Departamento de Ingeniería Química
y Química Inorgánica
Universidad de Cantabria (SPAIN)

SUSTAINABLE AND INNOVATIVE PROCESSES FOR CARBON CAPTURE AND RECYCLING

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Sosprocan DePRO
Desarrollo de Procesos Químicos
y Control de Contaminantes

Contents

1. Introduction

- Carbon dioxide Capture and geological Storage (CCS) is a bridging technology that will contribute to mitigating climate change.

- Preliminary estimates to assess the impact of the EU Directive 2009/31/EC [1] ➔ 7 million tonnes of CO_2 could be stored by 2020, and up to 160 million tonnes by 2030.

- "CCS components (capture, transport and storage) still need to be integrated into a complete CCS process, technological costs need to be reduced, and more and better scientific knowledge has to be gathered" [1].

- CCS: risks of permanent storage of CO_2?

  ↪ New interest in chemical technologies for **CARBON CAPTURE and RECYCLING PROCESSES**

[1] **Directive 2009/31/EC of 23 April 2009 on the geological storage of carbon dioxide, *O J L* 140: 114-35**

Aims of this presentation

- To discuss and present our view of the state of the art regarding **Carbon Capture and Recycling processes**, which include combustion, CO_2 separation/concentration and CO_2 transformation into useful products

- To outline the main aspects of the **"ENVIRONFRIEND-CONSOLIDER-Ingenio 2010" project proposal**, whose objective is to make a significant progress in the knowledge and development of **Sustainable and Innovative Processes for Carbon Capture and Recycling**

Contents

Carbon capture and mitigation processes

- Conditions of pressure and temperature and gas stream composition determine the CO_2 capture processes

GAS STREAM → **CARBON CAPTURE** → ***EMISSION***

- Conditions: P, T
- Composition: CO_2
  byproducts
  impurities

→ **Adsorption** technology

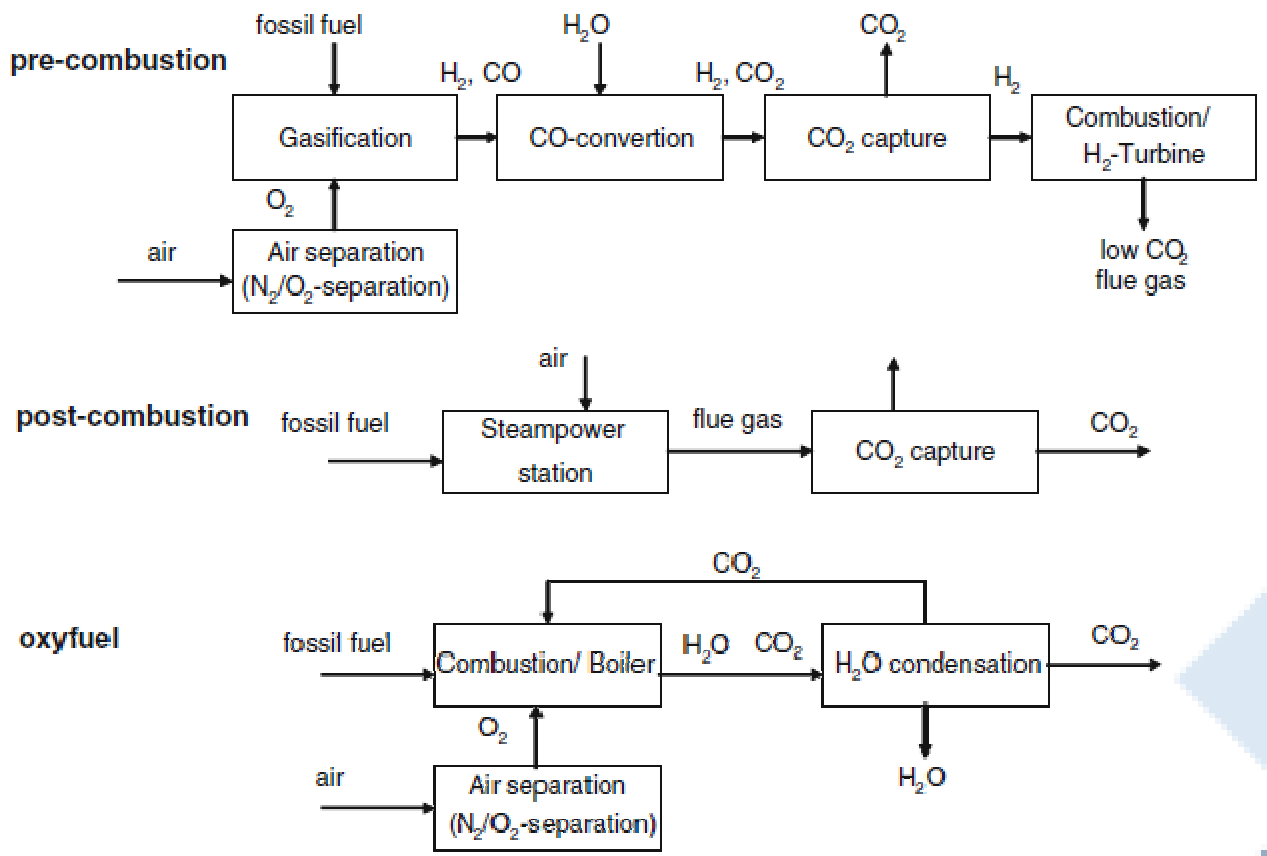
→ **Absorption** technology

→ **Membrane** technology

- Mitigation efficiency: % of CO_2 in emission with respect to % of CO_2 in input gas stream

2.1. Carbon capture and combustion processes

- Currently available processes to capture CO_2 [1]:

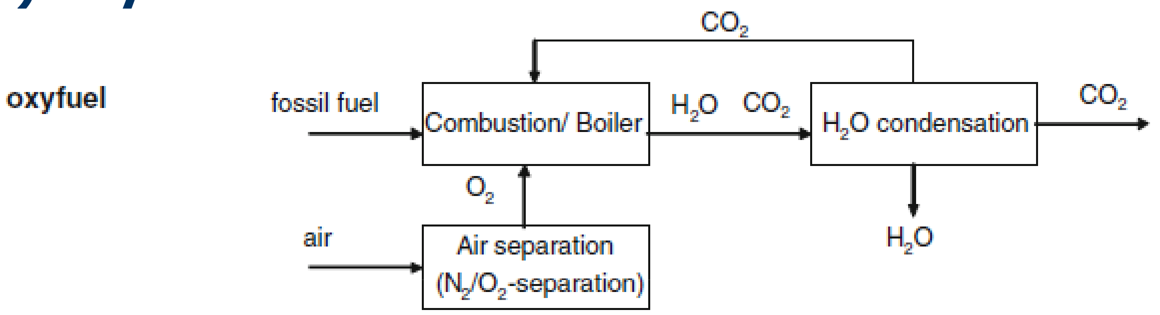


[1] Screiber et al., 2009, *Int J Life Cycle Assess* 14:547-559

2.1. Carbon capture and combustion processes

- **Cleaner combustion processes**

a) Oxy-fuel combustion [1,2]



- Fuel is combusted in pure O_2 mixed with recycled flue gases rather than air ➔ a flue gas stream with high concentration of CO_2 is produced, making CO_2 separation easier
- However, important pollutants formed during combustion, such as NOx, SO_2 and even soot, should be removed

Research is needed to optimize the process of NOx reduction, sulphur capture and soot formation under oxy-fuel operating conditions

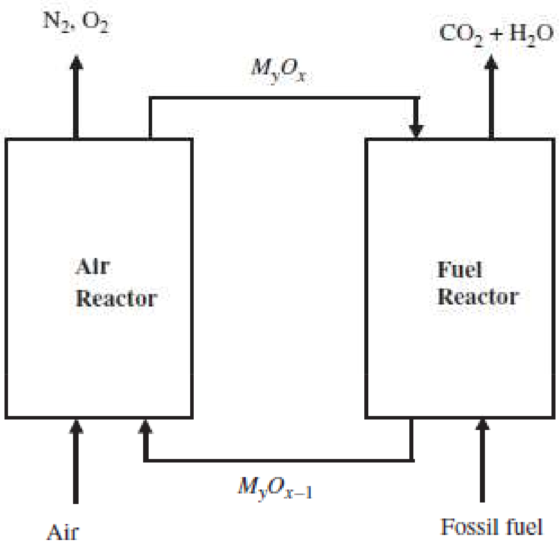
[1] **Buhre et al., 2005, *Energy Combust Sci* 31:283-307.** [2] **Screiber et al., 2009, *Int J Life Cycle Assess* 14:547-559**

2.1. Carbon capture and combustion processes

- **Cleaner combustion processes**

b) Chemical Looping Combustion [1,2]

- Two interconnected fluidized bed reactors (the fuel and air reactor) with an oxygen carrier (typically formed by metal oxide) circulated between units



- Two flue gas streams are generated:
  - Complete combustion in the fuel reactor produces CO_2 and water vapor (free nitrogen mixture)➔ the CO_2 formed can be readily recovered by condensing water vapor
  - Outlet gas stream from the air reactor: N_2 and unreacted O_2

[1] Hossain & de Lasa, 2008, *Chem Eng Sci* 63:4433-51. [2] Leion et al., 2008, *Int J Greenh Gas Con* 2:180-93.

2.1. Carbon capture and combustion processes

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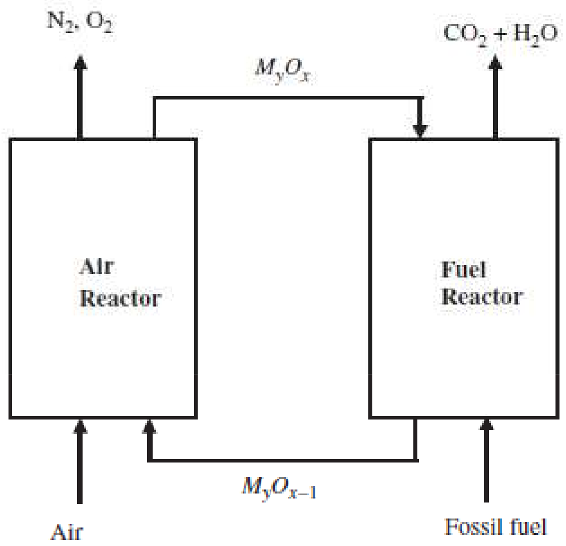


- Two interconnected fluidized bed reactors (the fuel and air reactor) with an oxygen carrier (typically formed by metal oxide) circulated between units

- Main advantages:
  - Promising technology with low energy penalty
  - CO_2 separation from flue gases is avoided
  - Formation of NOx is also reduced

Need to develop suitable oxygen carrier materials which are both active and stable

[1] Hossain & de Lasa, 2008, *Chem Eng Sci* 63:4433-51. [2] Leion et al., 2008, *Int J Greenh Gas Con* 2:180-93.

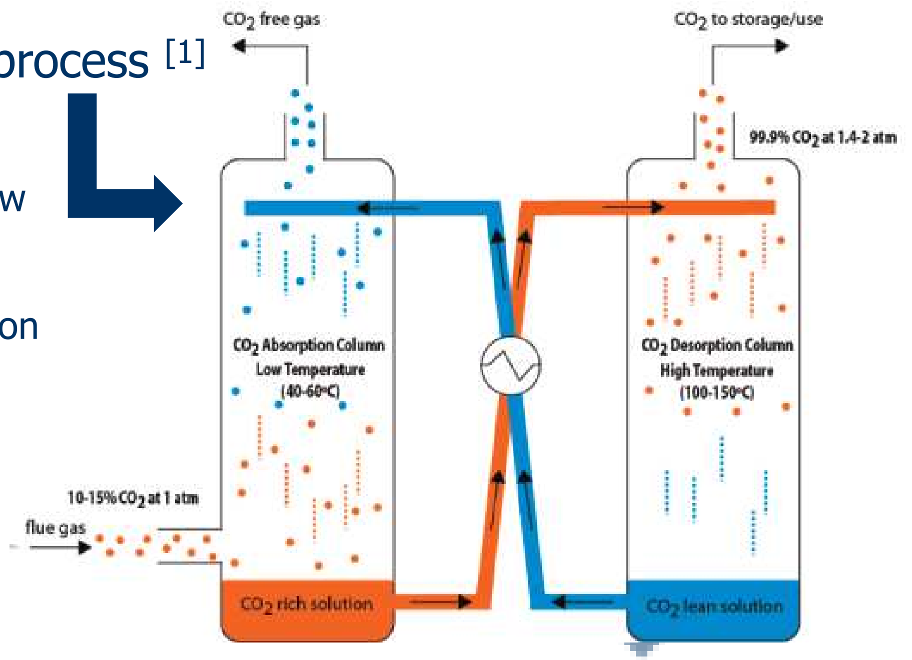
2.2. CO_2 separation processes

- The most mature and applied technology for the post-combustion capture of CO_2 from the flue gas and subsequent release is **cyclic chemical absorption/ desorption using an aqueous amine solution of monoethanolamine (MEA) 30% w/w [1]**
- Aqueous solutions of other amines that have better performance characteristics than MEA are also available from commercial suppliers
- Standard absorption/desorption process [1]

  - Gas and amine solution: counter-current contact in a packed absorber column at low T (40 °C) and atmospheric P

  - Absorbed CO_2 is released in the desorption column at high T (120 ºC)

  - Regenerated amine solution → recirculated to absorber



[1] **Puxty et al., 2009, *Environ Sci Technol* 43:6427-33.**

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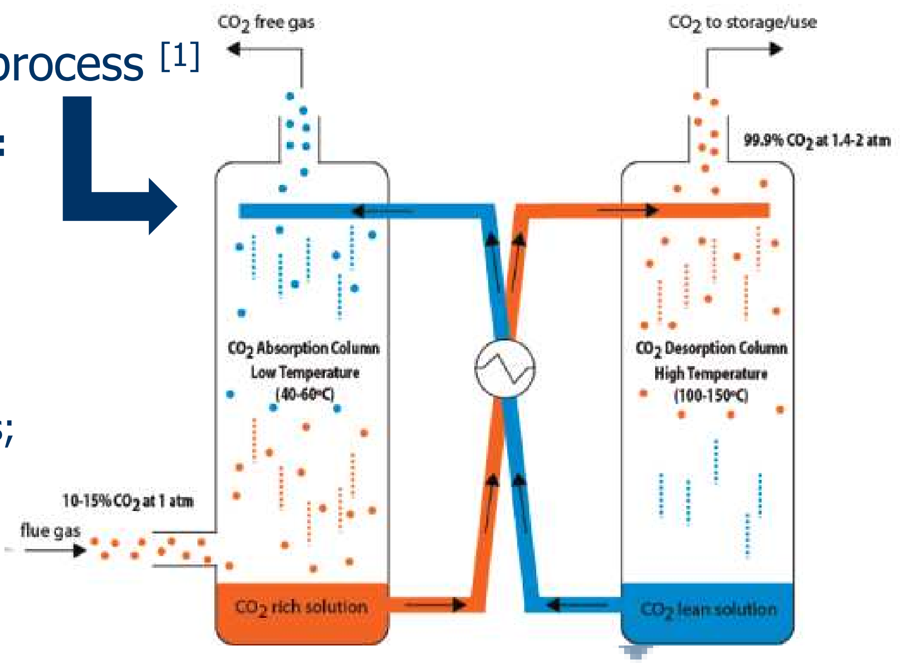
Many limitations and disadvantages:

- Significant amount of energy required (especially in the regeneration step)
- Large scale equipment needed
-Amines are corrosive and susceptible to degradation by trace flue gas components; atmospheric losses require adding new solvent



[1] Puxty et al., 2009, *Environ Sci Technol* 43:6427-33.

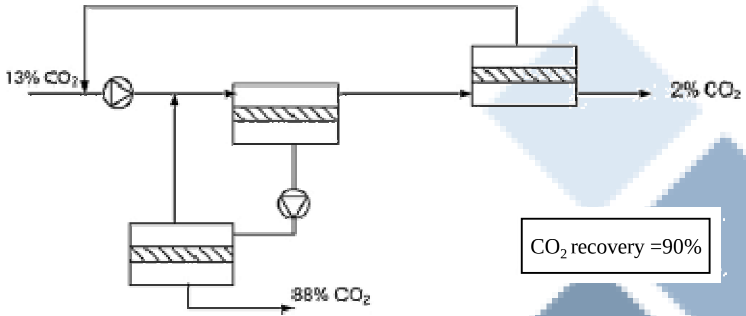
2.2. CO_2 separation processes

- The identification of a capture process which would fit the needs of target separation performances, together with a minimal energy penalty, is a key issue

Separation processes based on **membrane technologies intensified by ionic liquids** appear as one of the main innovations

- Because of their fundamental engineering and economic advantages over competing separation technologies, **membrane operations are, now, being explored for CO_2 capture** from power plant emissions [1]

- E.g. Three stage membrane process proposed for CO_2 separation from coal power plant flue gas (90% CO_2 recovery, 88% of purity) [2]



[1] Brunetti et al., 2009, *J Membr Sci*, in press. [2] Baker, 2008, Proceedings of 12th Aachener membrane kolloquim

2.2. CO_2 separation processes

- Selectivity and permeability: important membrane properties to consider.

  ↳ But research is also needed to study the influence of process variables (e.g. T, P, humidity, configuration)

- **Advanced Separation/Concentration Processes based on membrane technologies can be developed in three main ways [1,2]:**

  1) **Gas permeation**, based on fast and selective **dense membranes** and advanced configurations.
  2) **Non-Dispersive absorption** processes combining absorption selectivity and permeation.
  3) **Supported-Liquid Membrane** processes able to increase membrane selectivity.

[1] Scovazzo, 2009, *J Membr Sci* 343:199-211. [2] Hasib-ur-Rahman et al., 2010, *Chem Eng Process* 49:313-22.

2.2. CO_2 separation processes

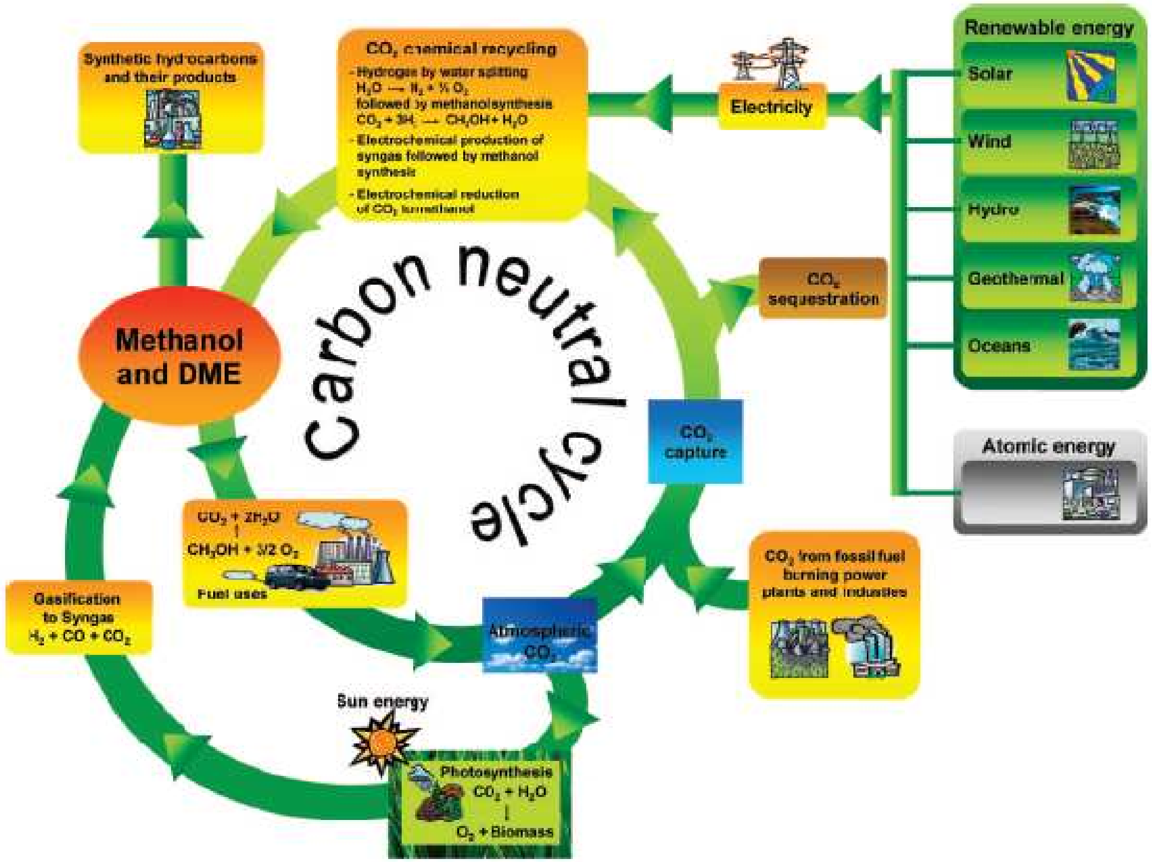
- **Intensification using Ionic Liquids:**
  - CO_2 capture by absorption with ILs is currently being studied (e.g. [1-4])
  - Reliable guidelines exist for selecting ILs with particular solubility and selectivity properties related to CO_2-based separations, with imidazolium-based salts at the centre of this research effort
  - Process temperature and the chemical structures of the cation and anion have significant impacts on CO_2 absorption performance
  - A great potential of ILs for CO_2 separations has been related to their ability to chemically capture CO_2 when used in combination with amines as functional groups of the cation or the anion

[1] Gurkan et al., 2010, *J Amer Chem Society* 132:2116-7. [2] Kurnia et al., 2009, *J Chem Therm* 41:1069-73.
[3] Yokozeki et al., 2008, *J Phys Chem B* 112:16654-63. [4] Bara et al., 2008, *Ind Ing Chem Res* 48:2739-51.

2.3. Processes for CO_2 recycling

- **CO_2 recycling ➔** conversion of the previously captured CO_2 into carbon fuels and derived hydrocarbon products with added value

  - E.g. Carbon dioxide recycling in the "Methanol Economy" proposed by Olah et al. [1]



[1] **Olah et al., 2009, *J Org Chem* 74:487-98**

2.3. Processes for CO_2 recycling

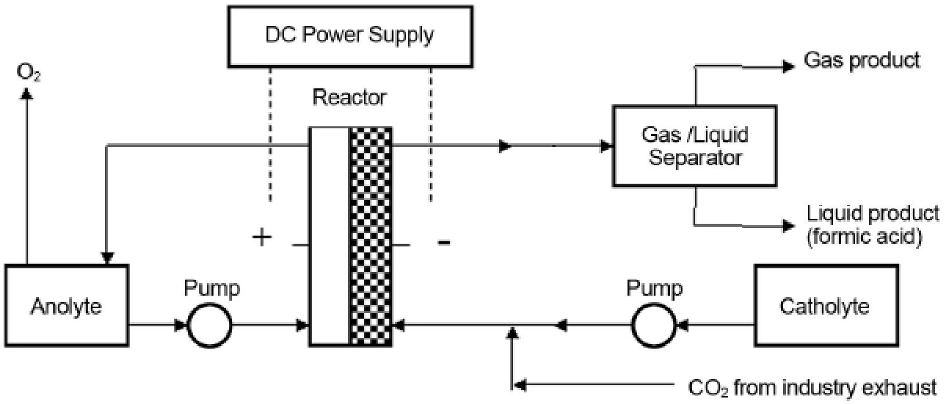
- **Electrochemical Reduction of CO_2 (ERC)**
  - Main products obtained highly depend on the nature of the material used as cathode and the supporting electrolyte

    E.g. Major products from the ERC using different electrode metals in aqueous media [1,2]:

    -Cu ➔ hydrocarbons (CH_4, C_2H_4) and alcohols (EtOH, PrOH)

    -Pb, Hg, In, Sn, Bi, Cd, Tl ➔ Formic acid (HCOOH)

  - Recent development of ERC commercial process to produce formic acid by Mantra™ Venture Group *(http://www.mantraenergy.com/home.html):*



http://www.mantraenergy.com/home.html

[1] **Hori et al., 1994, *Electrochim Acta* 39:1833-9.** [2] **Sánchez-Sánchez et al., 2001, *Pure Appl Chem* 73:1917-27**

2.3. Processes for CO_2 recycling

- **Electrochemical Reduction of CO_2 (ERC)**
  - **Key issues that need to be solved:**

-Cathodic reduction of CO_2 is normally accompanied by hydrogen evolution
-The reduction takes place at much more negative potentials than the reversible potential
-Selectivity of the reaction is low in many cases→ mixtures of reaction products are obtained
-Short electrode lifetime
-Mass transport limitations in aqueous media due to low solubility of CO_2
-Large consumption of electric energy needed for the reduction

RESEARCH

- Need to find electrodes with high electrocatalytic activity, high product selectivity and satisfactory lifetime

-Improvement of CO_2 solubility: use of organic solvents, high pressure...

- Integration of ERC with renewable energy sources (e.g. photovoltaic solar, wind power)

2.4. Process integration and sustainability assessment

- **Life Cycle Thinking (LCT)**

Evaluation of innovative chemical processes and/or products considering **Life Cycle Assessment (LCA)** & **Supply Chain Management (SCM)** [1,2]

- **Process integration** considers the influence of innovative changes (Process Intensification [3]) in carbon capture

But decision-making tools need to be developed to clarify the advantages ➔ development of **Sustainability Metrics** of intensified processes

[1] Azapagic,1999, *Chem Eng J* 73:1-21. [2] Grossmann, 2004, *Comput Chem Eng* 29:29-39.
[3] Stankiewicz & Moulijn, 2002, *Ind Eng Chem Res* 41:1920-4

Contents

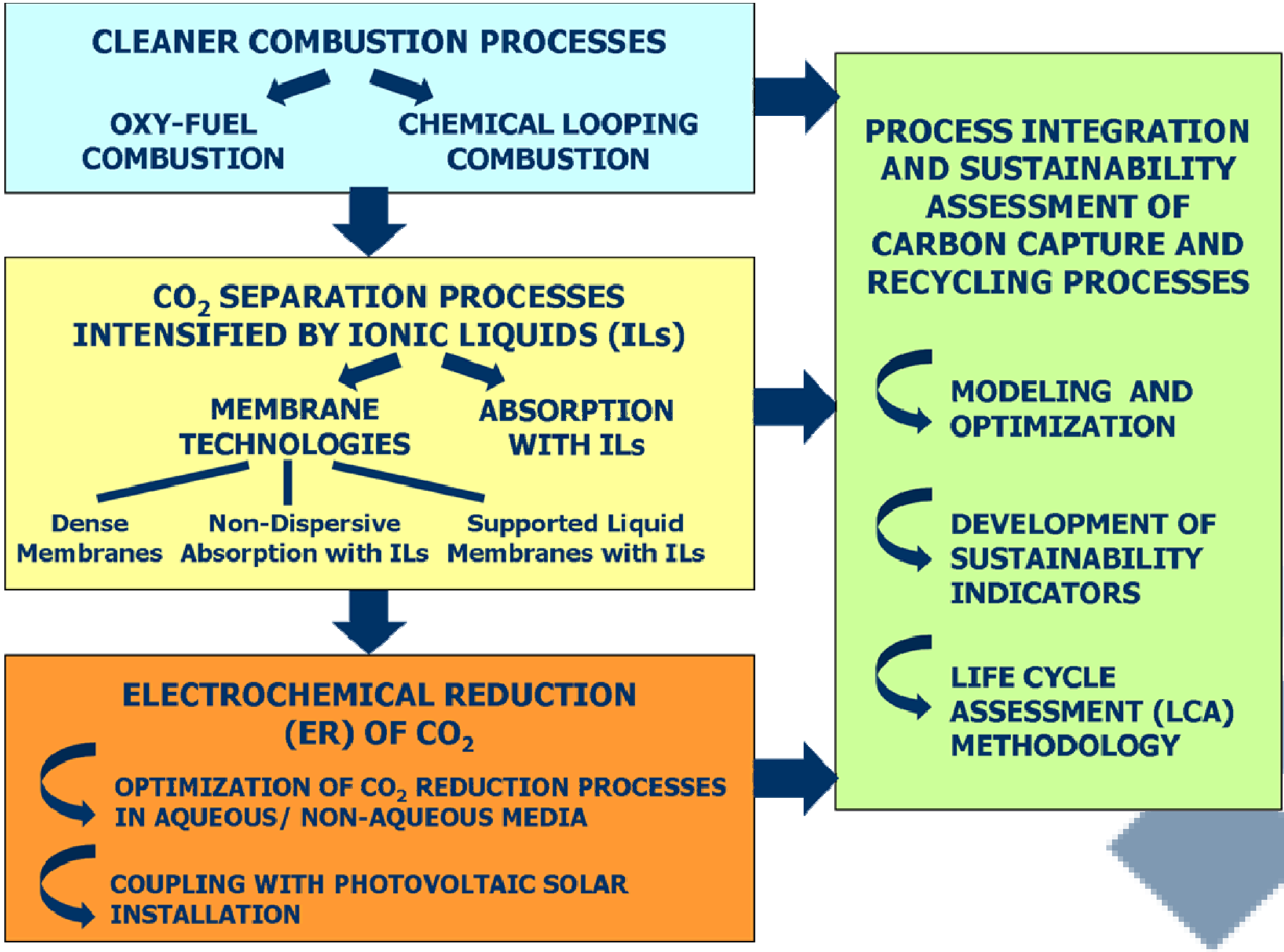
3.1. CONSOLIDER-Ingenio 2010 Programme

- Programme of the Spanish Ministry of Science and Innovation, which seeks to achieve research excellence
- "CONSOLIDER" ➔ financial help for CONSOlidated groups that are LEADERS within Spanish scientific community
- Strategic funding is awarded to teams comprising groups of high-level researchers which present a research project for joint implementation leading to significant progress in a high-level scientific activity.
- Beneficiaries: Research teams comprising research groups from R&D centres (Universities, PROs recognized by Spanish law, Technological Centres…)
- Long-term (5 years), large-scale (€5 mill.) funding is awarded in competitive call

3.2. Project proposal outline

- **"ENVIRONFRIEND-CONSOLIDER-Ingenio 2010" project proposal**

Global research approach: INTENSIFICATION AND INTEGRATION of innovative processes for the different steps of carbon capture & recycling



3.2. Project proposal outline

- Universities and CSIC Institutes involved:

Instituto de Carboquímica ICB-CSIC

Universidad Autónoma de Madrid (UAM)

Universidad Complutense de Madrid (UCM)

Universidad de Alicante (UA)

Universidad de Cantabria (UC)

Universidad de Castilla La Mancha (UCLM)

Universidad de las Palmas de Gran Canaria (ULPGC)

Universidad de Santiago de Compostela (USC)

Universidad de Vigo (UVigo)

Universidad de Zaragoza (UNIZAR)

Universidad del País Vasco (UPV/EHU)

Universitat Politècnica de Catalunya CTM-UPC.

Universitat Rovira i Virgili (URV)

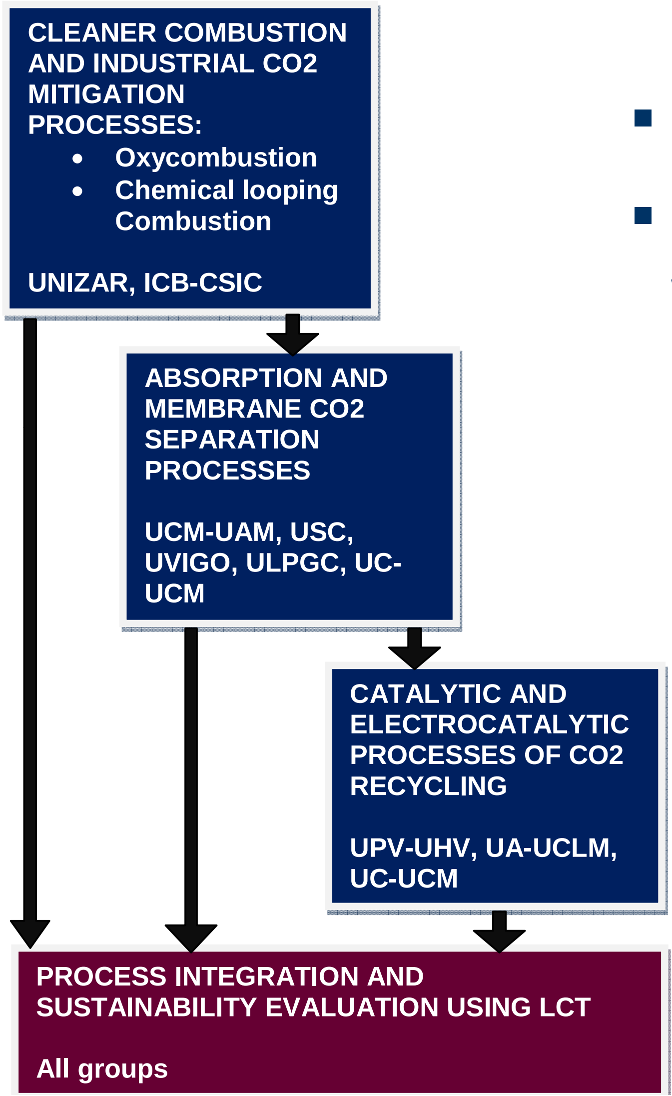
3.2. Project proposal outline

- Project coordinator: Angel Irabien (UC, University of Cantabria)
- Main researchers and topics

Main Researchers (Units)	Main Research Topic
R Bilbao (UNIZAR)	Cleaner Combustion
U Alzueta (UNIZAR)	Cleaner Combustion
J Adanez (ICB/CSIC)	Cleaner Combustion
L de Diego (ICB/CSIC)	Cleaner Combustion
F Rodriguez Somolinos (UCM)	Absorption Desorption with Ionic Liquids
A Irabien (UC)	Membrane Processes
J Palomar (UAM)	Molecular Design of Ionic Liquids
A Arce (USC)	Applications of ionic liquids (Absorption)
A Soto (USC)	Applications of ionic liquids
E Tojo (UVigo)	Synthesis of Ionic Liquids
A Dominguez (UVigo)	Properties of Ionic Liquids
JA Ortega (ULPGC)	Physical-Chemical properties of IL
I Nuez (ULPGC)	Physical-Chemical properties of IL
J Bilbao (UPV-EHU)	Catalytic Processes
M Olazar (UPV-EHU)	Catalytic Processes
E Herrero (UA)	Electrocatalytic Processes
F Feliu (UA)	Electrocatalytic Processes
J Lobato (UCLM)	Electrocatalytic Processes
F Castells (URV)	Life Cycle Assessment
L Jimenez (URV)	Process Systems Engineering
A Romero (UCM)	Chemical Process Development
J de Pablo (CTM-UPC)	Knowledge and Technology Transfer
M Rovira (CTM-UPC)	Knowledge and Technology Transfer

3. CONSOLIDER-Ingenio project proposal

3.2. Project proposal outline



- Functional structure of the project
- Coordination among the groups working in different parts of the project

3.3. Final Remarks

- **Knowledge transfer** to the Technology Platforms and Cenit projects (large collaborative projects of industrial research) and **promotion of the international cooperation** are also priorities in the project

  - Interest in demonstration projects and innovation partners for technology transfer

  - Interest in collaborations with other international research groups

- One-year funding has already been obtained for non-dispersive absorption processes and electrochemical reduction of CO_2, and three-year funding is under consideration for the main research group.

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«We know what we have to do to achieve the sustainability, now it's time to do it »