SUSTAINABLE AND INNOVATIVE PROCESSES FOR CARBON CAPTURE AND RECYCLING

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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**

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1. Introduction

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**.
1. Introduction

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Carbon Capture and Recycling: our view of the state of the art

Carbon capture and mitigation processes

- Conditions of pressure and temperature and gas stream composition determine the CO$_2$ capture processes

**GAS STREAM**
- Conditions: P, T
- Composition: CO$_2$, byproducts, impurities

**CARBON CAPTURE**

**EMISSION**

- Adsorption technology
- Absorption technology
- Membrane technology

- Mitigation efficiency: % of CO$_2$ in emission with respect to % of CO$_2$ in input gas stream
2. Carbon Capture and Recycling: our view of the state of the art

2.1. Carbon capture and combustion processes

- Currently available processes to capture CO$_2$\cite{screiber2009}:

\[\text{fossil fuel} \rightarrow \text{Gasification} \rightarrow \text{CO-conversion} \rightarrow \text{CO$_2$ capture} \rightarrow \text{Combustion/ H$_2$-Turbine}\]

\[\text{fossil fuel} \rightarrow \text{Steampower station} \rightarrow \text{CO$_2$ capture}\]

\[\text{fossil fuel} \rightarrow \text{Combustion/ Boiler} \rightarrow \text{H$_2$O condensation} \rightarrow \text{CO$_2$}\]

\[\text{Air separation (N$_2$/O$_2$-separation)}\]

\[\text{O$_2$} \rightarrow \text{Air separation (N$_2$/O$_2$-separation)}\]

\[\text{H$_2$O} \rightarrow \text{H$_2$O condensation}\]

\[\text{low CO$_2$ flue gas}\]

\[\text{1 Screiber et al., 2009, Int J Life Cycle Assess 14:547-559}\]
2. Carbon Capture and Recycling: our view of the state of the art

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 \(\rightarrow\) 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.

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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) $\Rightarrow$ the CO$_2$ formed can be readily recovered by condensing water vapor
    - Outlet gas stream from the air reactor: N$_2$ and unreacted O$_2$

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2. Carbon Capture and Recycling: our view of the state of the art

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

- Main advantages:
  
  - Promising technology with low energy penalty
  - \(\text{CO}_2\) 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

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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 °C)
  - Regenerated amine solution → recirculated to absorber

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2. Carbon Capture and Recycling: our view of the state of the art

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 \[1\]

**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

2. Carbon Capture and Recycling: our view of the state of the art

2.2. CO₂ 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 CO₂ capture from power plant emissions [1].

- E.g. Three stage membrane process proposed for CO₂ separation from coal power plant flue gas (90% CO₂ recovery, 88% of purity) [2].

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2.2. \( \text{CO}_2 \) separation processes

- Selectivity and permeability: important membrane properties to consider.
  But research is also needed to study the influence of process variables (e.g. \( T, P, \text{humidity, configuration} \)).

- 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 \textit{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.

Carbon Capture and Recycling: our view of the state of the art

2.2. CO₂ separation processes

- Intensification using Ionic Liquids:
  - CO₂ 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 CO₂-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 CO₂ absorption performance
  - A great potential of ILs for CO₂ separations has been related to their ability to chemically capture CO₂ when used in combination with amines as functional groups of the cation or the anion

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 $\rightarrow$ hydrocarbons (CH$_4$, C$_2$H$_4$) and alcohols (EtOH, PrOH)
  
  - Pb, Hg, In, Sn, Bi, Cd, Tl $\rightarrow$ Formic acid (HCOOH)

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

![ERC process diagram](http://www.mantraenergy.com/home.html)

2.3. Processes for CO\textsubscript{2} recycling

- Electrochemical Reduction of CO\textsubscript{2} (ERC)
  
  - Key issues that need to be solved:
    - Cathodic reduction of CO\textsubscript{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\textsubscript{2}
    - Large consumption of electric energy needed for the reduction
  
  - Need to find electrodes with high electrocatalytic activity, high product selectivity and satisfactory lifetime
  - Improvement of CO\textsubscript{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

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   - 3.1. CONSOLIDER-Ingenio 2010 Programme
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3. CONSOLIDER-Ingenio project proposal

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. CONSOLIDER-Ingenio project proposal

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

**CLEANER COMBUSTION PROCESSES**
- OXY-FUEL COMBUSTION
- CHEMICAL LOOPING COMBUSTION

**CO₂ SEPARATION PROCESSES INTENSIFIED BY IONIC LIQUIDS (ILs)**
- MEMBRANE TECHNOLOGIES
  - Dense Membranes
  - Non-Dispersive Absorption with ILs
  - Supported Liquid Membranes with ILs

**ELECTROCHEMICAL REDUCTION (ER) OF CO₂**
- OPTIMIZATION OF CO₂ REDUCTION PROCESSES IN AQUEOUS/ NON-AQUEOUS MEDIA
- COUPLING WITH PHOTOVOLTAIC SOLAR INSTALLATION

**PROCESS INTEGRATION AND SUSTAINABILITY ASSESSMENT OF CARBON CAPTURE AND RECYCLING PROCESSES**
- MODELING AND OPTIMIZATION
- DEVELOPMENT OF SUSTAINABILITY INDICATORS
- LIFE CYCLE ASSESSMENT (LCA) METHODOLOGY
3. CONSOLIDER-Ingenio project proposal

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)
  - Universitat d’Alacant
  - Universidad de Cantabria (UC)
  - Universitat Rovira i Virgili (URV)
  - Universidad de Castilla La Mancha (UCLM)
  - Universidad de las Palmas de Gran Canaria (ULPGC)
  - Universidade 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. CONSOLIDER-Ingenio project proposal

3.2. Project proposal outline

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

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<th>Main Research Topic</th>
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<td>U Alzueta (UNIZAR)</td>
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<td>A Irabien (UC)</td>
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<td>J Palomar (UAM)</td>
<td>Molecular Design of Ionic Liquids</td>
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<td>A Arce (USC)</td>
<td>Applications of ionic liquids (Absorption)</td>
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<td>A Soto (USC)</td>
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<td>E Tojo (UVigo)</td>
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<td>M Rovira (CTM-UPC)</td>
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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

CLEANER COMBUSTION AND INDUSTRIAL CO2 MITIGATION PROCESSES:
  - Oxycombustion
  - Chemical looping Combustion

UNIZAR, ICB-CSIC

ABSORPTION AND MEMBRANE CO2 SEPARATION PROCESSES

UCM-UAM, USC, UVIGO, ULPGC, UC-UCM

CATALYTIC AND ELECTROCATALYTIC PROCESSES OF CO2 RECYCLING

UPV-UHV, UA-UCLM, UC-UCM

PROCESS INTEGRATION AND SUSTAINABILITY EVALUATION USING LCT

All groups
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 »