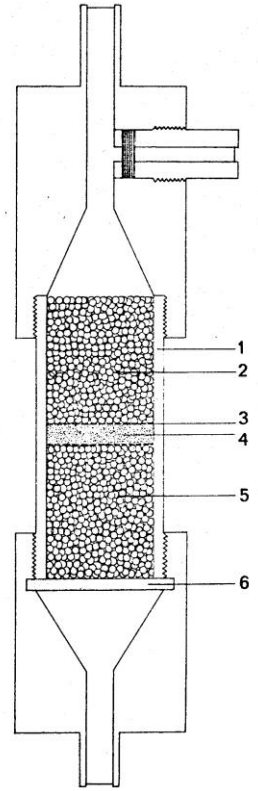
I thought I had now won the battle I had fought for fifteen years. But my paper before the Faraday Society actually made no impression.[4] It seems that by this time the opinion that my theory was false had hardened to a point where the reasons for which it had been rejected were forgotten. Hence my refutation of these objections had no effect.

# Measuring intraparticle diffusion, film mass transfer…

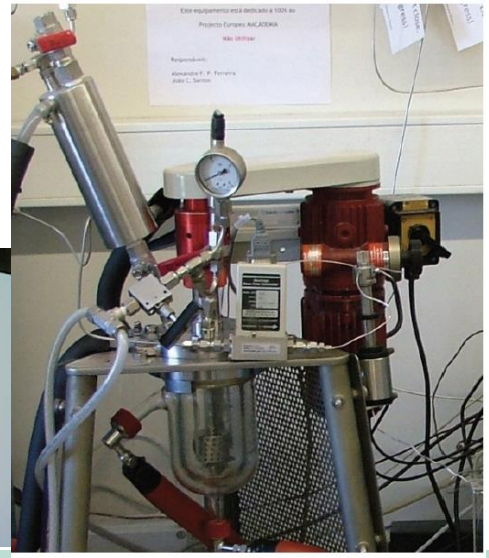



**Basket adsorber** used in the thesis of C. Costa
in batch and open mode
I was inspired by the Carberry basket reactor



**Shallow bed**
…later more fancy ZLC

# Don De Vault, 1943

## Equilibrium theory of adsorption columns

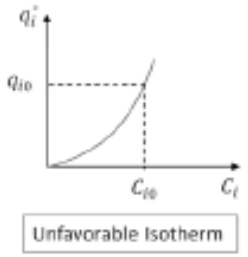
**“Modèle simplissime” – Pierre Le Goff**

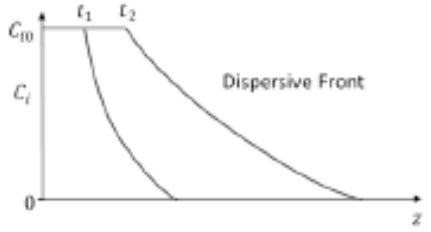
**Isothermal; negligible pressure drop, plug flow,**

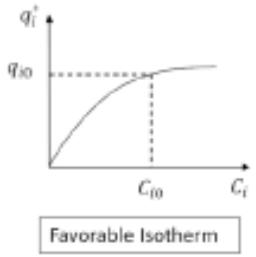
**Dilute systems; no mass /heat transfer resistances**

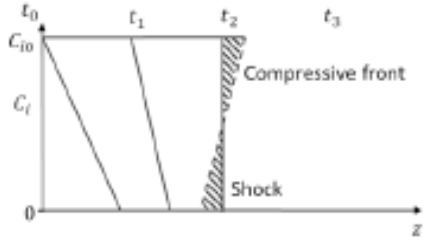
$$u_0 \frac{\partial c_i}{\partial z} + \varepsilon \frac{\partial c_i}{\partial t} + (1-\varepsilon)\frac{\partial q_i^*}{\partial t} = 0$$

$$q_i^* = f(c_i)$$

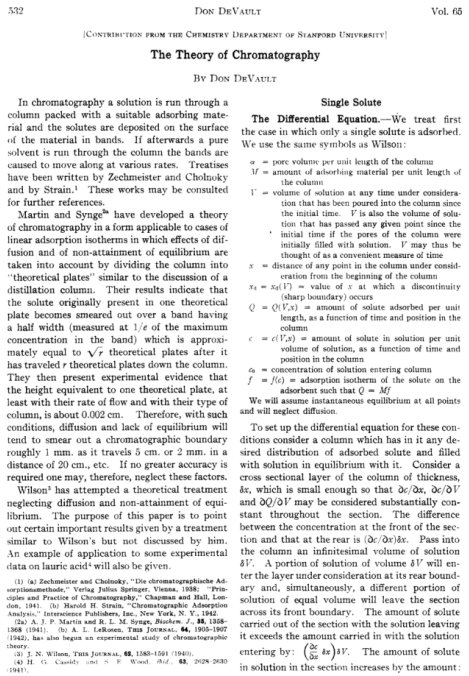



**Dispersive and Compressive concentration fronts**



532 DON DEVAULT Vol. 65

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF STANFORD UNIVERSITY]

**The Theory of Chromatography**

BY DON DEVAULT

In chromatography a solution is run through a column packed with a suitable adsorbing material and the solutes are deposited on the surface of the material in bands. If afterwards a pure solvent is run through the column the bands are caused to move along at various rates. Treatises have been written by Zechmeister and Cholnoky and by Strain.[1] These works may be consulted for further references.

Martin and Synge[2a] have developed a theory of chromatography in a form applicable to cases of linear adsorption isotherms in which effects of diffusion and of non-attainment of equilibrium are taken into account by dividing the column into "theoretical plates" similar to the discussion of a distillation column. Their results indicate that the solute originally present in one theoretical plate becomes smeared out over a band having a half width (measured at $1/e$ of the maximum concentration in the band) which is approximately equal to $\sqrt{r}$ theoretical plates after it has traveled $r$ theoretical plates down the column. They then present experimental evidence that the height equivalent to one theoretical plate, at least with their rate of flow and with their type of column, is about 0.002 cm. Therefore, with such conditions, diffusion and lack of equilibrium will tend to smear out a chromatographic boundary roughly 1 mm. as it travels 5 cm. or 2 mm. in a distance of 20 cm., etc. If no greater accuracy is required one may, therefore, neglect these factors.

Wilson[3] has attempted a theoretical treatment neglecting diffusion and non-attainment of equilibrium. The purpose of this paper is to point out certain important results given by a treatment similar to Wilson's but not discussed by him. An example of application to some experimental data on lauric acid[4] will also be given.

(1) (a) Zechmeister and Cholnoky, "Die chromatographische Adsorptionsmethode," Verlag Julius Springer, Vienna, 1938; "Principles and Practice of Chromatography," Chapman and Hall, London, 1941. (b) Harold H. Strain, "Chromatographic Adsorption Analysis," Interscience Publishers, Inc., New York, N. Y., 1942.

(2a) A. J. P. Martin and R. L. M. Synge, *Biochem. J.*, **35**, 1358-1368 (1941). (b) A. L. LeRosen, THIS JOURNAL, **64**, 1905-1907 (1942), has also begun an experimental study of chromatographic theory.

(3) J. N. Wilson, THIS JOURNAL, **62**, 1583-1591 (1940).

(4) H. G. Cassidy and N. F. Wood, *Ibid.*, **63**, 2628-2630 (1941).

**Single Solute**

**The Differential Equation.**—We treat first the case in which only a single solute is adsorbed. We use the same symbols as Wilson:

$\alpha$ = pore volume per unit length of the column
$M$ = amount of adsorbing material per unit length of the column
$V$ = volume of solution at any time under consideration that has been poured into the column since the initial time. $V$ is also the volume of solution that has passed any given point since the initial time if the pores of the column were initially filled with solution. $V$ may thus be thought of as a convenient measure of time
$x$ = distance of any point in the column under consideration from the beginning of the column
$x_0 = x_0(V)$ = value of $x$ at which a discontinuity (sharp boundary) occurs
$Q = Q(V,x)$ = amount of solute adsorbed per unit length, as a function of time and position in the column
$c = c(V,x)$ = amount of solute in solution per unit volume of solution, as a function of time and position in the column
$c_0$ = concentration of solution entering column
$f = f(c)$ = adsorption isotherm of the solute on the adsorbent such that $Q = Mf$

We will assume instantaneous equilibrium at all points and will neglect diffusion.

To set up the differential equation for these conditions consider a column which has in it any desired distribution of adsorbed solute and filled with solution in equilibrium with it. Consider a cross sectional layer of the column of thickness, $\delta x$, which is small enough so that $\partial c/\partial x$, $\partial c/\partial V$ and $\partial Q/\partial V$ may be considered substantially constant throughout the section. The difference between the concentration at the front of the section and that at the rear is $(\partial c/\partial x)\delta x$. Pass into the column an infinitesimal volume of solution $\delta V$. A portion of solution of volume $\delta V$ will enter the layer under consideration at its rear boundary and, simultaneously, a different portion of solution of equal volume will leave the section across its front boundary. The amount of solute carried out of the section with the solution leaving it exceeds the amount carried in with the solution entering by: $\left(\frac{\partial c}{\partial x}\delta x\right)\delta V$. The amount of solute in solution in the section increases by the amount:

$$u_{c_i} = \left.\frac{\partial z}{\partial t}\right|_{c_i} = \frac{u_0}{\varepsilon + (1-\varepsilon) f'(c_i)}$$

# De Vault equation (1943)

# Gordon Conference, New Hampshire 1982

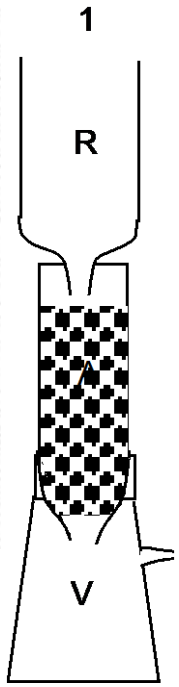
With my co-supervisor **Daniel Tondeur** and **Mr Grammont** from Diaprosim… provided Duolite resins to the lab

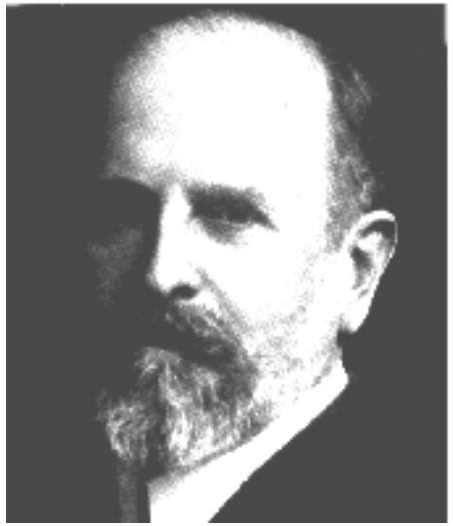
**EFCE congress Montpellier 2002**

# Learning from the past: Chromatography- Who is the father?

**M. Tsweet**

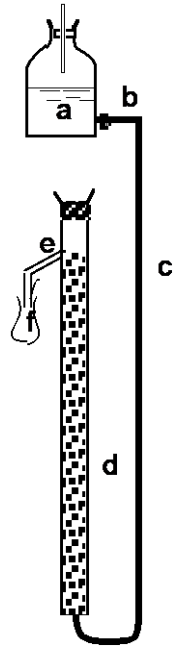
**(1850-1906)**



**D. T. Day**

**(1855-1893)**

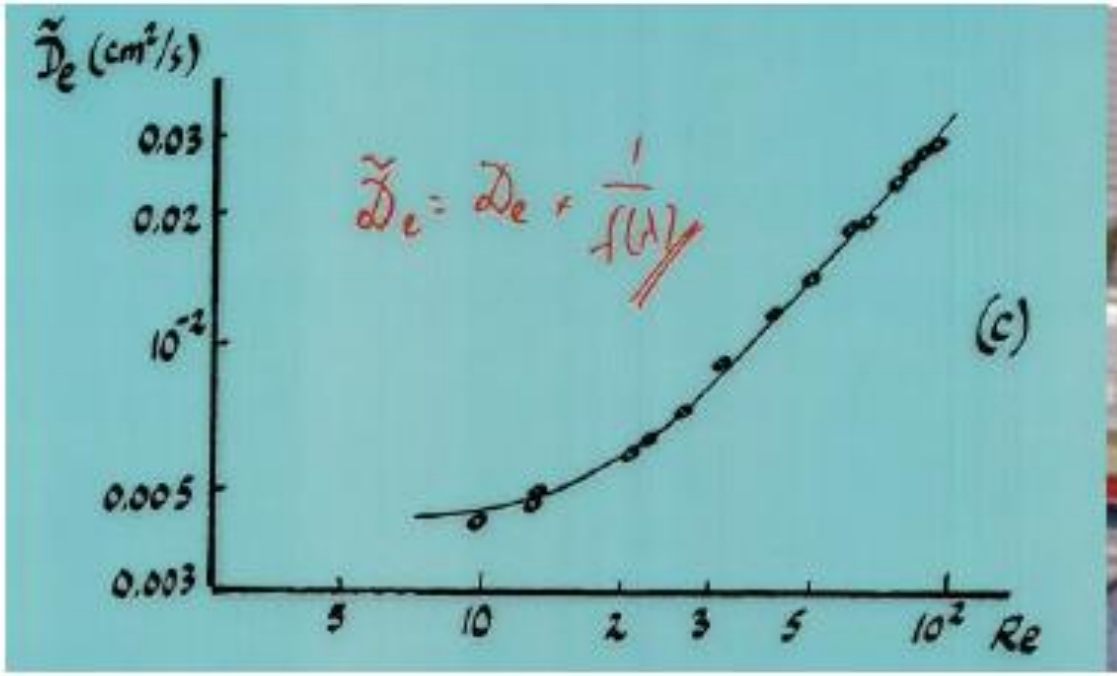



PONA analysis

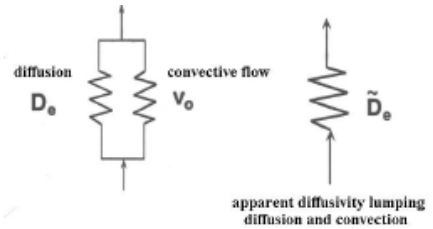

Grave of Michail Semyenovich Tsvet with the inscription:

**"He invented chromatography, separating molecules but uniting peoples."**

# The era of perfusion chromatography




**UT Compiègne-Analyzing data from Ahn (1980)**
**Intraparticle convection in large-pore catalysts**

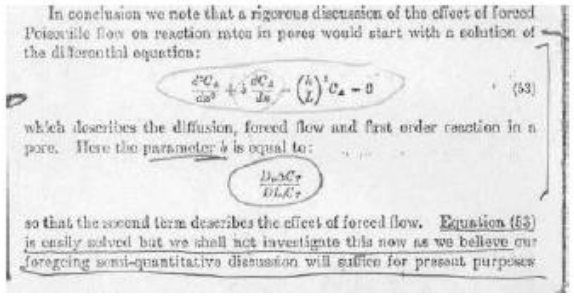



Conventional model – lumped or apparent pore diffusion

$$\widetilde{D_e}\frac{\partial^2 c}{\partial z^2} = \varepsilon_p \frac{\partial c}{\partial t}$$

Complete diffusion/convection model

$$D_e\frac{\partial^2 c}{\partial z^2} - v_0\frac{\partial c}{\partial z} = \varepsilon_p \frac{\partial c}{\partial t}$$



In conclusion we note that a rigorous discussion of the effect of forced Poiseuille flow on reaction rates in pores would start with a solution of the differential equation:

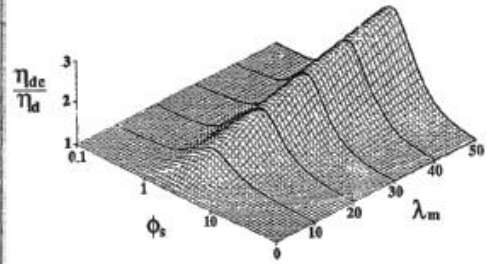
$$\frac{\partial^2 C_A}{\partial x^2} + \frac{1}{r}\frac{\partial C_A}{\partial r} - \left(\frac{h}{L}\right)^2 C_A = 0 \qquad (53)$$

which describes the diffusion, forced flow and first order reaction in a pore. Here the parameter $h$ is equal to:

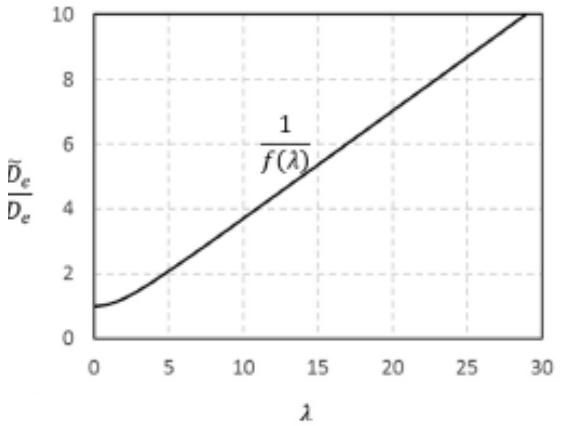
$$\frac{D_e \partial C_T}{DLC_T}$$

so that the second term describes the effect of forced flow. Equation (53) is easily solved but we shall not investigate this now as we believe our foregoing semi-quantitative discussion will suffice for present purposes

Wheeler (1951)




Nir and Pismen (1977)




$$\widetilde{D_e} = D_e\frac{1}{f(\lambda)}. \qquad f(\lambda) = \frac{3}{\lambda}\left(\frac{1}{tanh\lambda} - \frac{1}{\lambda}\right)$$

**From CRE to protein separation!**
**Cross fertilization**

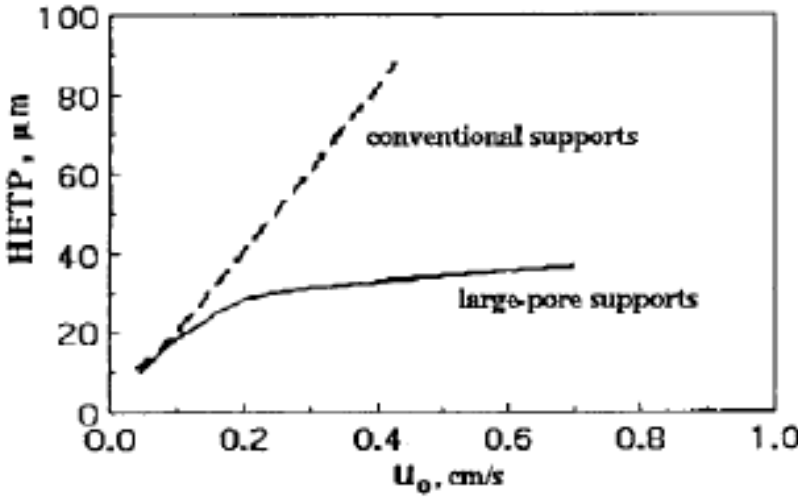


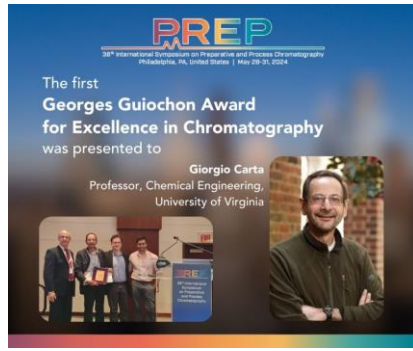
A.E. Rodrigues et al., AIChEJ 28, 95-930 (1982)

# Extended Van Deemter equation (Rodrigues equation)

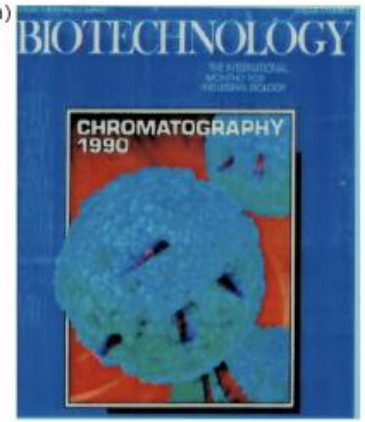
a) b)

$$HETP = A + \frac{B}{u_o} + Cf(\lambda)u_o$$

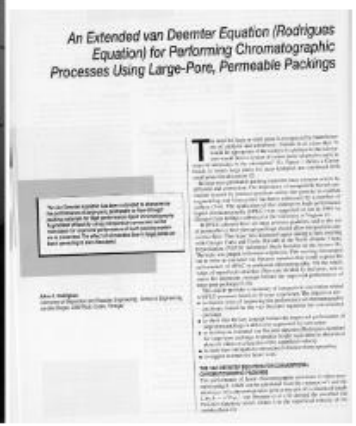


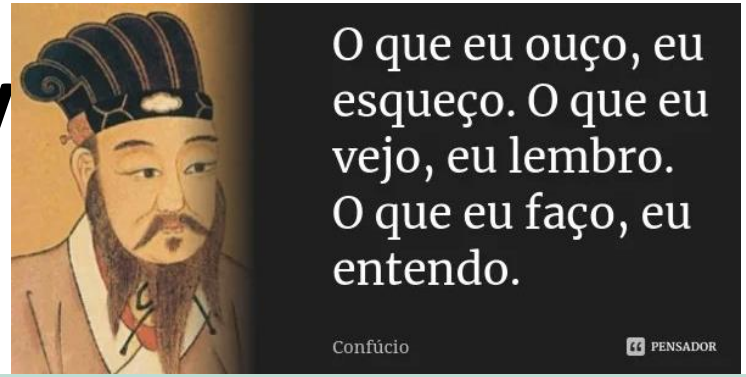

a) b)








# Perfusion Chromatography




The Power List 2013

## Georges Guiochon

**Georges Guiochon**

Distinguished Professor, Analytical Chemistry, Department of Chemistry, The University of Tennessee, Knoxville, USA

**Snapshot**: "In 1984, I decided to come to the US. There were too many smart people in LC and GC, so I decided to go into something that no-one else was doing seriously – preparative chromatography. Chemical engineers had no idea about the subtleties of the stationary phase, for instance, and analysts had no ideas about chemical engineering. I didn't have much idea either but I knew enough to marry them together.

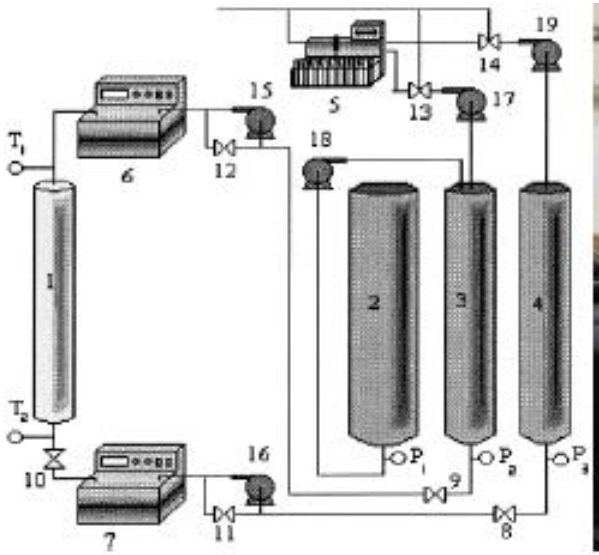
"Computers were starting to play a bigger role and I was able to solve numerically the mass balance equation for mass transfer in chromatography. I published a lot of papers and made my reputation with that [...] Now I'm doing supercritical fluid chromatography."

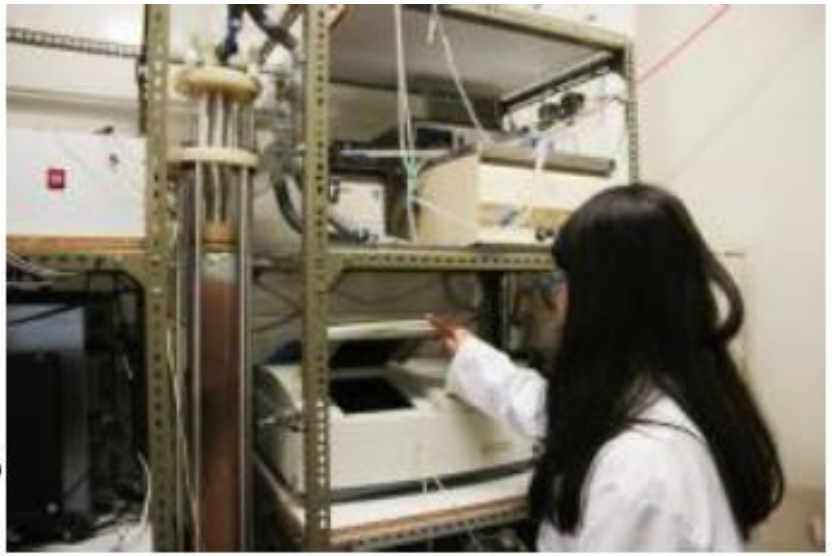
**Main motivation**:"Understanding phenomena, solving problems, and training people."

www.chem.utk.edu/Faculty/guiochon

*Sitting Down With... theanalyticalscientist.com/issues/0613/601*

# The era of cyclic adsorption/reaction processes



**NATO Research Grant with Doug LeVan** 1989-1993
Dynamics of pressure swing adsorption

**EEC JOULE 0052 C 1989-1993**
The methodology of gas adsorption process design, etc

**MACADEMIA** "MOFs as catalysts and adsorbents. Discovery and engineering of materials for industrial applications", **2009-2013**

**1-bed PSA** F. Da Silva and JAC Silva
**2-bed PSA** C. Grande
**ESA** C. Grande and Rui Ribeiro
**"Each researcher has to put his fingerprint in the lab"**

## First EU project 1987-1990

Purification of wastewaters by parametric pumping and ion exchan
(with **Mario Diaz** from **Universidad de Oviedo**)

## Parametric pumping is a Temperature Swing Adsorption (TSA) with flow reversal

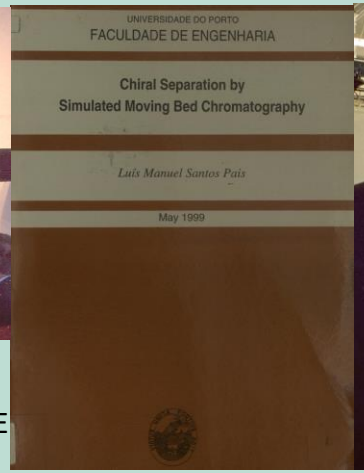
Lab-scale PSA units :single column unit and 2-bed PSA. Electric Swing Adsorption

# SMB technology at LSRE


InfoChimie Magazine
The history of NOVASEP through the eyes of its founder Roger-Marc Nicoud (2022)

"Finally in 1992 I had the opportunity of participating in a BRITE-EURAM project on Chiral Separations using SMB chromatography. The leader was R.M. Nicoud from Separex and after one year we got the pilot SMB in our lab (Fig 1). I remember: it was a Saturday in the old building of Rua dos Bragas and the equipment could not go in the elevator (no space!). We had to get help of a student passing by (J.A.C. Silva who later got a PhD with me) and it was put in the lab with "human force" (I did not contribute much for that task…). By the end of the project a new company NOVASEP was started for the SMB business towards pharmaceutical industries and life sciences. The company is now the world leader in this technology; the first industrial unit started at UCB Pharma in 1999 and the biggest plant is at AMPAC Fine Chemicals near Sacramento (1 m diameter columns). So I entered SMB area with chiral separations (PhD of Luís Pais); followed by sugars and later xylenes…" in Life stories (Chap. 3-2010)


**Broughton and Gerhold (1961) UOP Sorbex technology**


**Luís Pais**
First CUF award for the best PhD thesis in ChE
for the period 1999-2001
2003-02-21 , Cordoaria Nacional

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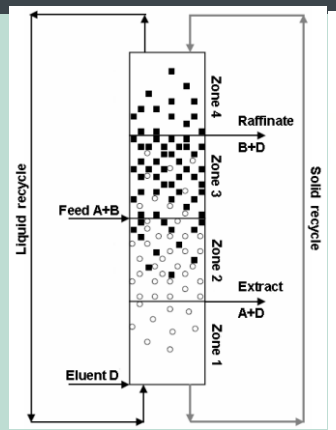
UNIVERSIDADE DO PORTO

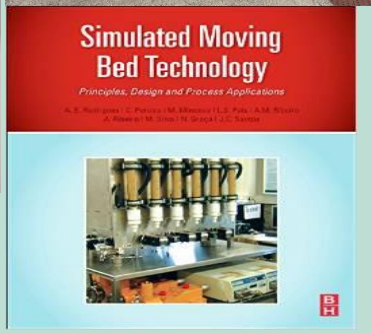
# SMB…FlexSMB…Gas-phase SMB

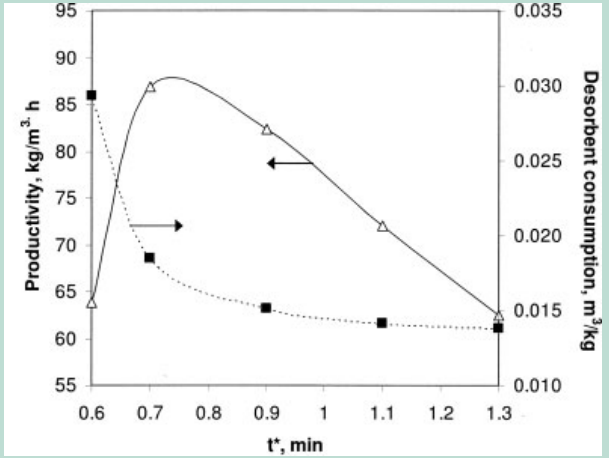
LSRE-LCM

Shaking the Present
Shaping the Future

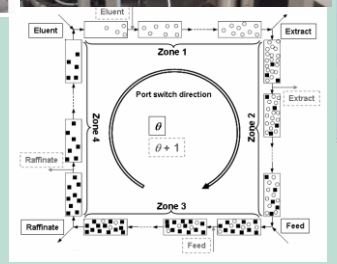


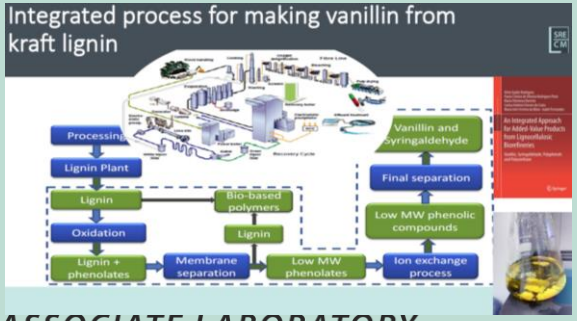

Free consulting on SMB…

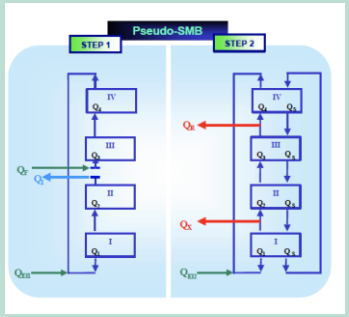



## Around PAREX…

## Gas-phase SMB

## Future…

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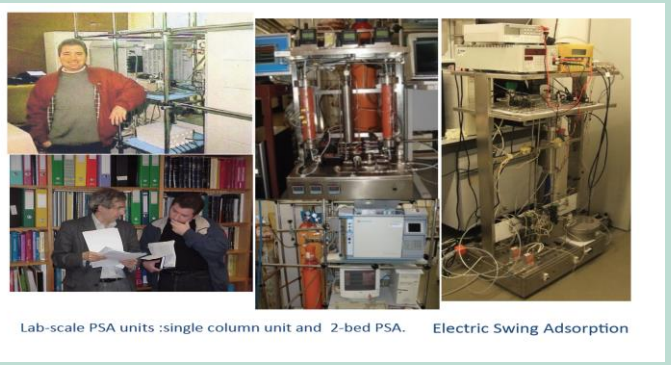
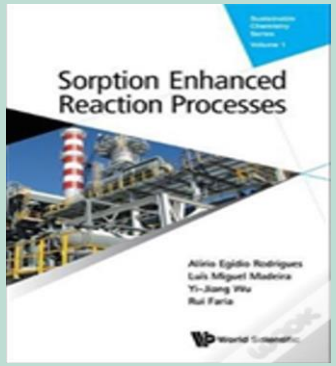
## Contribuições para Ciência 2008 do LSRE/LCM

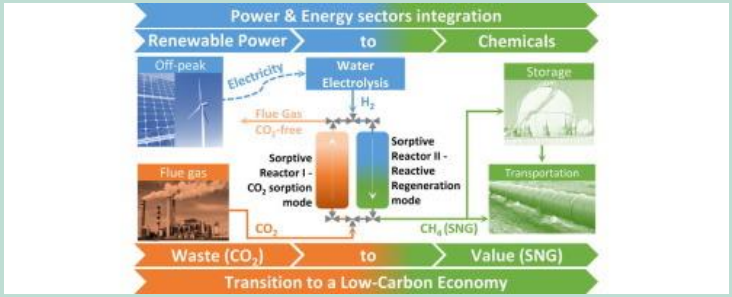
**Carlos Grande/Alírio Rodrigues**

**Novos processos para atingir metas de Kyoto: captura de CO2, bio-metano e produção de hidrogénio.**

No quadro da estabilização de emissões de CO2 para cumprir metas de Kyoto apresentam-se :
i) novo processo (electric swing adsorption) para captura de CO2 de flue gases;
ii) nova tecnologia para obter bio-metano a partir de biogas;
iii) recuperação de H2 de waste gas do reforming por PSA/membranes e
iv) Novo conceito (SERP) para produzir H2 a partir do reforming de NG ou etanol com adsorção in-situ de CO2.

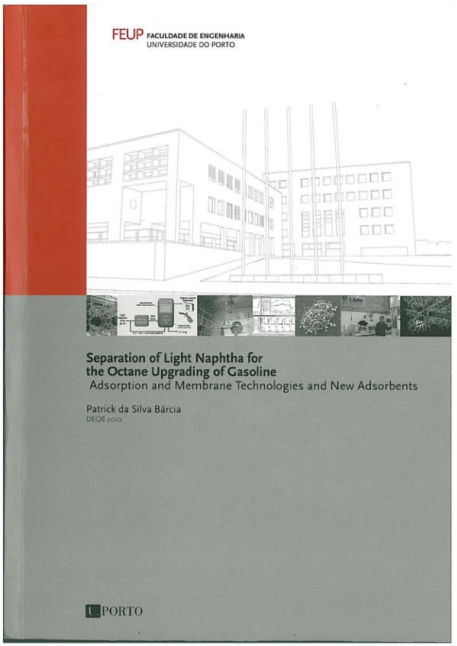



# CO2 capture from flue gas- pilot plant in Shangai (Zhen Liu)

# Biogas upgrading…biomethane

Patrick Bárcia
patrick.barcia@sysadvance.com

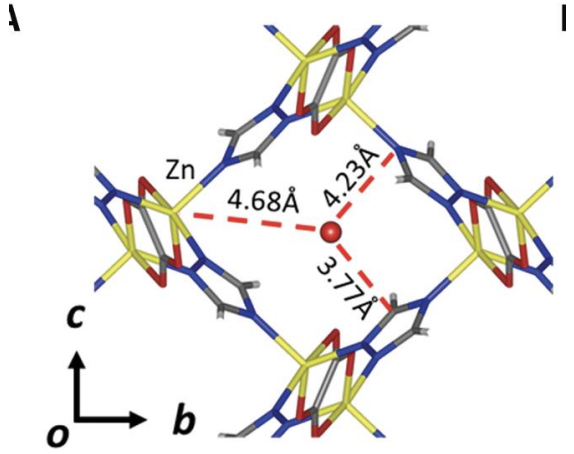




sysadvance®

**URL**:
https://www.sysadvance.com/#!/

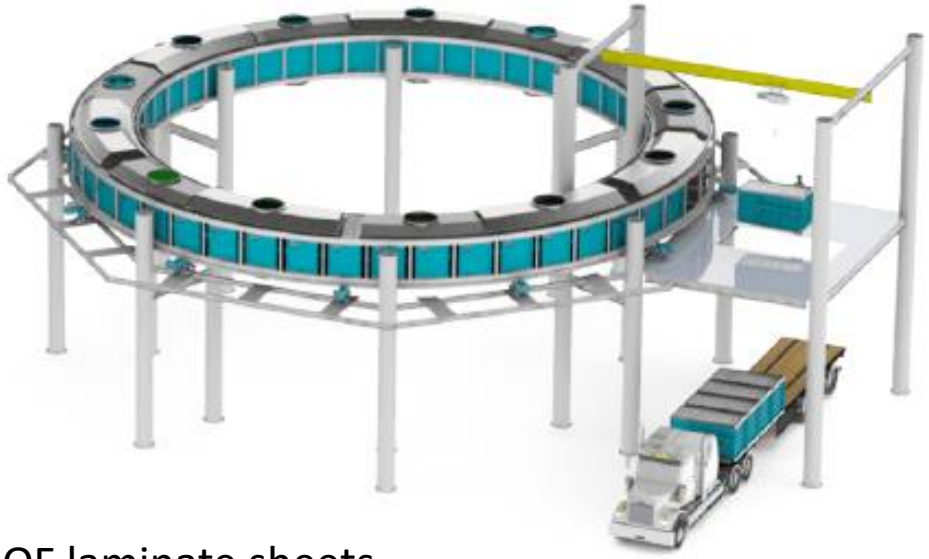
# SVANTE technology for CO2 capture

CALF-20 is composed of layers of 1,2,4-triazolate-bridged zinc(II) ions pillared by oxalate ions to form a 3D lattice and 3Dpore structure

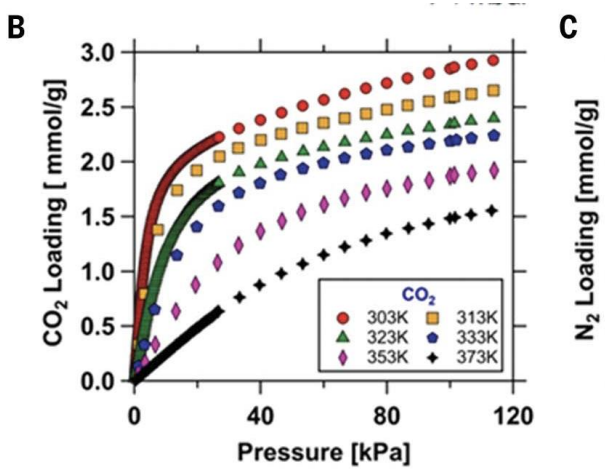



**URSA 2000**

Captures approximately 2,000 tonnes of $CO_2$ per day



MOF laminate sheets




2019 World's first 30 TPD $CO_2$ capture plant comes online in SK, Canada

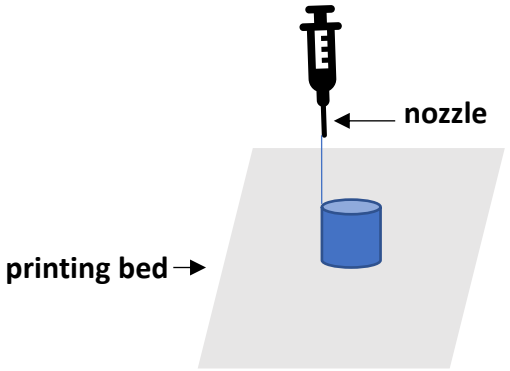
$CO_2$MENT Pilot Plant Project at Lafarge Canada in Richmond, BC, Canada, capturing one tonne per day for its use in building materials

Lin et al., Science 374, 1464–1469 (2021) MOF CALF-20

2022 Chevron demo carbon capture plant launched in Bakersfield, CA, USA

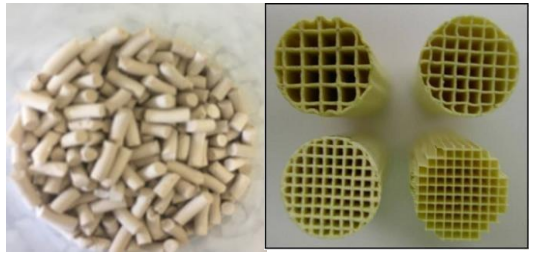
# Development of structured adsorbent materials using additive manufacturing techniques

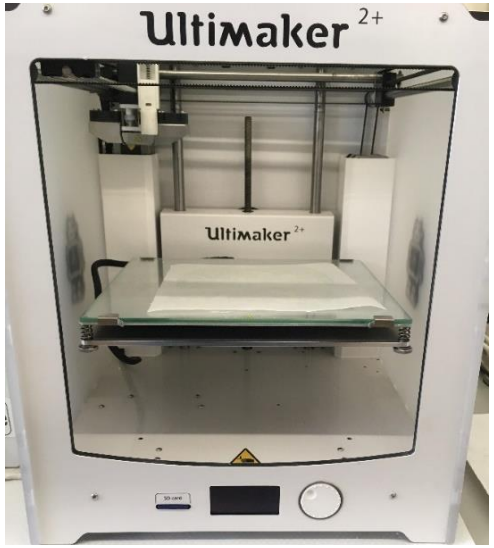
## *Robocasting (Direct Ink Writing* -DIW)

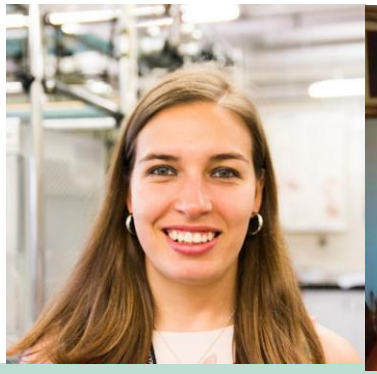



Viscous ink (that contains the adsorbent) with pseudoplastic properties

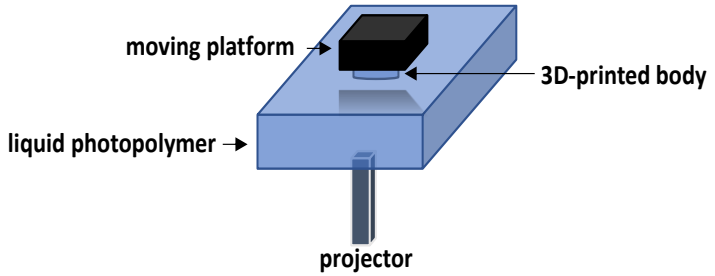
Wide range of materials that can be applied





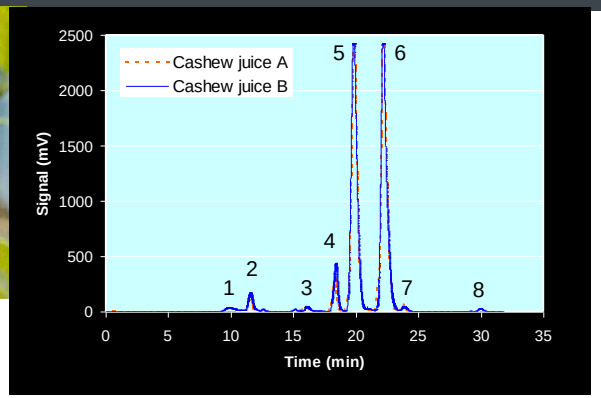
## *Digital Light Processing* (DLP)

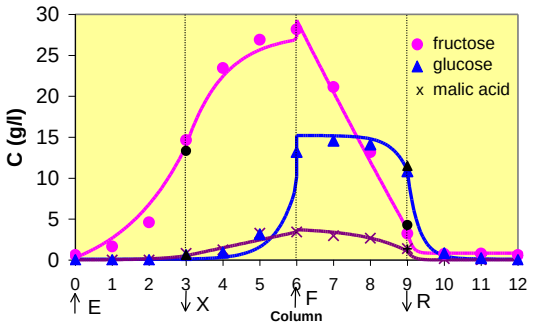



UV source + photocurable resin (that contains the adsorbent)

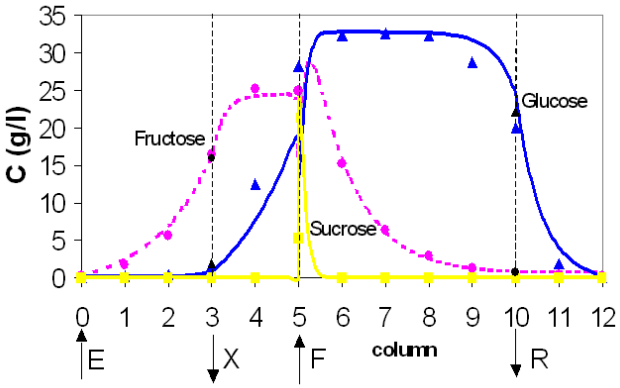
Materials with high resolution

# Process intensification by SMBR

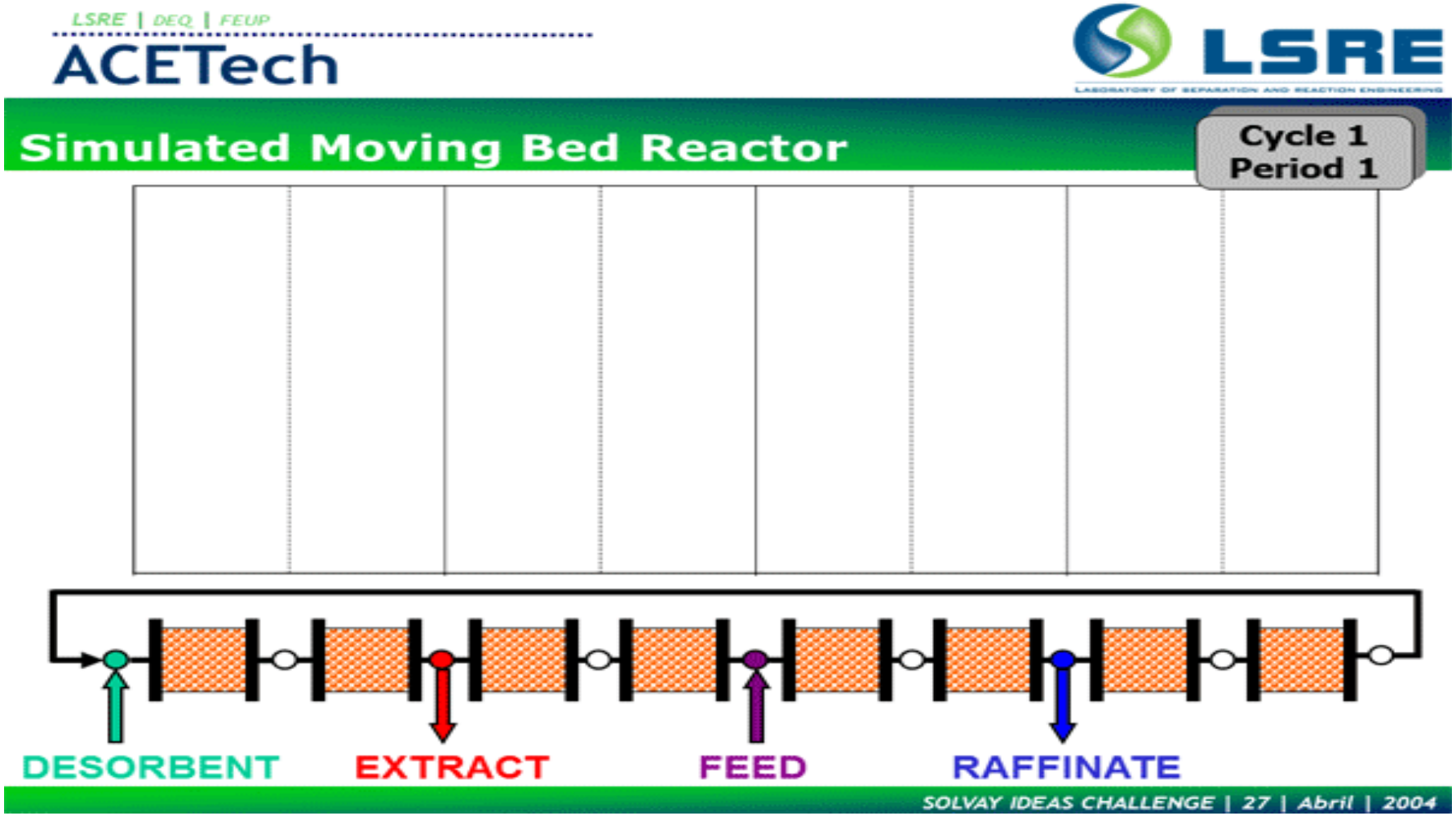

## Combining reaction and adsorption





# AceTech – Green diesel additives

## New and versatile process by Simulated Moving Bed Reactor

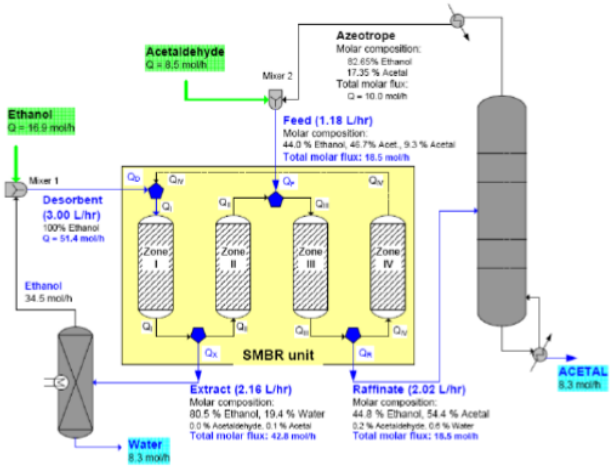


# Process intensification (SMBR) and re-intensification (PermSMBR)

## Solvay Ideas Challenge (2004)
## IChemE award (2008)

AceTech – **Green** diesel additves

**New and versatile process by means of SMBR**




- Diethylacetal is a green additive produced from bioethanol, that enhances the renewable fraction in diesel, and blends with 10% of acetal leads:
  - 13% reduction in CO
  - 8% reduction in CO2
  - 21% reduction in PM
- Diethylacetal production cost was estimated to be 0.75 €/liter using this technology.

Awards for innovation and excellence 08 Winner

PCT (10) International Publication Number WO 2005/113476 A1

Brazil, EUA, Sweden, France, Germany, Spain, The Netherlands, United Kingdom, Switzerland, Finland, Hungary, Italy

V.T.M. Silva and A.E. Rodrigues, "A Novel Process for Diethylacetal Synthesis", AIChEJ, 51(10) 2752-2768 (2005)

2008
AIChE 100 years

The PSE Model-Based Innovation Prize 2012

Winning paper

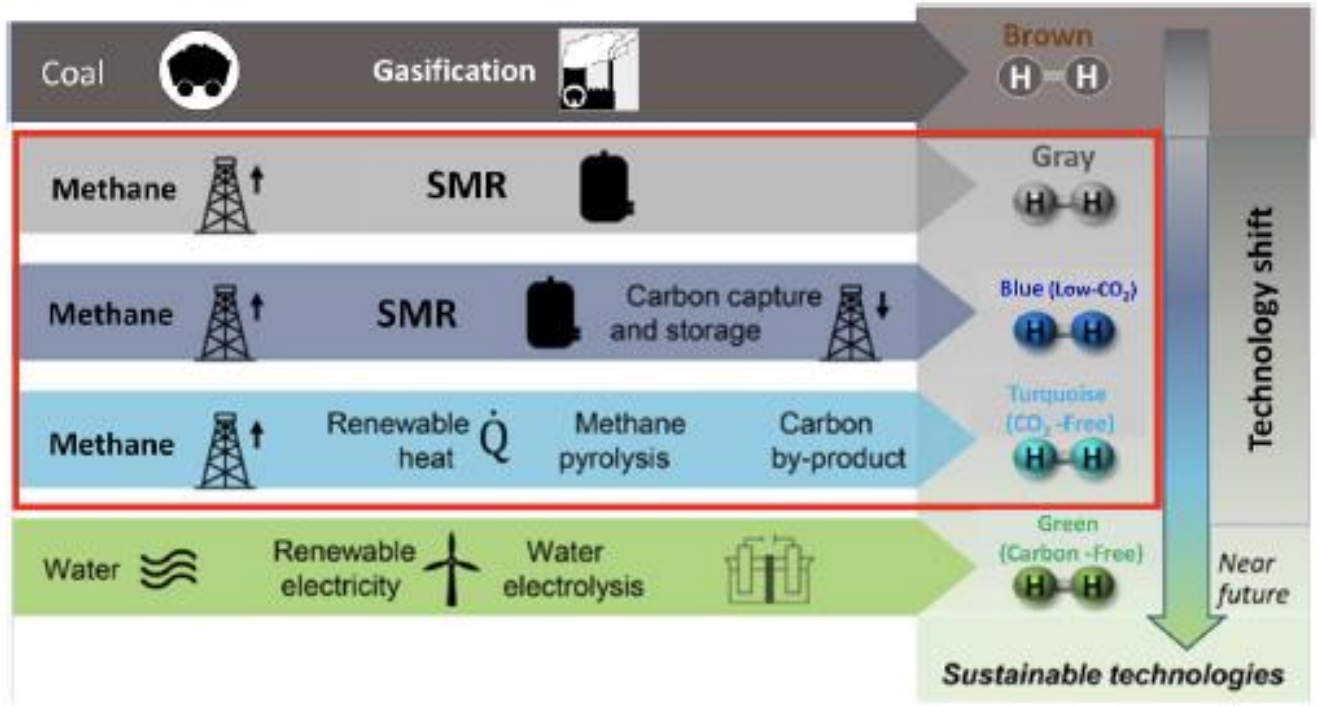
PermSMBRA New Hybrid Technology: Application on Green Solvent and Biofuel Production by **Viviana M. T. M. Silva, Carla S. M. Pereira, and Alírio E. Rodrigues** of Faculdade de Engenharia da Universidade do Porto (FEUP)

**2021**
**18th Annual SCI**
**Gordon E. Moore Medal**

# $H_2$ in colours…

Table 1. Concept map of hydrogen categories and production pathways

| Type of hydrogen | | Feedstock | Energy source | Process | Products | Comment |
|---|---|---|---|---|---|---|
| Brown/Black | | Coal or lignite | Coal | SMR in combination with gasification | $H_2$ + CO + $CO_2$ (released) | Established process used in industries that convert organic or fossil-based carbon materials into CO, $H_2$, and $CO_2$. |
| White | | Naturally occurring | | | $H_2$ | Naturally occurring geological hydrogen, found in underground deposits and created through fracking. |
| Grey | | Natural Gas | Natural Gas | SMR | $H_2$ + $CO_2$ (released) | Sources are derived from fossil fuels. Grey hydrogen is currently the most common form of $H_2$ production, in which the hydrogen is created from natural gas (methane), using SMR, with no GHG capture process. |
| Blue | | Natural Gas | Natural Gas | SMR | $H_2$ + $CO_2$ (% captured and stored) | Produced mainly from natural gas, using SMR technology. $CO_2$ obtained as co-product, is captured using CCS technology. |
| Turquoise | | Natural Gas | Natural Gas | Pyrolysis | $H_2$ + C (solid) | Uses methane pyrolysis to produce $H_2$ and carbon materials. |
| Red | | Water | Nuclear Power | Catalytic splitting | $H_2$ + $O_2$ | Generated through catalytic splitting powered by nuclear energy. |
| Purple/Pink | | Water | Nuclear Power | Electrolysis | $H_2$ + $O_2$ | Generated through electrolysis powered by nuclear energy. |
| Green | RFNBO (non-biological origin) | Water | Renewable electricity | Water splitting processes (thermolysis, photolysis, electrolysis) | $H_2$ + $O_2$ | The best known green $H_2$ is obtained via electrolysis of water using clean electricity from surplus renewable energy sources, such as solar or wind power. |
| | Bio-hydrogen (biological origin) | Biogenic sources (biomass, Biogas, Biomethane | Biomass derived energy[22] | Biological, thermochemical and bioelectrochemical (See Chapter 2) | $H_2$ + biogenic $CO_2$ + co-product (digestate, C, biochar, others) | Can be C negative when combined with CCS or when obtained from feedstocks such as wastes and manure. Low electricity needs. |




S. Saeidi et al, Evolution paths from gray to turquoise hydrogen via catalytic steam methane reforming: current challenges and future developments, Renewable and Sustainable Energy Reviews 183(2023)113392

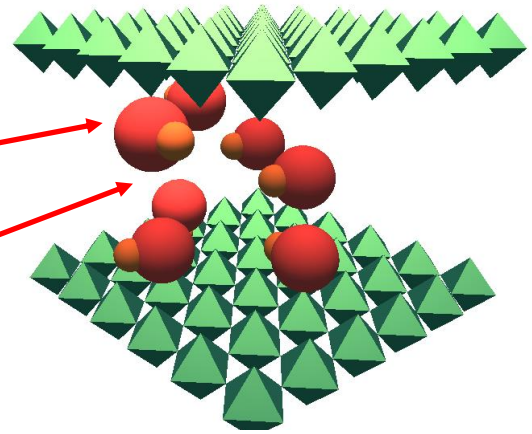
EBA European Biogas Association
Decarbonizing Europe's hydrogen production with biohydrogen, June 2023

## One possible improvement : Adsorptive reactor

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$

$$CO + H_2O \rightleftharpoons H_2 + CO_2$$

$$CH_4 + 2H_2O \rightleftharpoons 4H_2 + CO_2$$

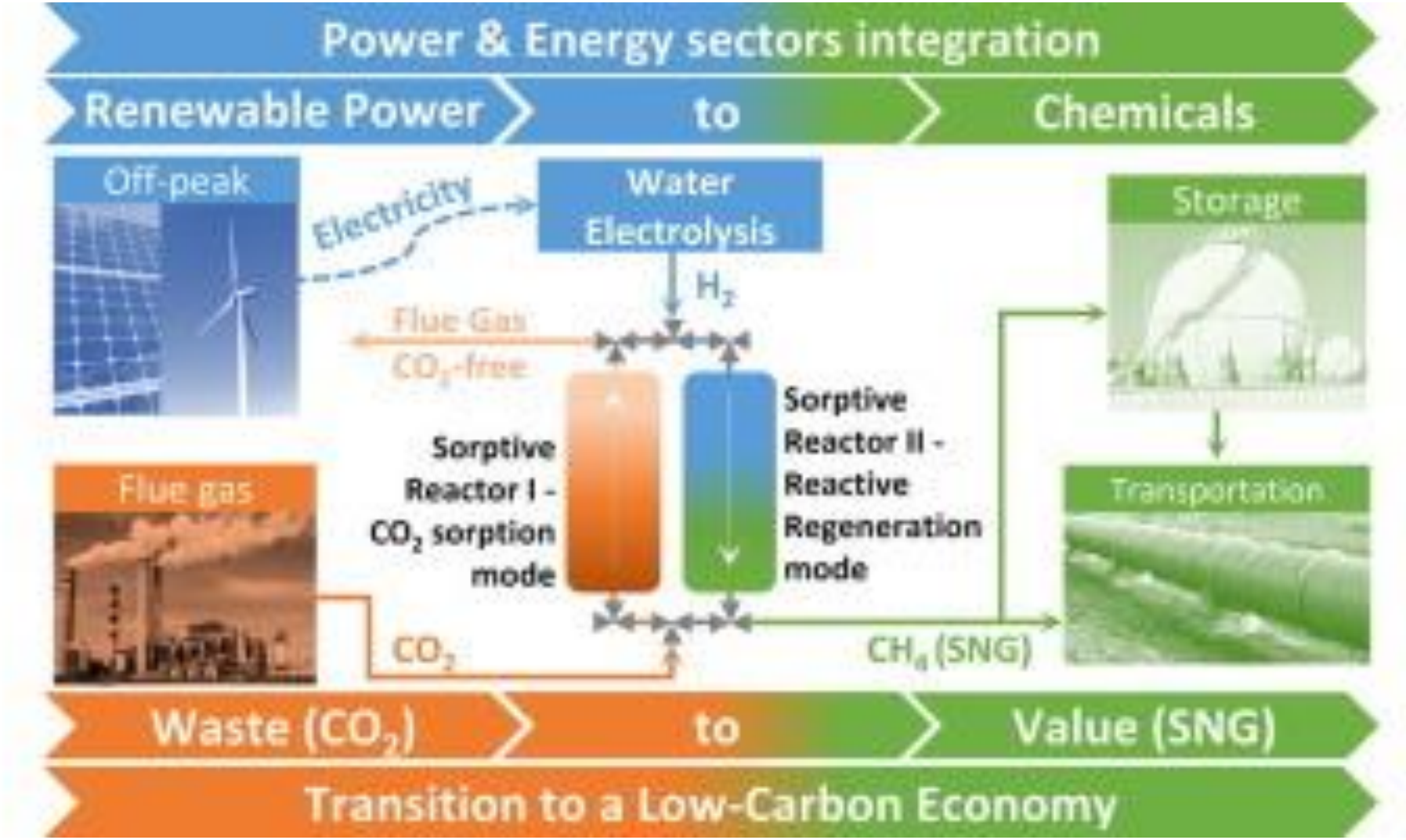



i-sensis

BASF

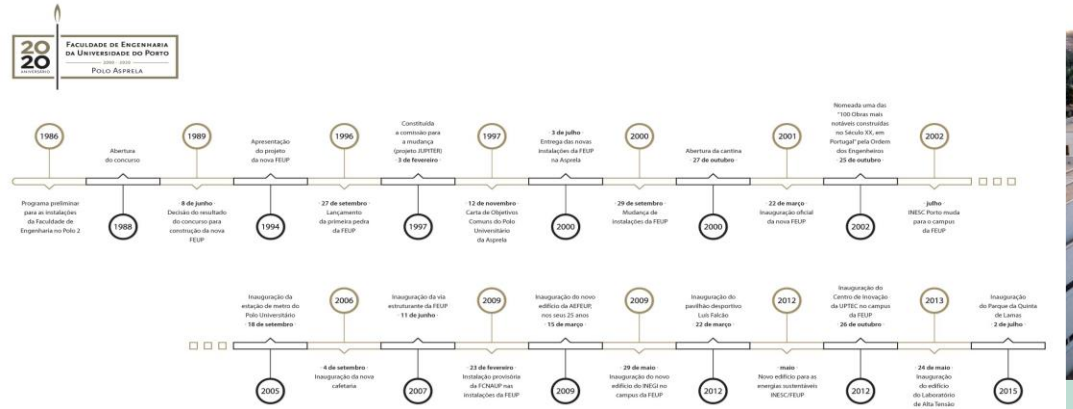
ICT Mumbai

# Power2Gas


Power & Energy sectors integration
Renewable Power
to
Chemicals
Off-peak
Electricity
Water Electrolysis
$H_2$
Flue Gas
$CO_2$-free
Storage
Sorptive Reactor I - $CO_2$ sorption mode
Sorptive Reactor II - Reactive Regeneration mode
Flue gas
Transportation
$CO_2$
$CH_4$ (SNG)
Waste ($CO_2$)
to
Value (SNG)
Transition to a Low-Carbon Economy

# Administration…someone has to do it…

1989- President of FEUP directory : the decision of choosing the winner “ideas competition” for the new campus-Architect Pedro Ramalho





Prémio de Excelência Científica FEUP 2009

AIChE, 2014
Atlanta

I&D+I CIBIQ, 2019
Santander


IAS Fellow 2020
Denver 2022

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**Knowledge modeling in ChE (Venkatasubramanian)**

**DAE**- **Amundson era** (1950s) modeling process units; first-principles
**Optimization MILP and MINLP**- **Sargent era** 1970s modeling process engineers, decision-making, constraints
**AI**- **Westerberg, Stephanopoulos, others** –modeling process engineers & data; symbolic statistics and relationships

Se os modelos em Engenharia Química fossem tão maus….


Público, 16.03.2013

# Research lines and Groups of LSRE-LCM

**New technologies of cyclic separations/reactions**

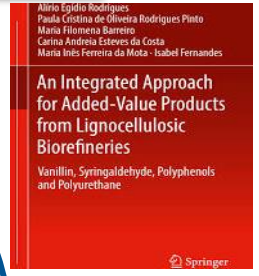
**Synthesis and formulation of high-added value products**

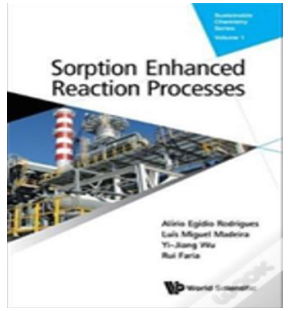
PRODUCT ENGINEERING

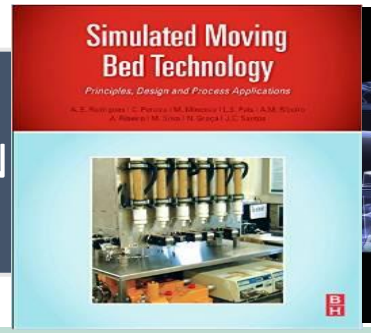
CATALYSIS & CARBON MATERIALS

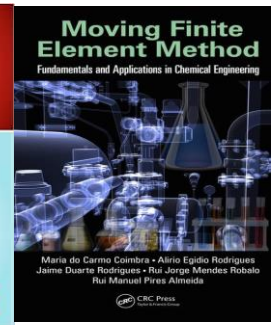
THERMOD. & ENVIRONMENT

CYCLIC ADSORPTION/REACTION PROCESSES


**Research Groups**

CYCLIC ADSORPTION/REACTION PROCESSES
- Cyclic Adsorption Processes
- Process Intensification
- Process Systems Engineering

PRODUCT ENGINEERING
- Mixing in Chemical Reactors
- Micro/Nano Structured Materials
- Perfume & Flavour Engineering
- Polymer Engineering
- Biovalorisation and Sustainability of Agrofood Products
- Industrial Processes Design
- Chemical Engineering Thermodynamics

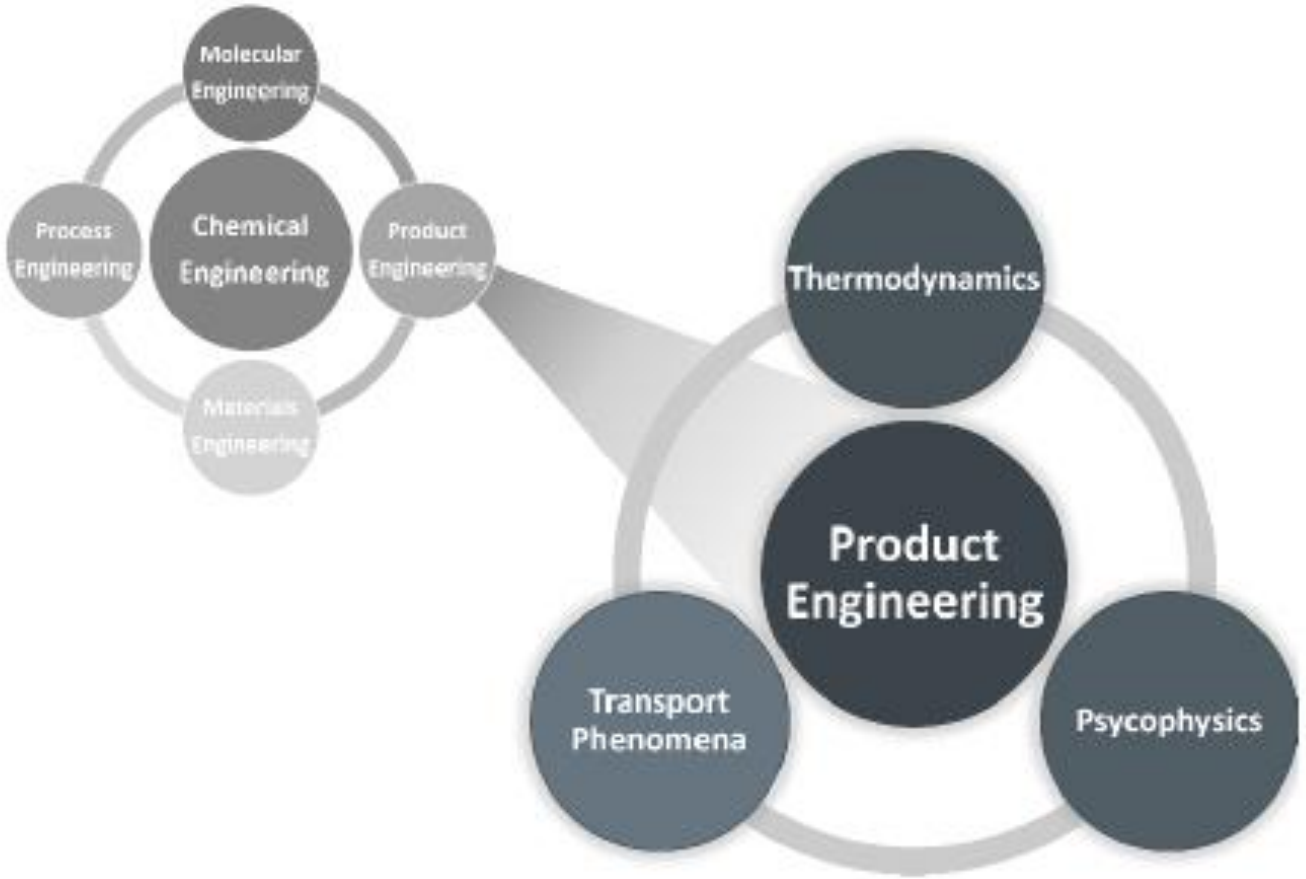
ENVIRONMENTAL ENGINEERING
- Water Management
- Technologies for Pollution Control
- Circular Economy: Recovery, Reuse & Valorisation

CARBON MATERIALS, CATALYSIS AND ENVIRONMENTAL ASSESSMENT
- Nanostructured Carbon Materials
- Environmental Catalysis and Technologies
- Energy, Fuels and Chemicals

PHOTO-ELECTRO-CHEMISTRY AND NATURE-INSPIRED SYSTEMS

**ChE=M2P2**

**To “make”,**
**to “service”,**
**to “care”**
**Solke Bruin**

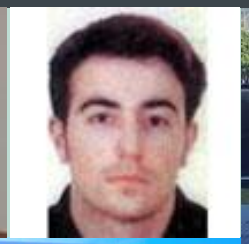


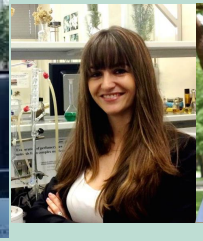

# Why apply Product Engineering to fragrances?

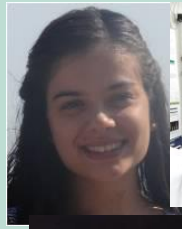


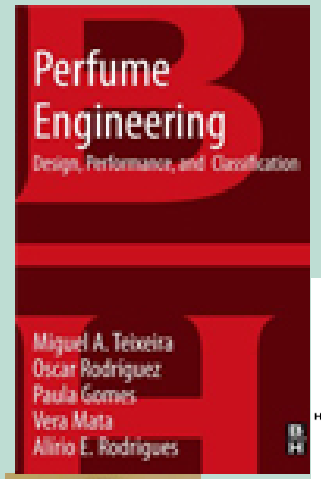
Rodrigues, A.E., et al., XXXIII Reunion Iberica de Adsorcion. Madrid, Spain, 13-14, 2008.

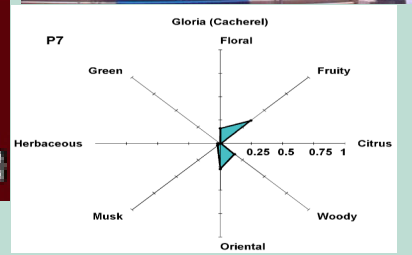










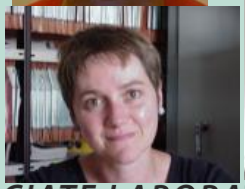

Miguel Teixeira
EFCE Award Best PhD 2015





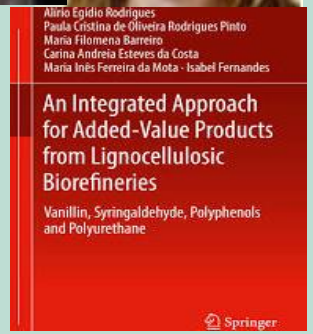








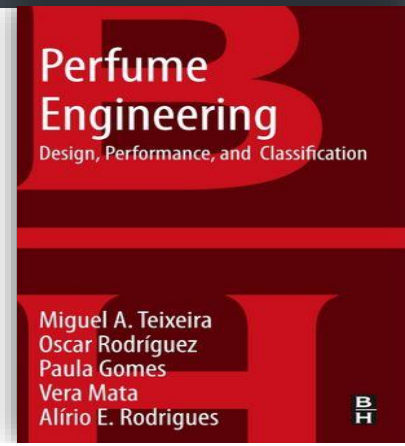




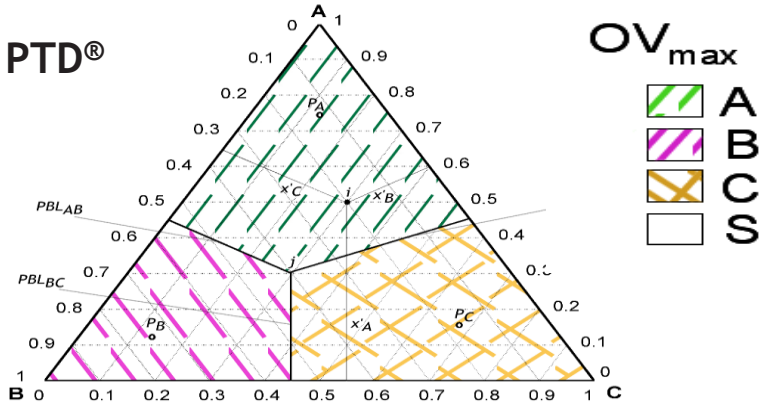
# Ask the right question…

**Looking back in 1997 when with posdoc Vera Mata I started Perfume Engineering at LSRE**

## What do we smell?
## Can we predict it?

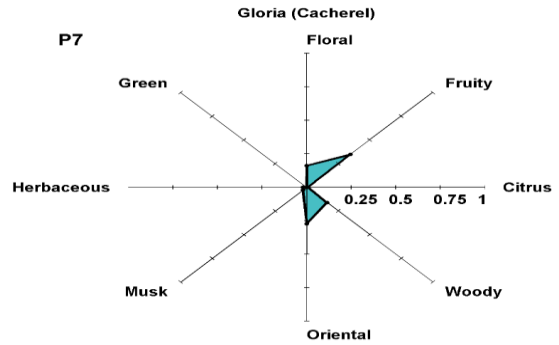




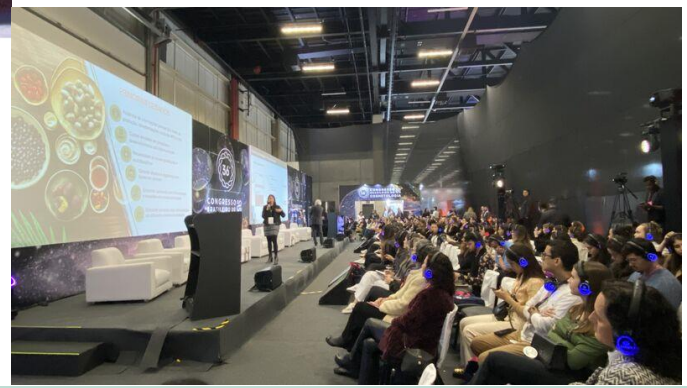






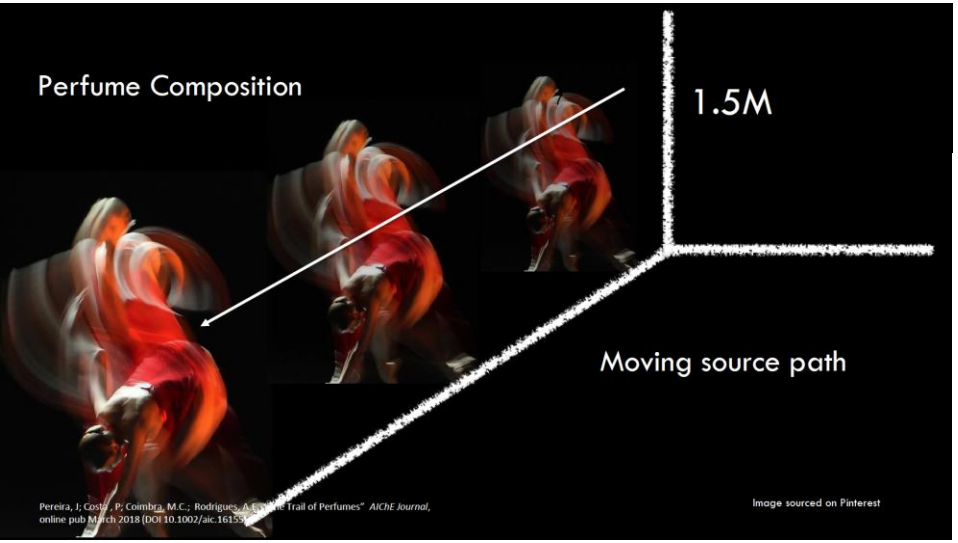



**Perfumery Ternary Diagram**
**Perfumery radar**
**The trail of perfumes**
**Microencapsulation of perfumes**
**The effect of skin on the performance**



**36 Congresso Brasileiro de Cosmetologia, São Paulo, 4-6 June 2024**

# Sillage in perfumery C Benaim and J Brahms, IFF – WPC 2018, Nice



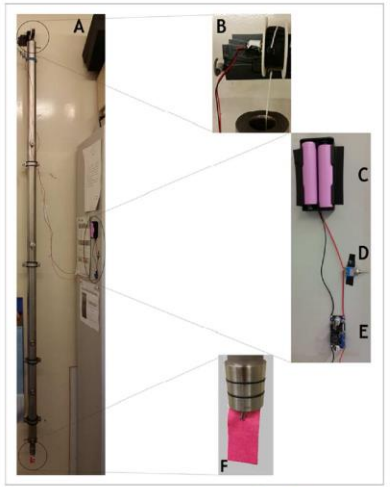
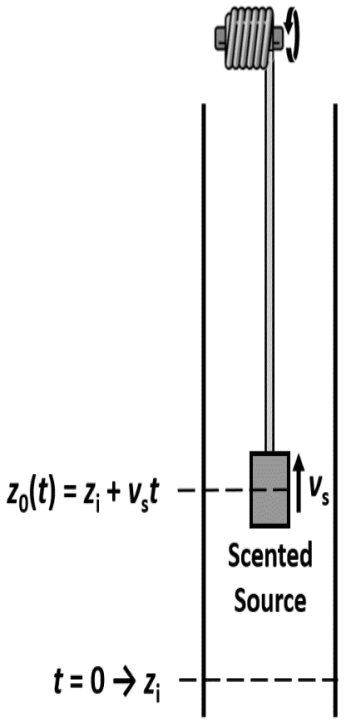





**Figure 2.** System developed in the laboratory; F1 – Zoom of the textile used as the source, and the respective dimensions.



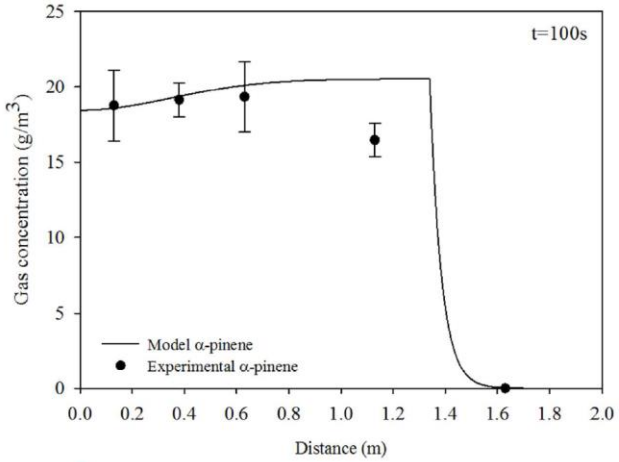
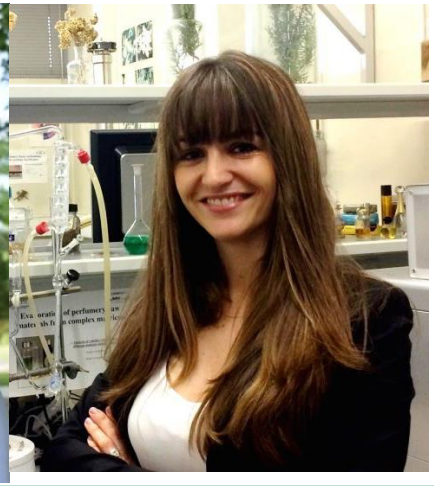




**Figure 3.** Theoretical and experimental gas concentration profiles of α-pinene over distance, at a fixed time of 100 s, of a source moving at $1.34 \times 10^{-2}$ m/s, and $D_{\alpha\text{-pin}}=6.04 \times 10^{-6}$ m$^2$/s.



# Sillage in perfumery C Benaim and J Brahms, IFF – WPC 2018, Nice

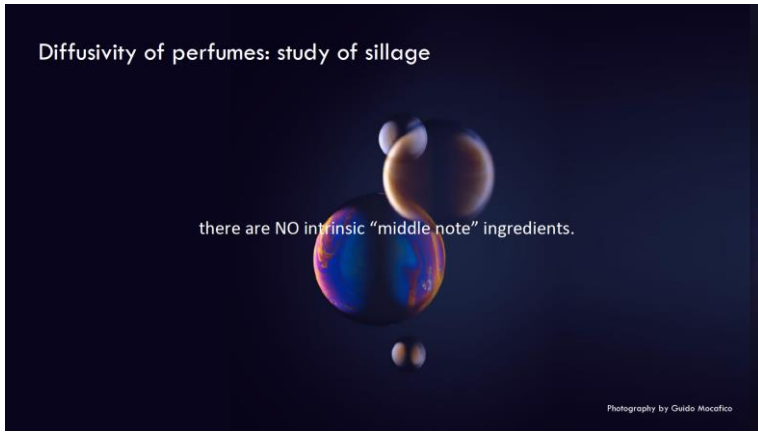
## Aura of aroma

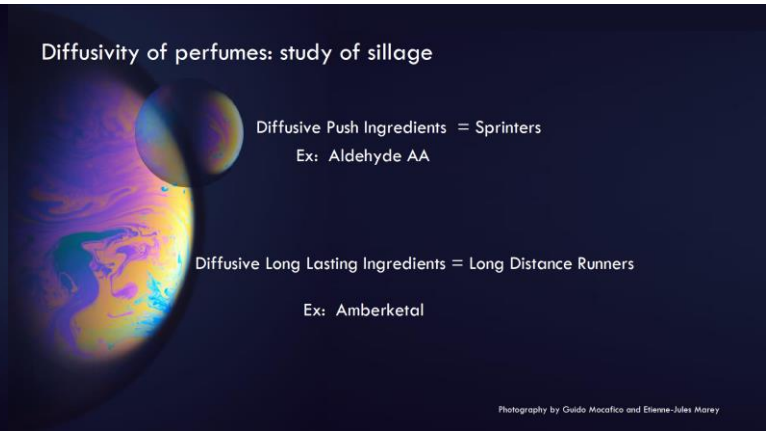
Observations: the amount of certain materials found in headspace over mixtures on skin was over-represented vs liquid phase concentration:

- Under-represented materials – limonene, hedione , benzyl sal
- Over-represented materials: linalool, linalyl-acetate, cashmeran and coumarin and ethyl vanillin

"Aura of Aorma®: A Novel Technology to Study the Emission of Fragrance from the Skin" Mookerjee, B. D.; Patel, S. M.; Trenkle, R. W.; Wilson, R. A.; in Flavours and Fragrances Karl A.D. Swift ed. Elsevier, 1997, Cambridge, UK. pp 36-47.

Image sourced on Pinterest




## Aura of aroma

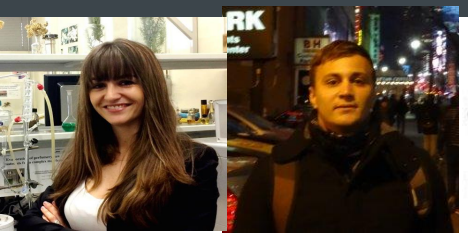
Technical study of aura: oriental scent skin vs oil

| Component | | Oil % | Aura on skin % |
|---|---|---|---|
| Limonene | Topnote | 30.0 | 20.4 |
| Linalool | Topnote | 1.7 | 17.9 |
| Linalyl Acetate | Topnote | 9.9 | 21.6 |
| Ethyl Vanillin | Middle Note | 0.2 | 1.6 |
| Coumarin | Middle Note | 1.7 | 7.8 |
| Methyl Ionone | Middle Note | 1.1 | 2.1 |
| Musk Xylol | Bottom Note | trace | 0.3 |

"Aura of Aorma®: A Novel Technology to Study the Emission of Fragrance from the Skin" Mookerjee, B. D.; Patel, S. M.; Trenkle, R. W.; Wilson, R. A.; in Flavours and Fragrances Karl A.D. Swift ed. Elsevier, 1997, Cambridge, UK. pp 36-47.

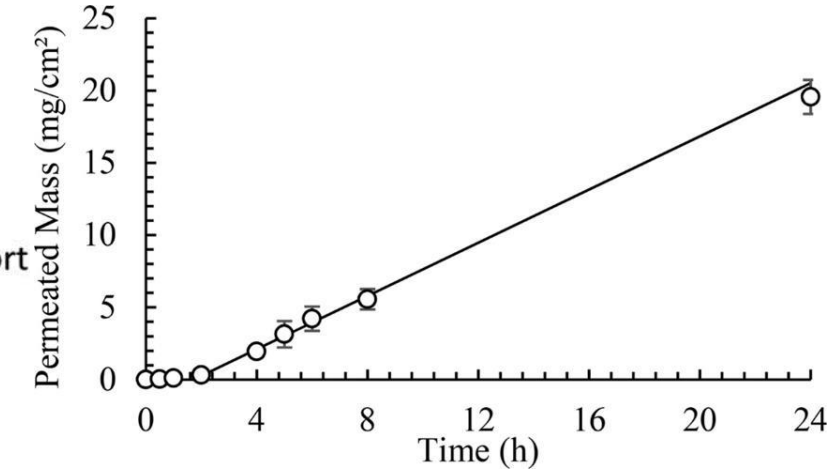
Image sourced on Pinterest

# The effect of skin-Franz cell for permeation of fragrances



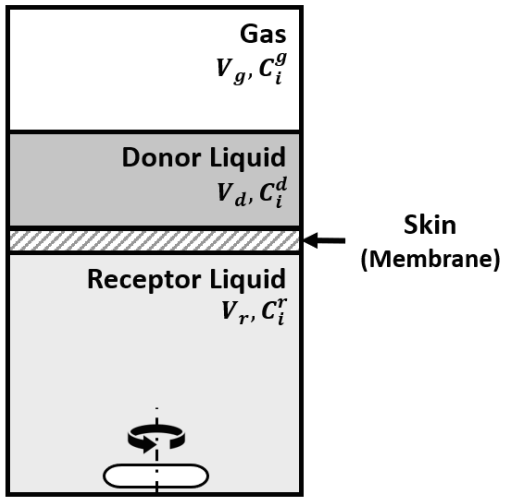




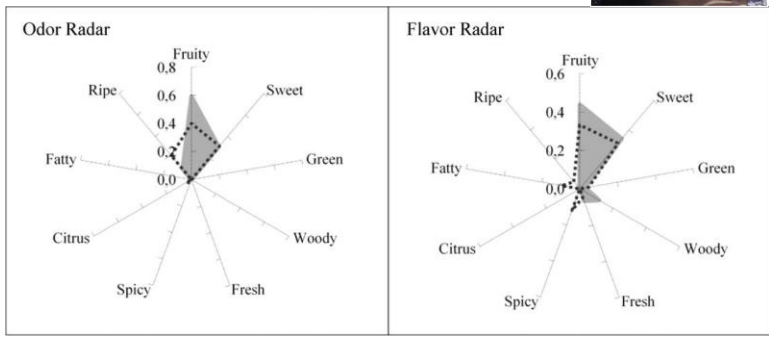

Permeation coefficients :
alfa-pinene 1.08x10-5 cm/h
limonene 8.25x10-6 cm/h
linalool 2.15x10-3 cm/h
Infinite-dose experiments …
diluted in ethanol
Measurements with 14 PRM

# Flavor engineering

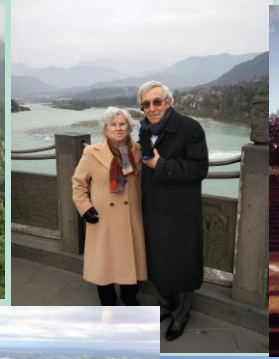



Flavor detection threshold FDTi - the lowest liquid concentration of component i at which it is detected by the retronasal route;
Flavor value FVi - the ratio between the gas phase concentration and its FDT

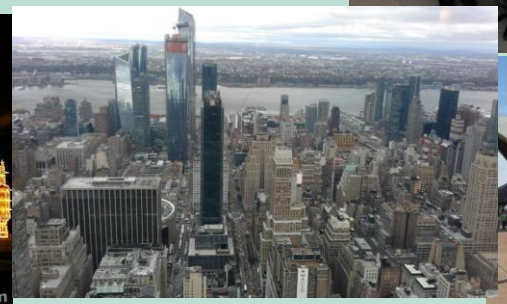
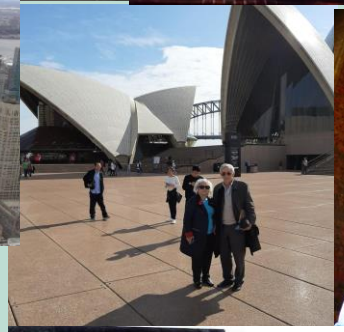
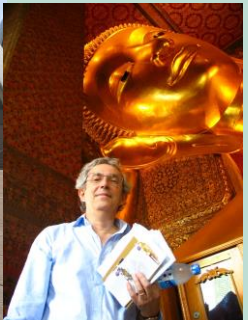
| | **ODT(**mg/m3) | **FDT**(mg/kg) |
|---|---|---|
| Ethyl butyrate (fruity, sweet, spicy) | 3.35 x10$^{-4}$ | 1.8x10$^{-3}$ |
| Isoamyl acetate (sweet, fruity, ripe) | 4.99x10$^{-1}$ | 5.7x10$^{-2}$ |
| Benzaldehyde (woody, fruity, sweet) | 6.0 | 5.3x10$^{-1}$ |
| Ethyl hexanoate (sweet, fruity, green) | 1.5x10$^{-2}$ | 8.0x10$^{-3}$ |
| Limonene (citrus) | 6.19x10$^{-1}$ | 2.1x10$^{-1}$ |
| Linalool (citrus, sweet, woody) | 9.33x10$^{-3}$ | 3.3x10$^{-3}$ |







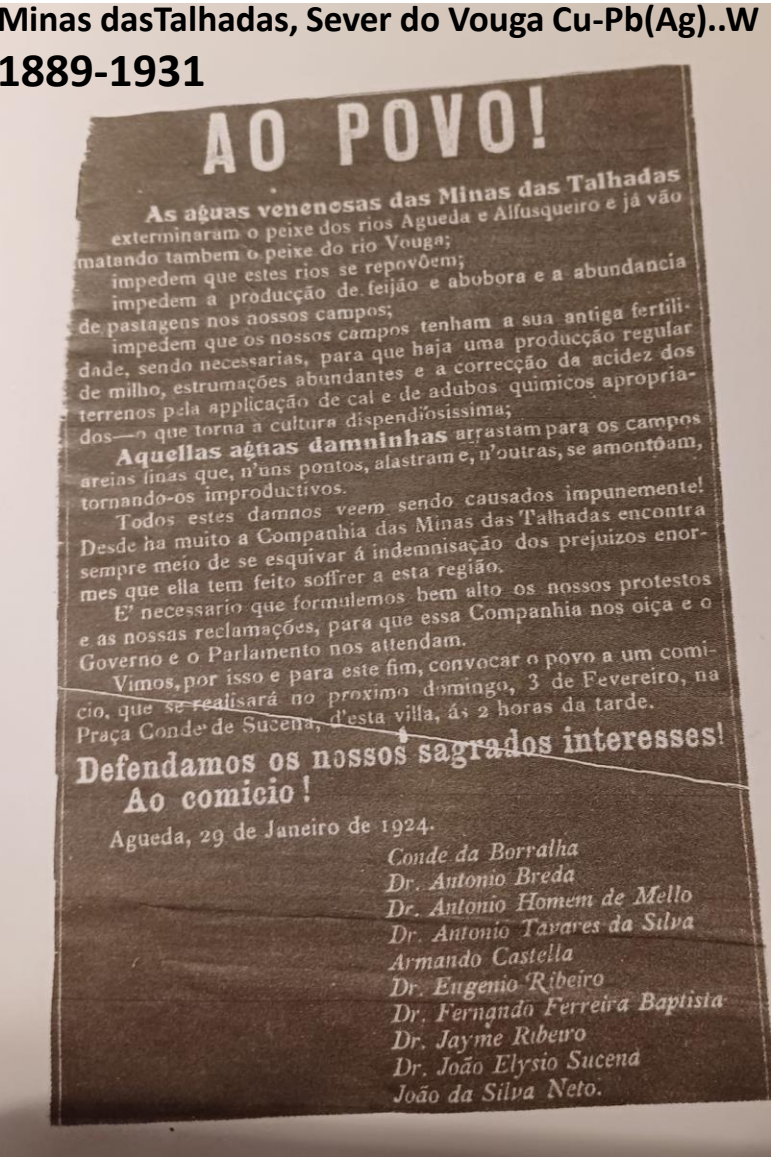

IndiaOuting.com







CAPE OF GOOD HOPE
THE SOUTH-WESTERNMOST POINT OF THE AFRICAN CONTINENT
34° 21' 25" SOUTH LATITUDE
18° 28' 26" EAST LONDITUDE

# People rights…in 1924 and today

**Minas dasTalhadas, Sever do Vouga Cu-Pb(Ag)..W**
**1889-1931**



AO POVO!

As aguas venenosas das Minas das Talhadas exterminaram o peixe dos rios Agueda e Alfusqueiro e já vão matando tambem o peixe do rio Vouga;
impedem que estes rios se repovôem;
impedem a producção de feijão e abobora e a abundancia de pastagens nos nossos campos;
impedem que os nossos campos tenham a sua antiga fertilidade, sendo necessarias, para que haja uma producção regular de milho, estrumações abundantes e a correcção da acidez dos terrenos pela applicação de cal e de adubos quimicos apropriados—o que torna a cultura dispendiosissima;
Aquellas aguas damninhas arrastam para os campos areias finas que, n'uns pontos, alastram e, n'outras, se amontôam, tornando-os improductivos.
Todos estes damnos veem sendo causados impunemente! Desde ha muito a Companhia das Minas das Talhadas encontra sempre meio de se esquivar á indemnisação dos prejuizos enormes que ella tem feito soffrer a esta região.
E' necessario que formulemos bem alto os nossos protestos e as nossas reclamações, para que essa Companhia nos oiça e o Governo e o Parlamento nos attendam.
Vimos, por isso e para este fim, convocar o povo a um comicio, que se realisará no proximo domingo, 3 de Fevereiro, na Praça Conde de Sucena, d'esta villa, ás 2 horas da tarde.

Defendamos os nossos sagrados interesses!
Ao comicio!

Agueda, 29 de Janeiro de 1924.

*Conde da Borralha*
*Dr. Antonio Breda*
*Dr. Antonio Homem de Mello*
*Dr. Antonio Tavares da Silva*
*Armando Castella*
*Dr. Eugenio Ribeiro*
*Dr. Fernando Ferreira Baptista*
*Dr. Jayme Ribeiro*
*Dr. João Elysio Sucena*
*João da Silva Neto.*

Álvaro de Castro (18 de dezembro de 1923 a 6 de julho 1924) – 201 dias

40 governos de 1910 (República) a 1926 (Golpe de 28 de Maio; ditadura)

**Lítio. Manifestação contra a mina em Boticas "bloqueia" acesso a escritório da Savannah**



**População de Covas do Barroso sai à rua, em defesa da região e contra a mina de lítio**

# I like to read books in paper…



80th anniversary…still 20 to go…(now 19)

3-10-2

c-gc-ggc