Academic Workshop on Chemical Looping
HUST - CSIC

Huazhong University of Science and Technology
Consejo Superior de Investigaciones Científicas

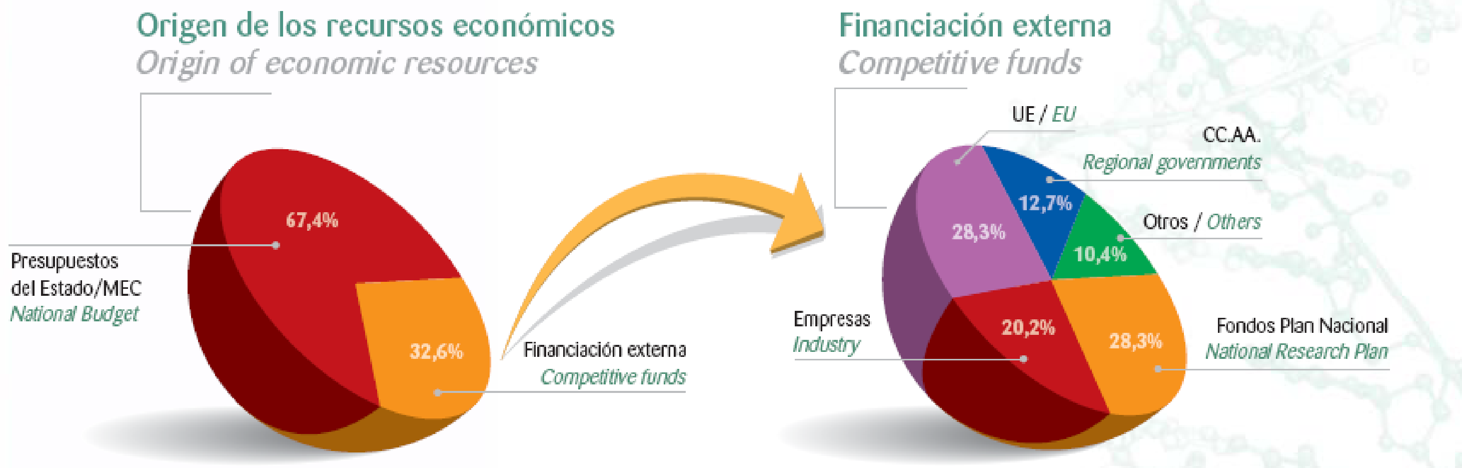
April 11th, 2025

Combustion and Gasification Group
Instituto de Carboquímica (ICB-CSIC)
Zaragoza, España

Spanish National Research Center

Consejo Superior de Investigaciones Científicas (CSIC)

“the largest public research body in Spain”



Total budget (2022) : 1286 M€

2022 Human resources (13888 personnel)

- 4489 Scientific personnel
- 1334 Pre and postdoctoral researchers
- 6705 Research support personnel
- 1360 Administration

➢ CSIC covers all fields of knowledge, from basic research to technological development

Society

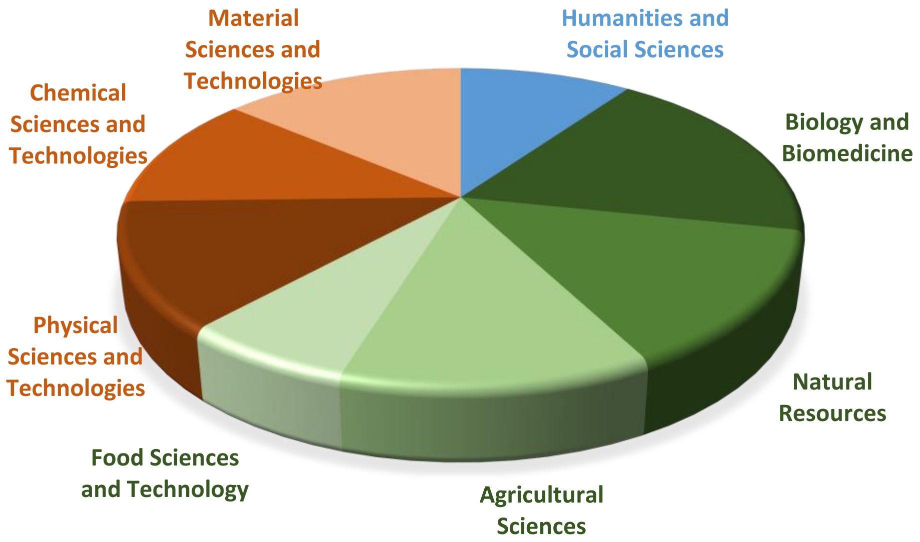
- Humanities and Social Sciences

Life

- Biology and Biomedicine
- Natural Resources
- Agricultural Sciences
- Food Sciences and Technology

Matter

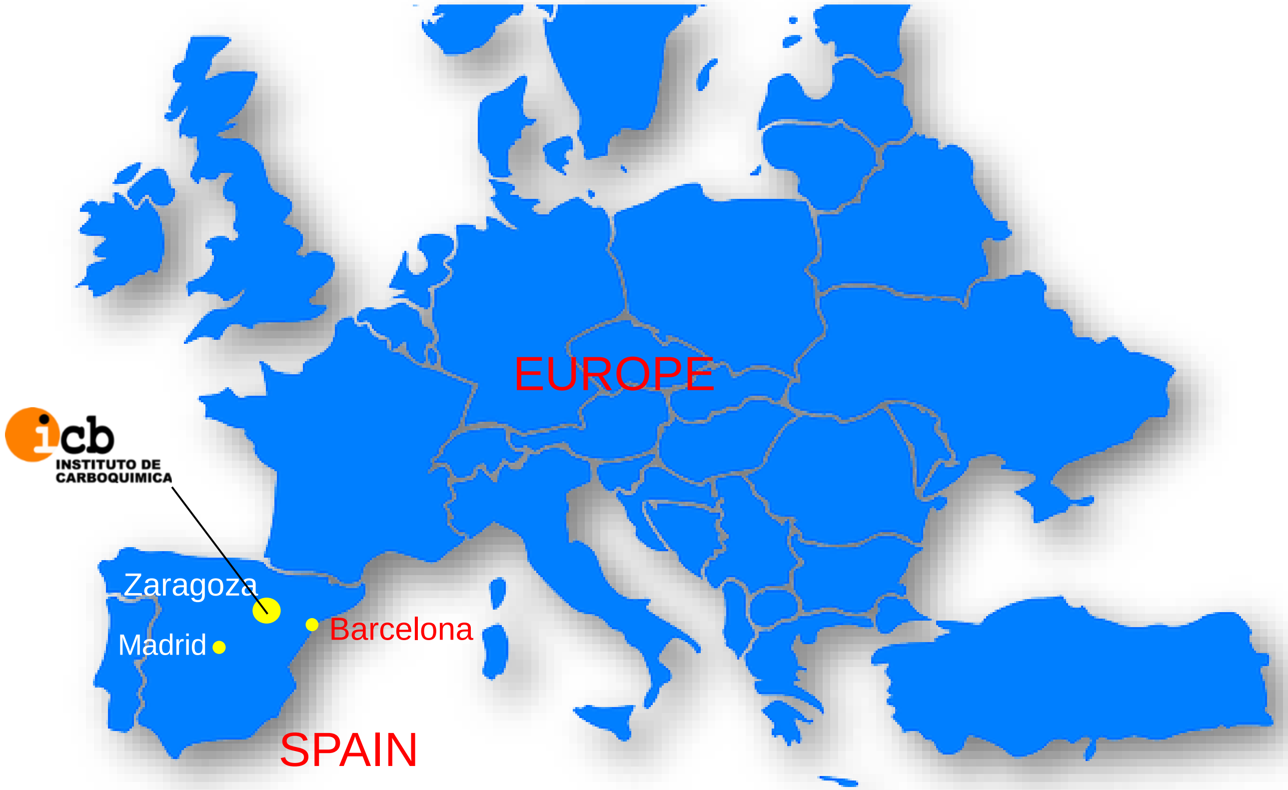
- Physical Sciences and Technologies
- **Chemical Sciences and Technologies** ⇨ icb INSTITUTO DE CARBOQUIMICA
- Material Sciences and Technologies



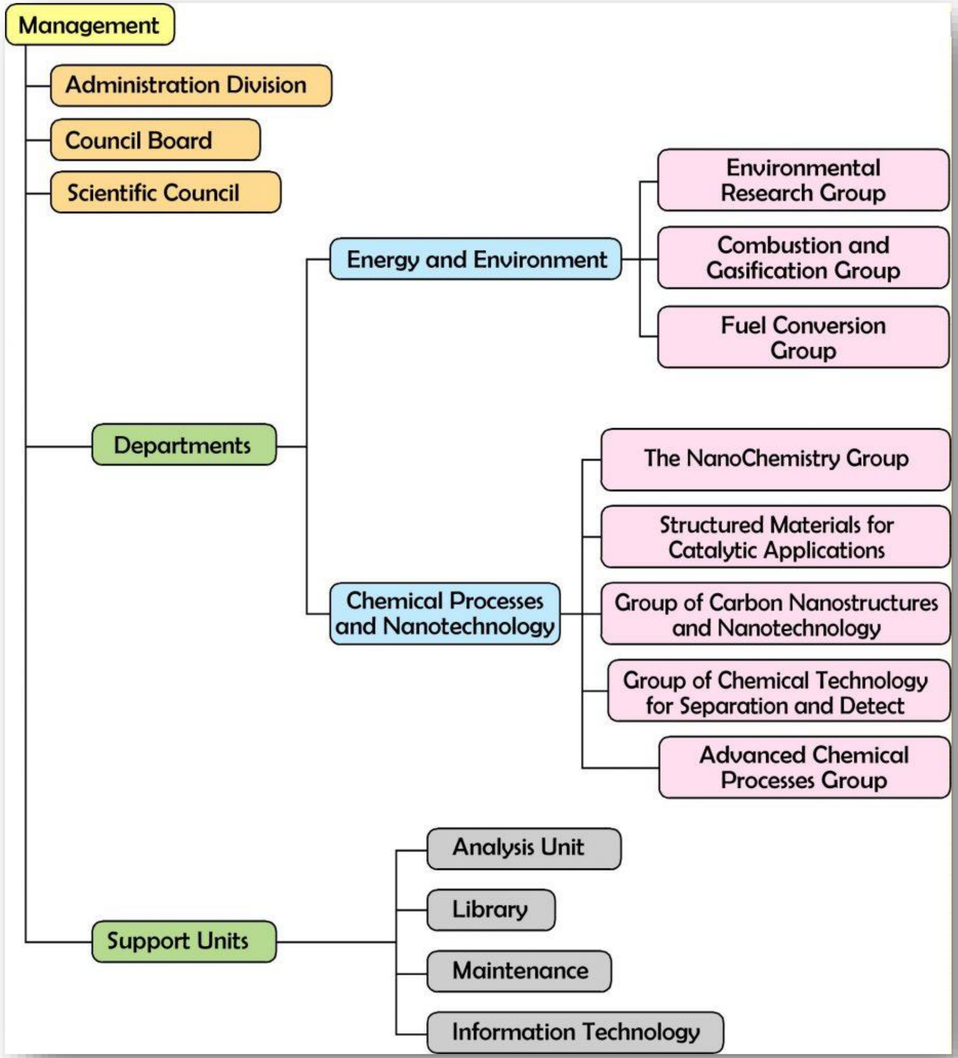
Consejo Superior de Investigaciones Científicas (CSIC)

- Spanish National Research Council (CSIC) -

Instituto de Carboquímica (ICB) Zaragoza

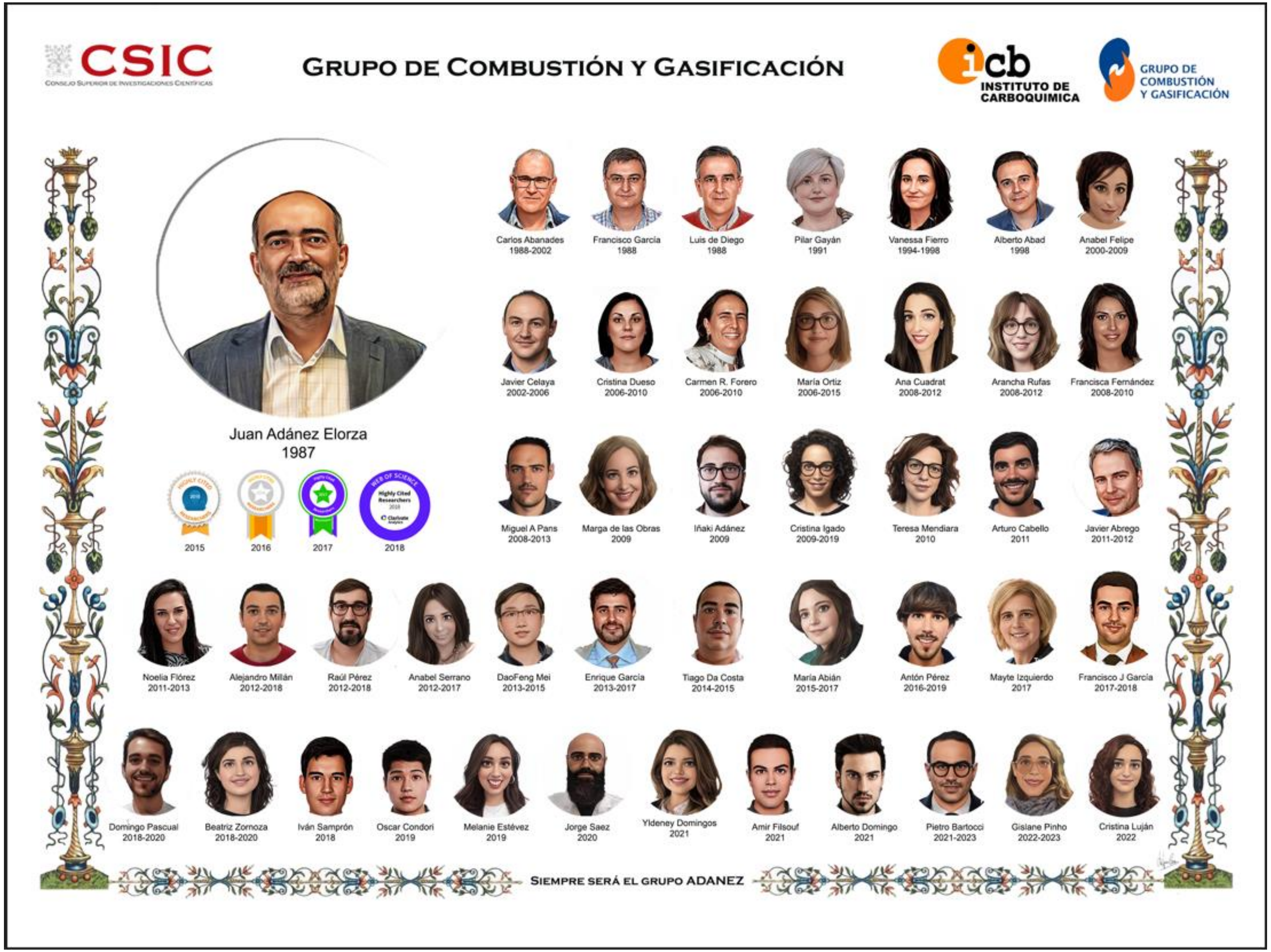


ICB organization



Combustion and Gasification Group

www.icb.csic.es/grupo/grupo-de-combustion-y-gasificacion/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Consejo Superior de Investigaciones Científicas
Grupo de Combustión y Gasificación
icb INSTITUTO DE CARBOQUIMICA
GRUPO DE COMBUSTIÓN Y GASIFICACIÓN
Juan Adánez Elorza
1987
2015
2016
2017
2018
Carlos Abanades 1988-2002
Francisco García 1988
Luis de Diego 1988
Pilar Gayán 1991
Vanessa Fierro 1994-1998
Alberto Abad 1998
Anabel Felipe 2000-2009
Javier Celaya 2002-2006
Cristina Dueso 2006-2010
Carmen R. Forero 2006-2010
María Ortiz 2006-2015
Ana Cuadrat 2008-2012
Arancha Rufas 2008-2012
Francisca Fernández 2008-2010
Miguel A Pans 2008-2013
Marga de las Obras 2009
Iñaki Adánez 2009
Cristina Igado 2009-2019
Teresa Mendiara 2010
Arturo Cabello 2011
Javier Abrego 2011-2012
Noelia Flórez 2011-2013
Alejandro Millán 2012-2018
Raúl Pérez 2012-2018
Anabel Serrano 2012-2017
DaoFeng Mei 2013-2015
Enrique García 2013-2017
Tiago Da Costa 2014-2015
María Abián 2015-2017
Antón Pérez 2016-2019
Mayte Izquierdo 2017
Francisco J García 2017-2018
Domingo Pascual 2018-2020
Beatriz Zornoza 2018-2020
Iván Samprón 2018
Oscar Condori 2019
Melanie Estévez 2019
Jorge Saez 2020
Yldeney Domingos 2021
Amir Filsouf 2021
Alberto Domingo 2021
Pietro Bartocci 2021-2023
Gislane Pinho 2022-2023
Cristina Luján 2022
Siempre será el grupo ADANEZ

Combustion & Gasification Research Group created in 1987

Staff	Dr. Francisco García	Senior scientific researcher	- **Head of research group**
7	Dr. Luis F. de Diego	Scientific Professor	
	Dra. Pilar Gayán	Senior scientific researcher	
	Dr. Alberto Abad	Senior scientific researcher	
	Dra. Mª Teresa Izquierdo	Senior scientific researcher	
	Dra. Teresa Mendiara	Senior scientific researcher	
	Dr. Arturo Cabello	Senior scientific researcher	
	Dra. Margarita Obras	Senior scientific researcher	
Post- doctoral	Dr. Iñaki Adánez-Rubio		
2	Dr. DaoFeng Mei		
Ph D student	D. Oscar Condori		
7	D. Yldenei Silva		
	D. Alberto García		
	D. Amir Filsouff		
	D. Javier Gonzalez		
	D. Laura García		
	D. Jose Ignacio		
Technician	D. Jorge Saez		
3	Dña. Melanie Estevez		
	Dña. Cristina Luján		

6th Int Conference on Chemical Looping at Zaragoza. 2022

COMBUSTION & GASIFICATION GROUP

INSTITUTO DE CARBOQUIMICA

➢ Research lines

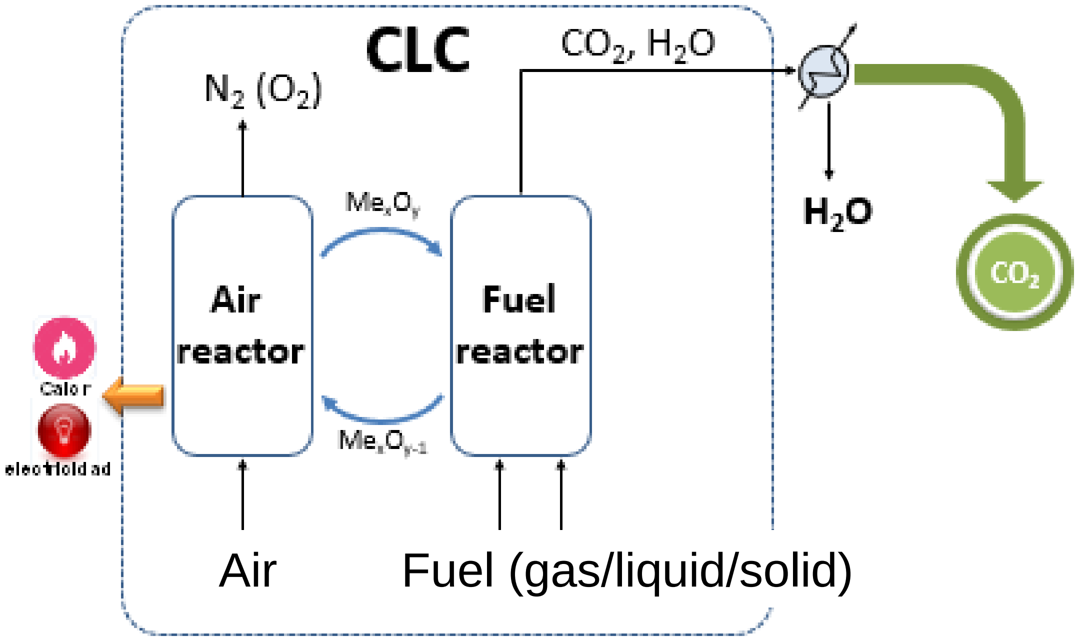
- **Combustion & Gasification**

  Renewable fuels (biogas, biomass, waste) in fluidized bed reactors

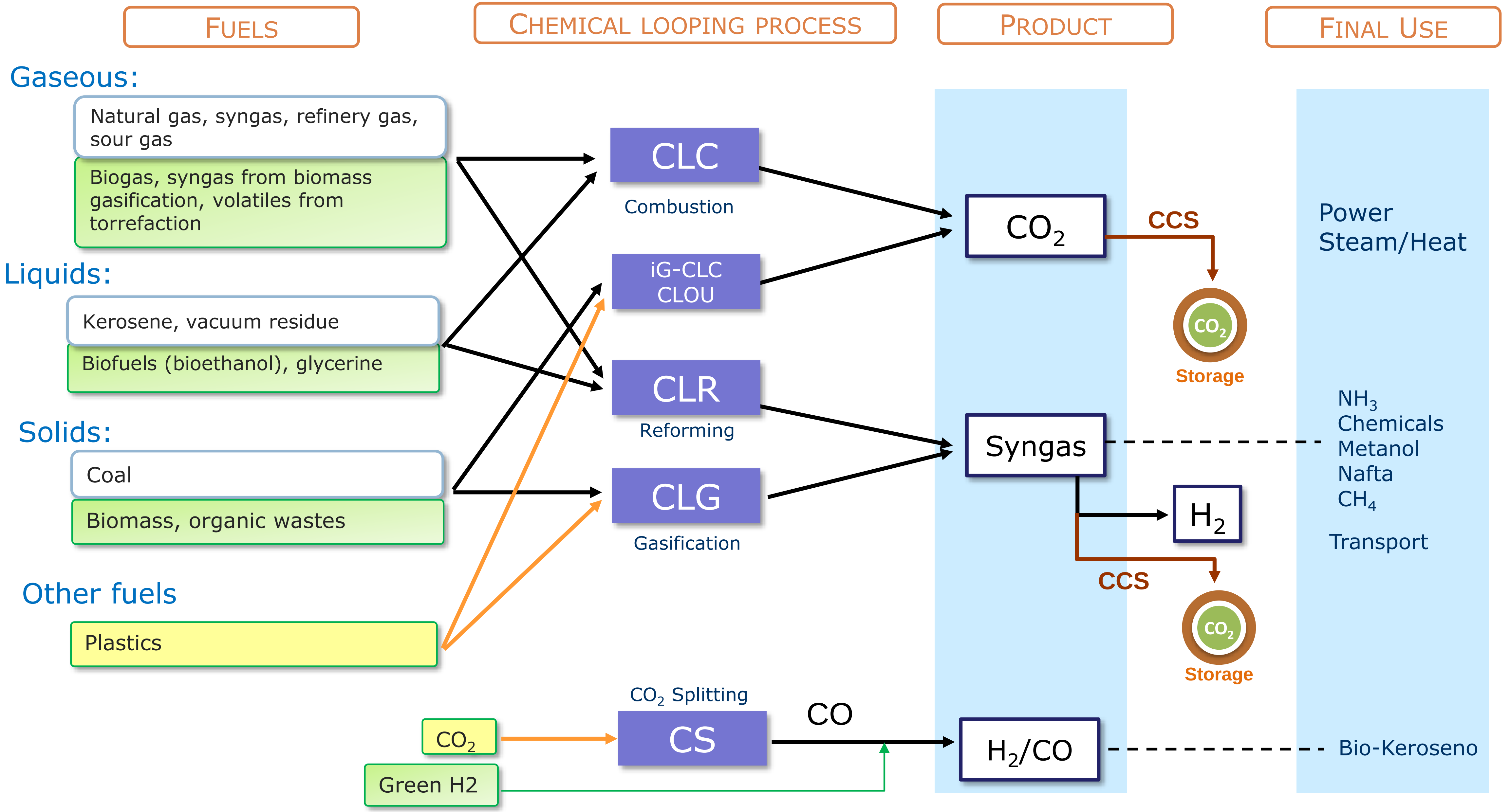
- **Hot gas cleaning of SO_2 and H_2S with calcium sorbents**

- **CO_2 capture**
  - **Chemical Looping Combustion (CLC)**
  - **Oxi-combustion in fluidized beds**

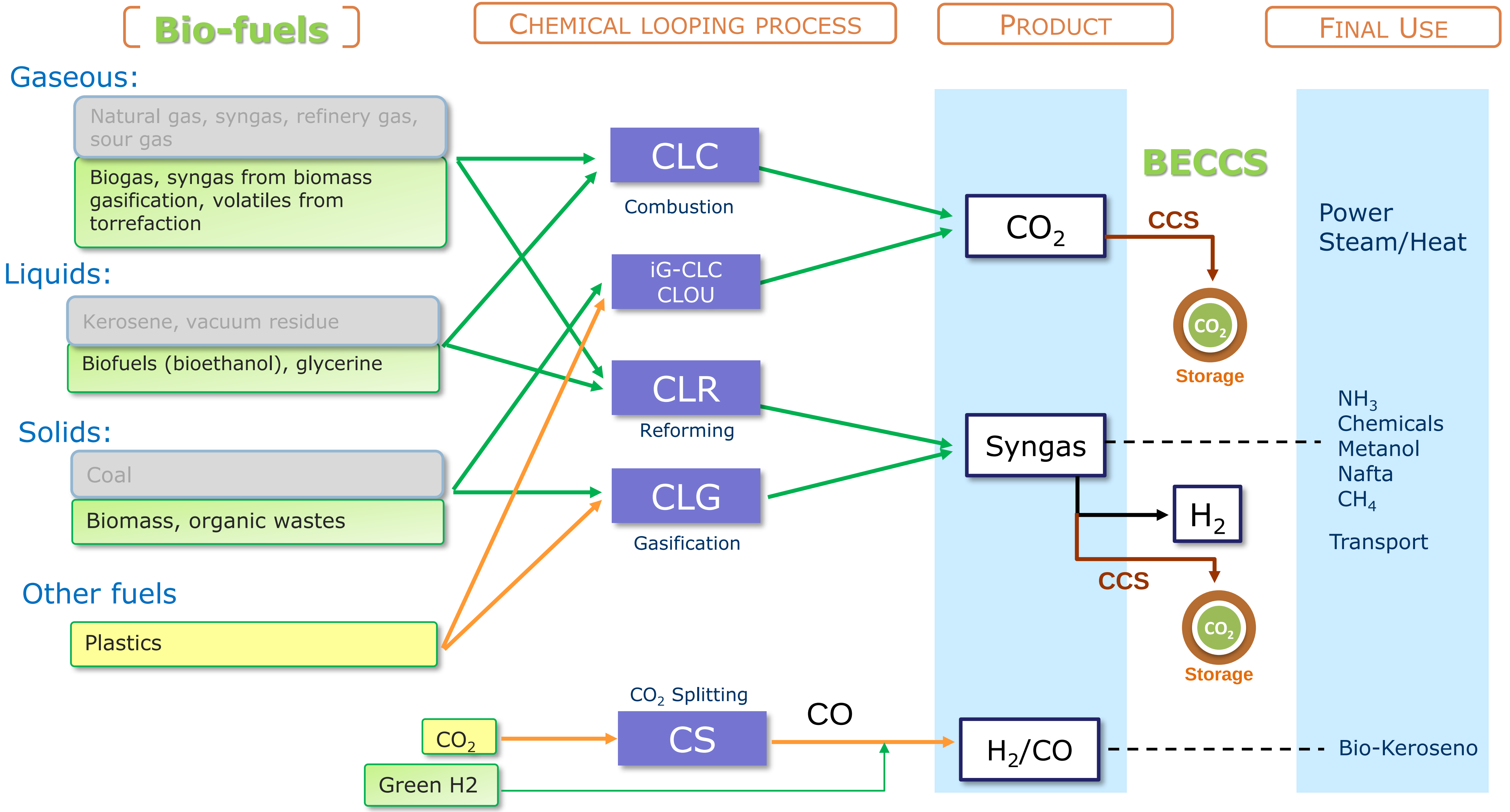
- **Syngas / H_2 production with CO_2 capture**
  - **Chemical Looping Reforming (CLG)**
  - **Sorption enhanced CLR**
  - **Chemical Looping Gasification (CLG)**



CHEMICAL LOOPING TECHNOLOGIES



BIO-FUELS CHEMICAL LOOPING TECHNOLOGIES



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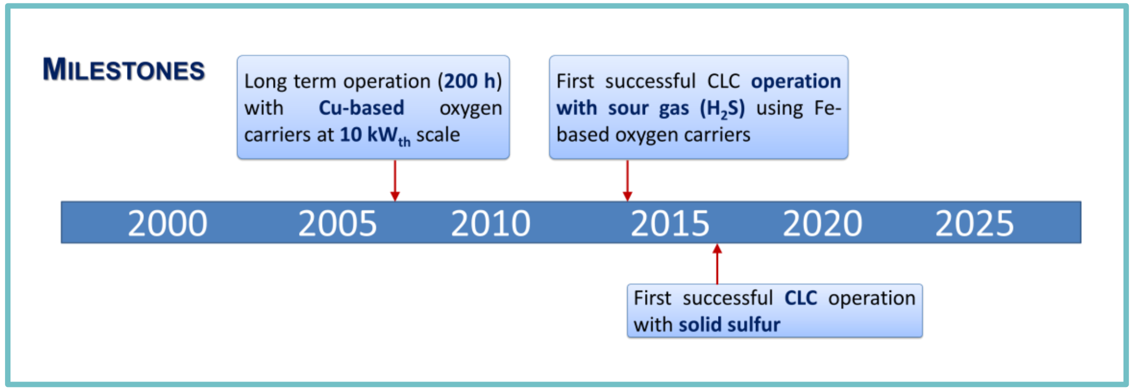
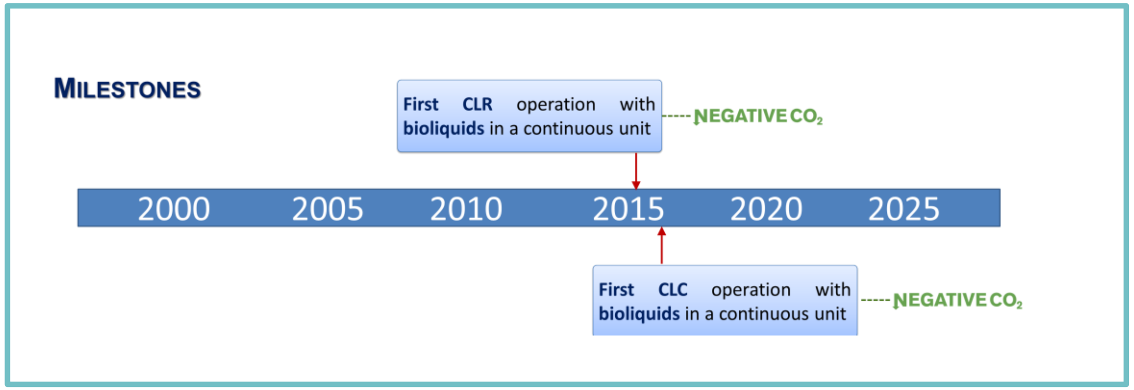
ICB-CSIC milestones in Chemical Looping

icb Instituto de Carboquimica — Grupo de Combustión y Gasificación

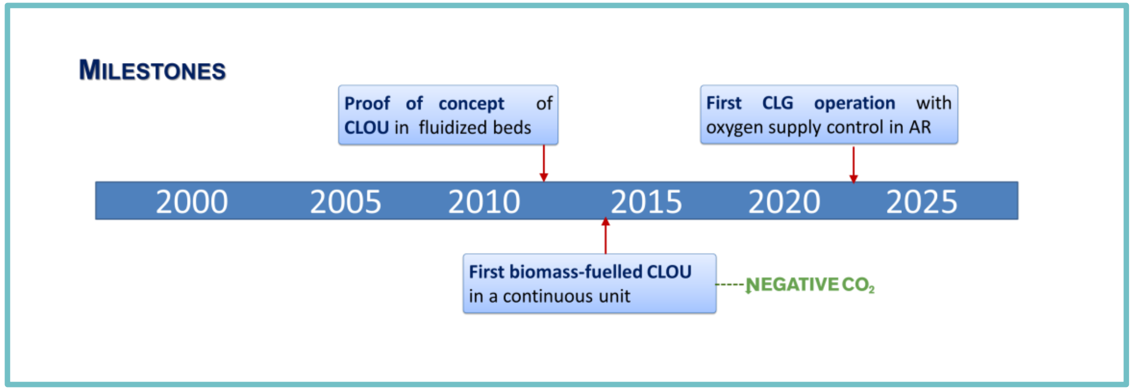
- **2000 h** continuous operation
- Special mentón to the use of fuels containing S compounds



- **500 h** continuous operation



- **+2000 h** continuous operation Combustion and Gasification



Oxygen carriers development | Testing in continuous units | Optimization

Preparation → **Caracterization - fluidization** → **kW / MW**

kg	mg - g	kg	ton

Pelletization
- Pelletizert

Impregnation
- ASTM-D-5757

Granulation
- Granulador Procell5, Glatt

Calcination muffles
- High capacity muffles

Patents CSIC

Granulator

Reactivity
- Thermobalances. CI Electronics. Setaram. Automatic system for gas and liquids feeding.
- Pressure Thermobalance. CAHN.

Atrition
- *Air jet attrition tester*. ATTRI-AS (MaTec). ASTM-D-5757.

Magentic properties
- Magnetic susceptibility meter. Bartington MS2G/MS3

Lixiviation
- System VELP ROTAX6.8. DIN38414 and UNE10802.

Determination of Hg
- Atomic absorption spectroscopy LECO AMA254. Liquid flows and in solids.

Reactioon in fluidized beds
- Batch fluidized beds. Redox cycles. Automatic system for mixtures gases&steam.

Thermobalance

Batch fluidized bed

Gaseous fuels

CLC/CLR – 500 W

CLC/CLR – 10 kW

Liquid fuels

CLC/CLR – 1 kW

Solid fuels

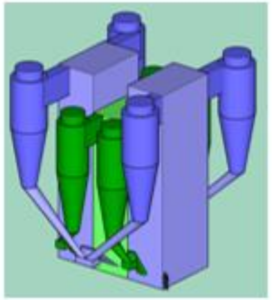
CLC/CLG/CLOU 1.5 kW

Solid fuels

CLC/CLG/iG-CLC/CLOU– 50 kW

Design, modelling, simulaiton
- Process optimization

Design/supply of pilots
- Continuous pliot plants (CLR/CLG). (Petrobras, Senai, Petrogalp)



Conceptual design of a hydrogen production plant (100,000 Nm^3/h) from diluted bioethanol (CLRa)

CLG – 1 MW TUD Darmstadt (Germany) Collaboration

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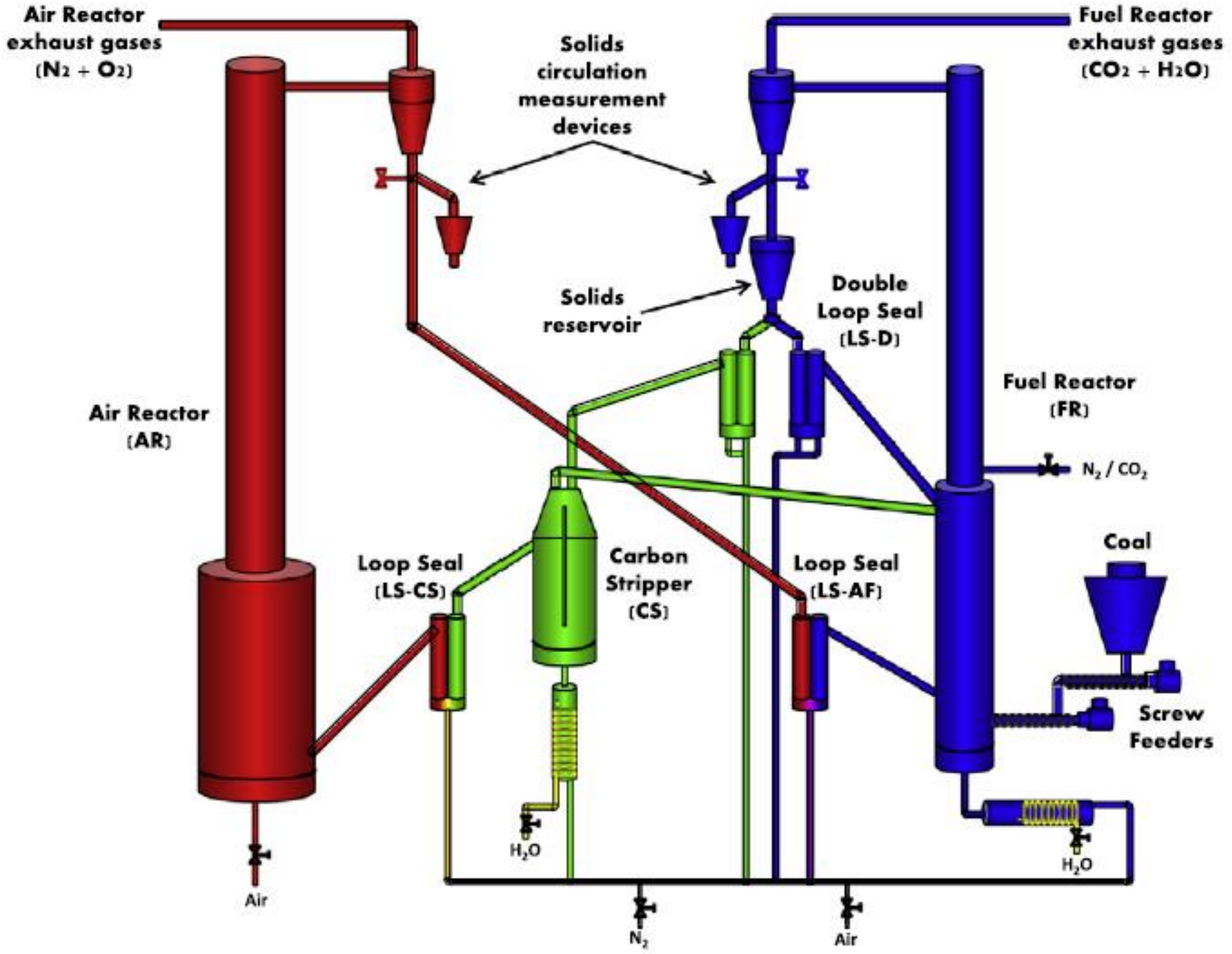
icb Instituto de Carboquímica

IG-CLC / CLOU   Coal- Biomass

CLC - 50 kW_{th}
Solid fuels



Recent and on-going ICB-CSIC research projects

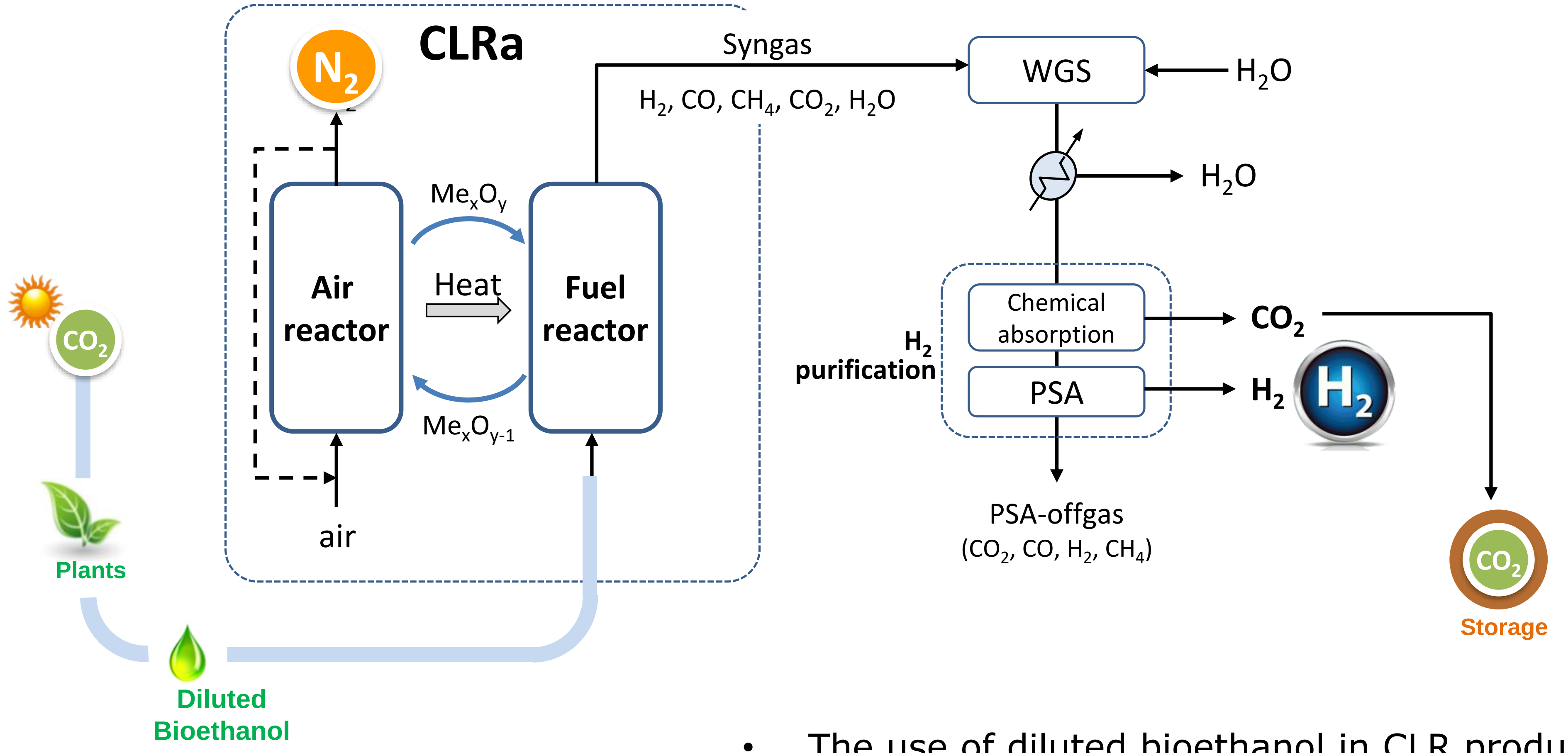
- Producción de H_2 a partir de Bioetanol diluido mediante proceso CLR. CTGAS-ER (PETROBRAS). Brasil. 2013 – 2016
- Diseño conceptual de una planta de producción 100.000 Nm^3/h de H_2 a partir de etanol diluido por reformado autotérmico (CLRa) con transportadores sólidos de oxígeno. SENAI-DR/RN, Brasil. 2019- 2020.

Hydrogen production from diluted bioethanol by Chemical Looping Reforming

Brasil is world leader in bioethanol production (sugar cane)

PETROBRAS needs H_2 in refineries

CL Reforming of bioethanol



- No ASU needs

- The use of diluted bioethanol in CLR produces pure streams of H_2, N_2 and CO_2 at autothermal conditions.

- Linked to CO_2 storage introduce the concept of **negative emissions** in the hydrogen production process.

CL Reforming of bioethanol

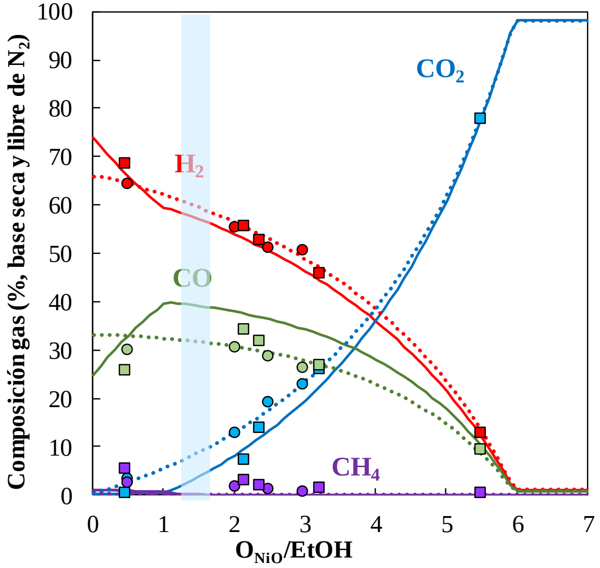
Oxygen carrier

$NiO18\text{-}\alpha Al_2O_3$

CSIC patent: WO2009/022046

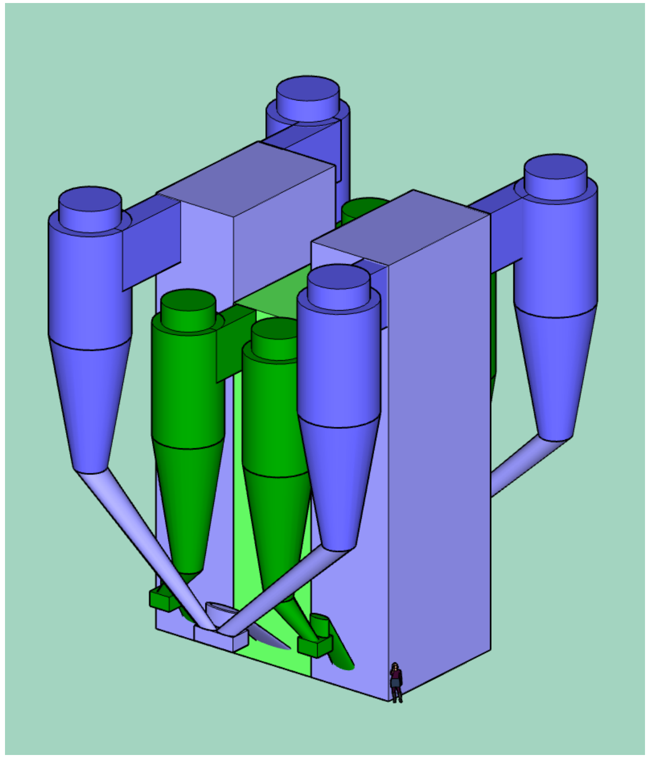
Autothermic

4.6 mol H_2/mol C_2H_3OH
Condiciones autotermicas



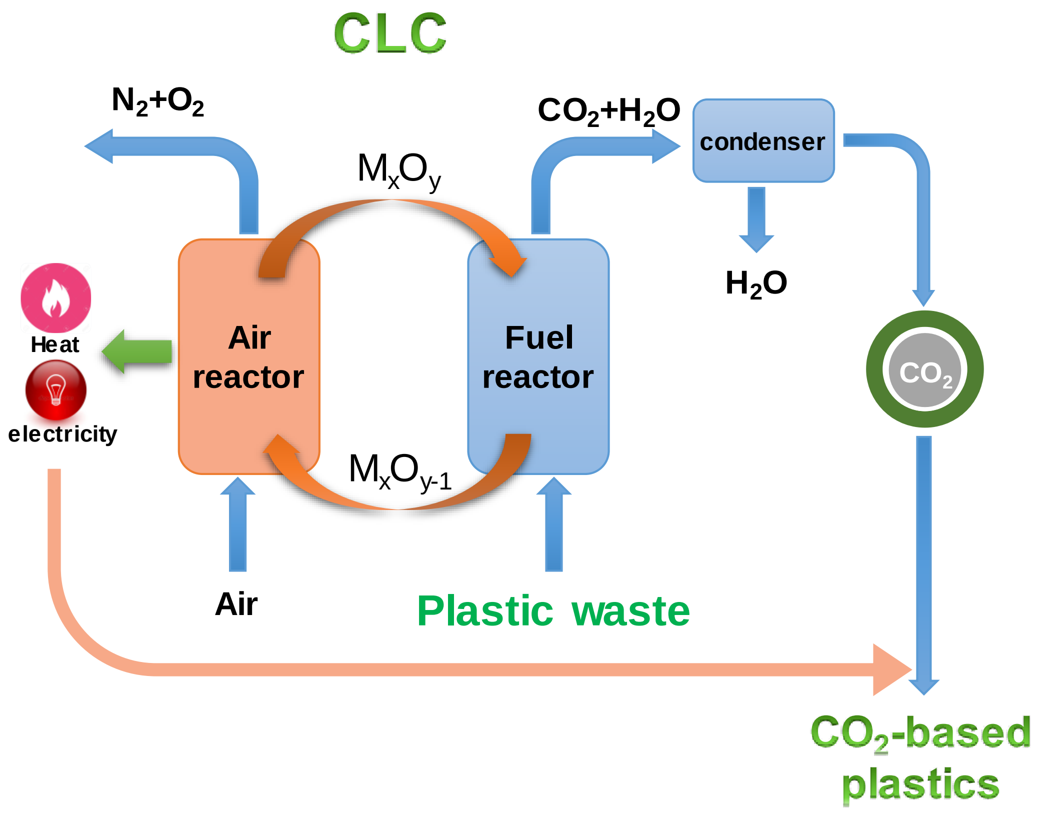
CLR unit for liquids

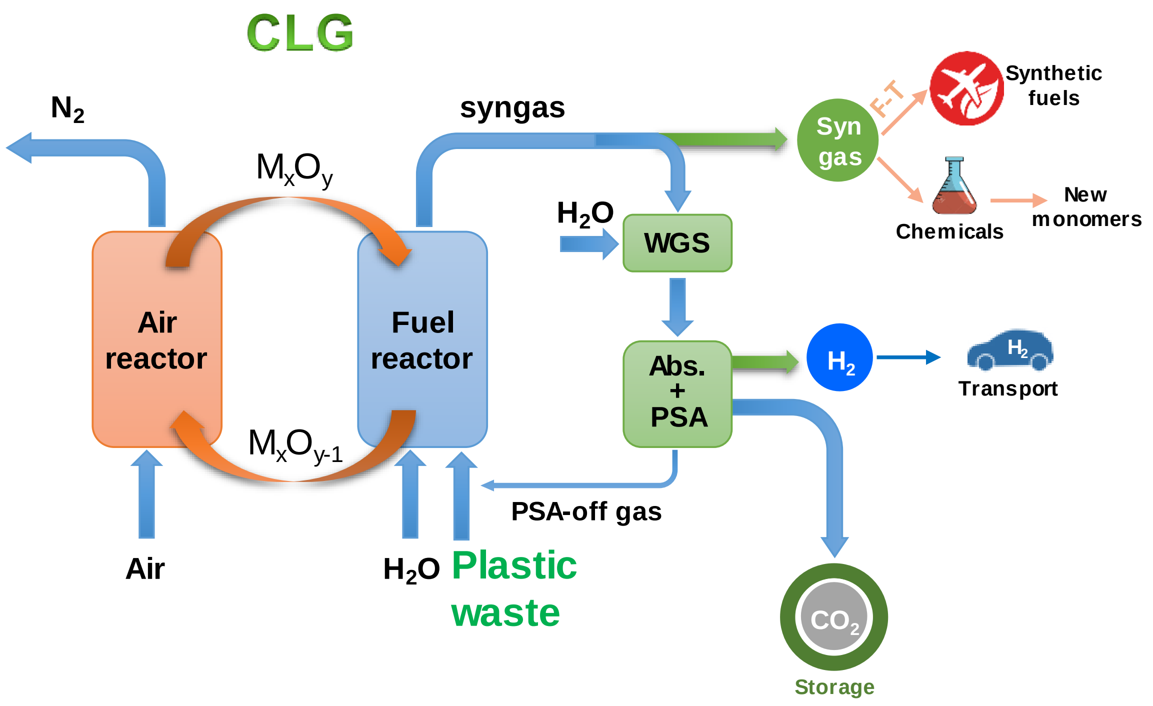
Turnkey project
to
CTGAS-Petrobras



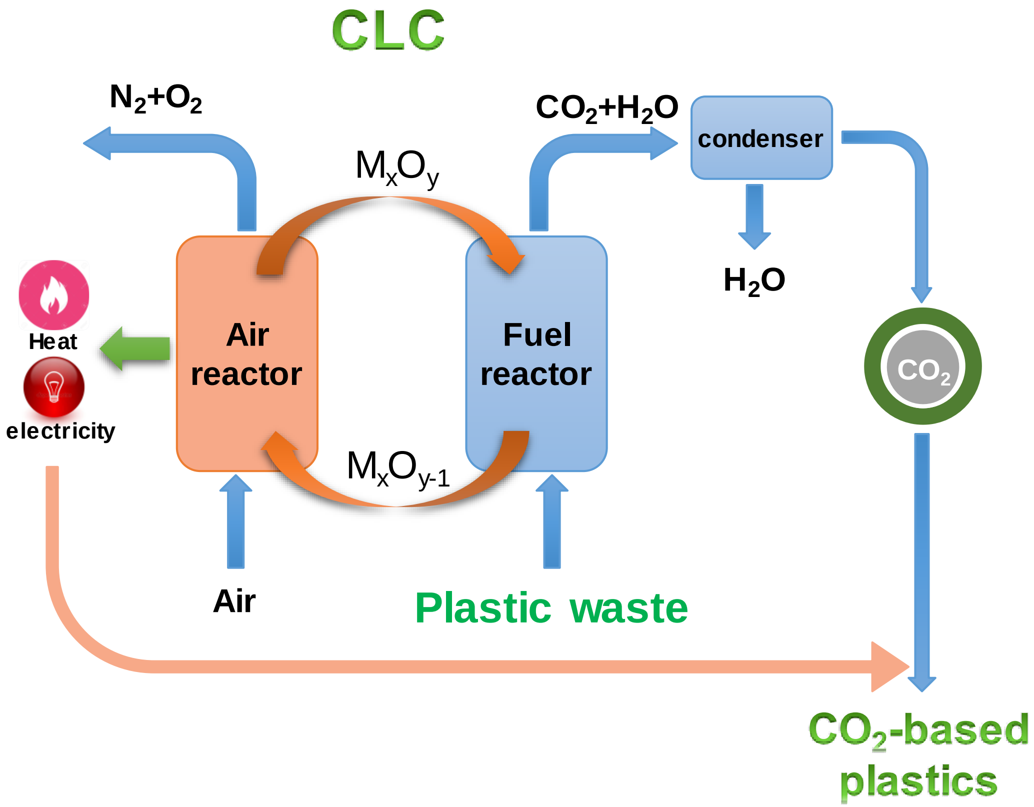
Conceptual design of a 100,000 Nm^3/h
H_2 production plant from diluted bioethanol
by autothermal reforming (CLRa)

Project: AEI proyectos de transición ecológica y transición digital 2021.
Circular economy of plastics based on Chemical Looping processes CIRCPLAS. TED2021-129842B-I00





CL of plastics



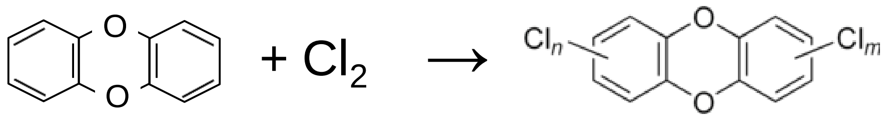
- No NOx
- No dioxines

Reason: Combustion **without** gaseous O_2

PCDDs formation

Deacon reaction $4\ HCl + O_2 \rightarrow 2\ Cl_2 + 2\ H_2O$

Chlorination of the benzene ring

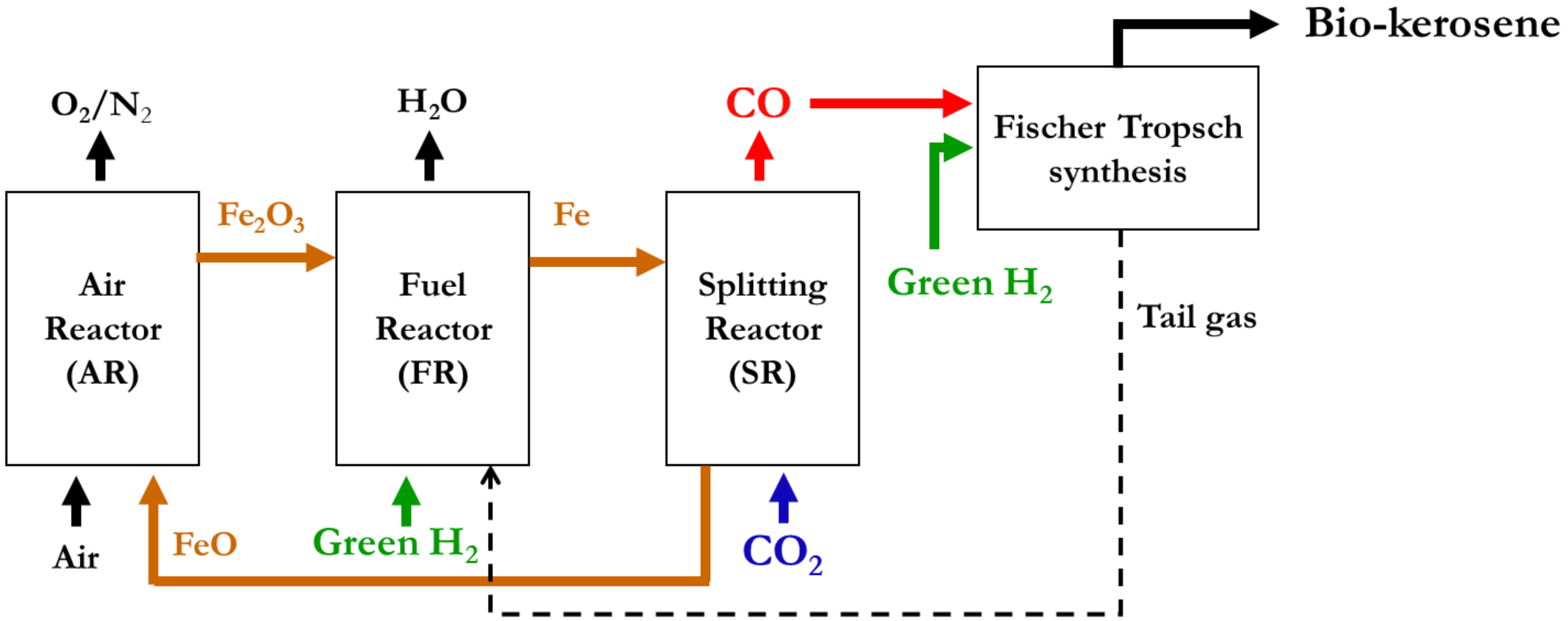


Polychlorinated dibenzodioxins (PCDDs)

New chemical looping process to obtain pure CO from CO_2 and green H_2 as a route for aviation biofuel production (CO2SPLIT) (PID2020-113131RB-I00)

The CO2SPLIT process uses **three reactors** instead of two commonly used in CLC.

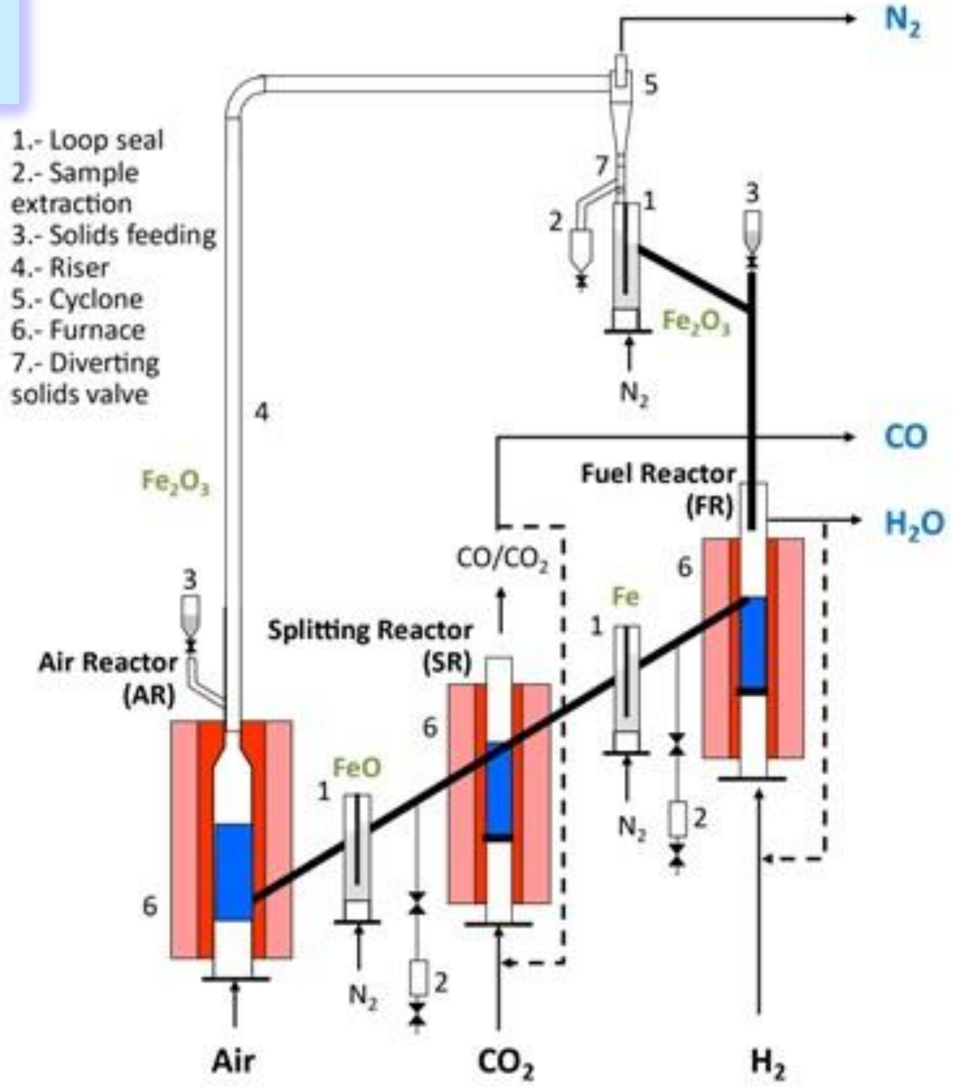
- Fuel Reactor (FR), the OC is reduced with green H_2 that is oxidized to H_2O (MeO_{x-2}/MeO_x).
- The reduced OC goes to the Splitting Reactor (SR) where it is partially oxidized by CO_2, generating CO (MeO_{x-2}/MeO_{x-1}).
- Air Reactor (AR), the OC is fully oxidized, being again prepared for a new cycle (MeO_{x-1}/MeO_x)



CO_2 splitting

Fuel Reactor:	$Fe_2O_3 + 3\ H_2$	$\longleftrightarrow$	$2\ Fe + 3\ H_2O$	$\Delta H>0$
Splitting Reactor:	$2\ Fe + 2\ CO_2$	$\longleftrightarrow$	$2\ FeO + 2\ CO$	$\Delta H>0$
Air Reactor:	$2\ FeO + 0.5\ O_2$	$\longleftrightarrow$	Fe_2O_3	$\Delta H<0$

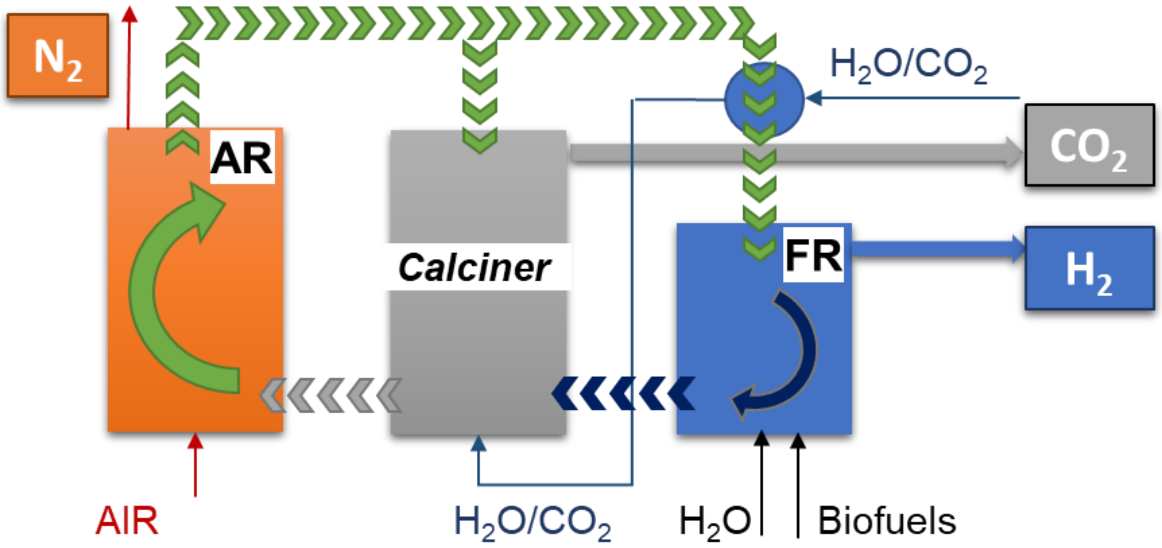
1 kWth *CO2SPLIT* plant at ICB-CSIC



Hydrogen production with CO2 capture by one-step and fuel-flexible sorption enhanced chemical looping reforming (HYSERLOOP). PID2022-138085OB-I00

The Sorption Enhanced Chemical Looping Reforming, SE-CLR, is a combination of the aCLR and Sorption Enhanced Reforming (SER) processes that allows obtaining separate streams of hydrogen and CO_2. **Three reactors** are used.

- **Elimination of the subsequent H_2 purification stages** needed in the aCLR process
- **Elimination of external energy supply** for the regeneration of the sorbent needed in the SER process



- Proof of concept using bifunctional materials (Metal and sorbent phase)
- Design and modeling of a SE-CLR unit

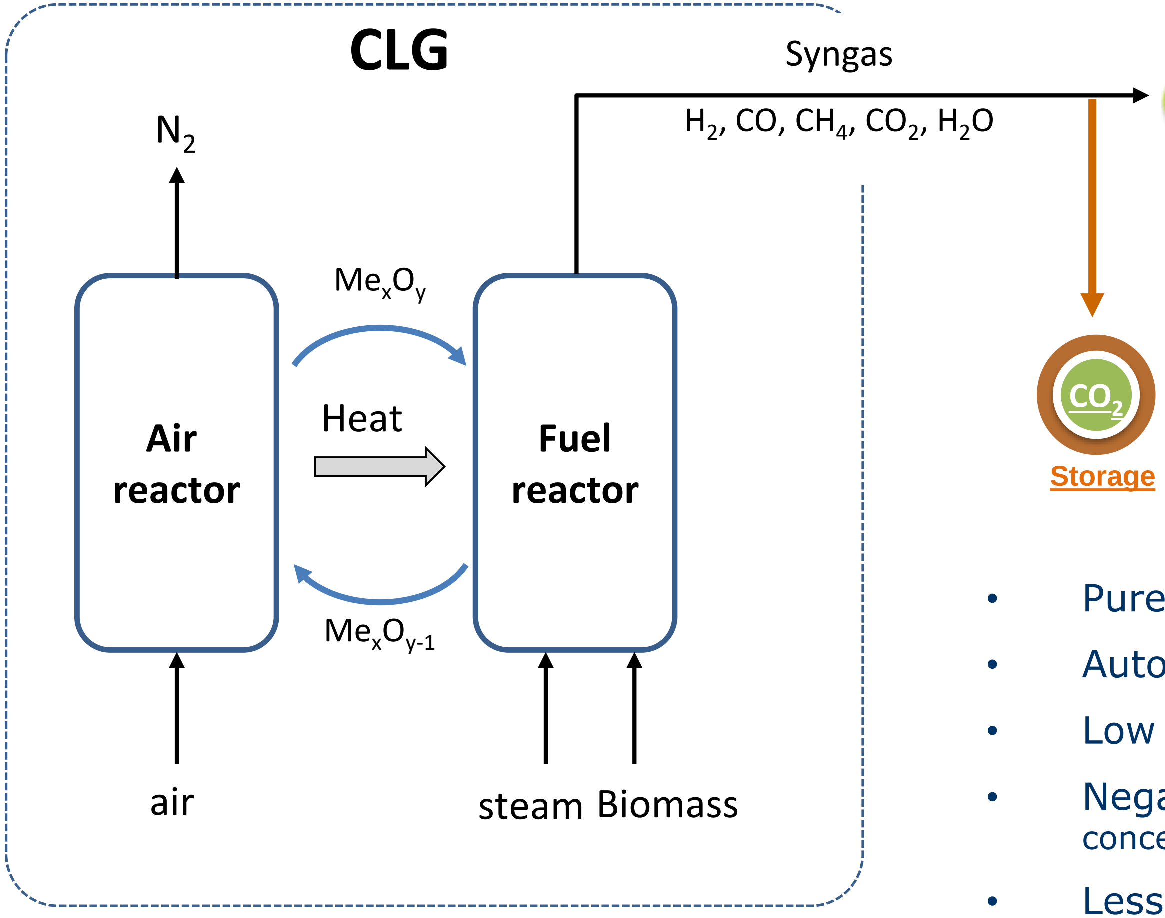
AR: $0.5\ O_2 + Ni \rightarrow NiO$ (R1)
$\Delta H_0 = -239.7$ kJ/mol

CR: $CaCO_3 + heat \rightarrow CaO + CO_2$ (R2)
$\Delta H_0 = 178.2$ kJ/mol

FR: $CH_4 + NiO \rightarrow CO + 2\ H_2 + Ni$ $\Delta H_0 = 203.8$ kJ/mol (R3)
$CH_4 + H_2O \rightarrow CO + 3\ H_2$ $\Delta H_0 = 205.9$ kJ/mol (R4)
$CO + H_2O \quad CO_2 + H_2$ $\Delta H_0 = -41.1$ kJ/mol (R5)
$CO_2 + CaO \quad CaCO_3$ $\Delta H_0 = -178.2$ kJ/mol (R6)

BIOMASS CHEMICAL LOOPING GASIFICATION

Biomass, wastes

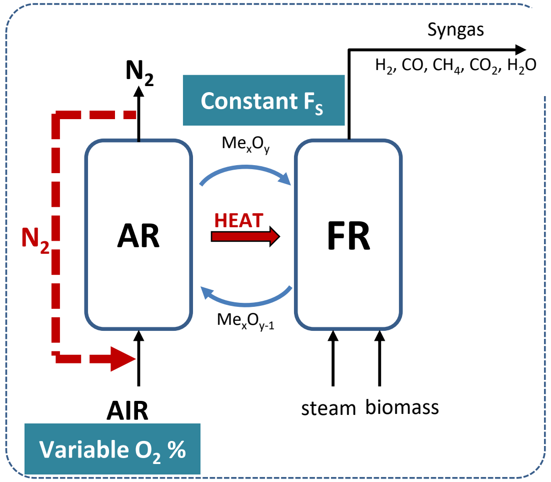


SYNGAS

- WGS-H_2 (NH_3)
- FT-diesel, gasoline
- Methanol (DME, MTBE)
- chemicals

- Pure syngas stream (no N_2 dilution and no ASU unit)
- Autothermic
- Low tar generation (catalytic properties of the Me_xO_y)
- Negative CO_2 emissions to the atmosphere (CO_2 concentrated in syngas)
- Less corrosion in heat exchangers (located in AR)

Control of the oxygen-to-fuel ratio

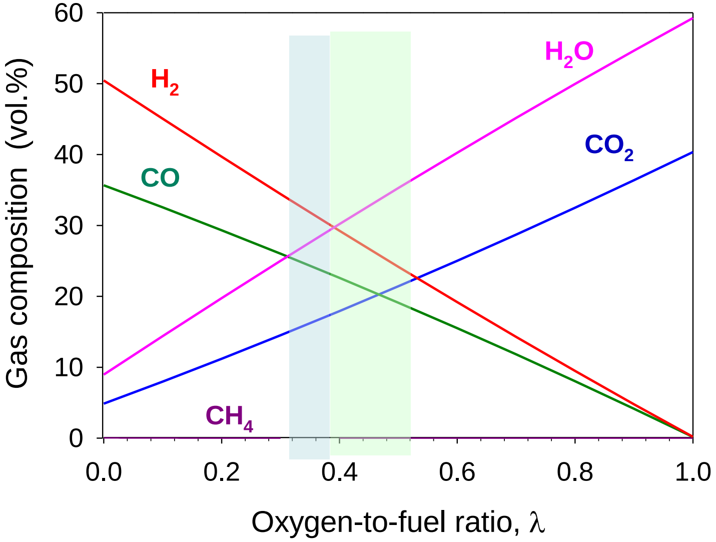


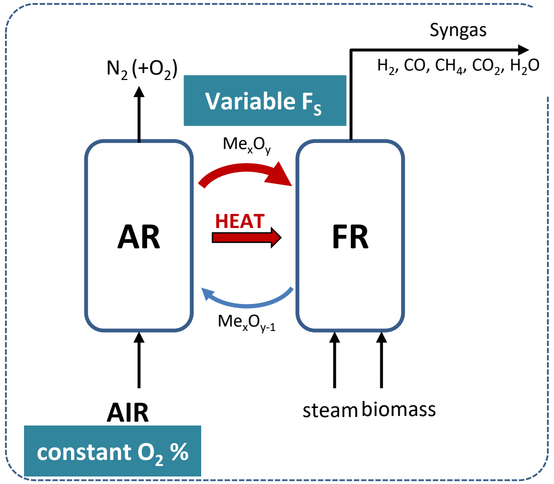
OCM-1

BY VARYING THE O_2 FED IN AR

- Allows operation at different ΔT and solid circulation rate (F_s) with any OC.
- Allows production of pure N_2
- Allows higher syngas yield at autothermal conditions

CLG units: 1 kW CSIC, 20 kW CSIC, 1 MW TUD



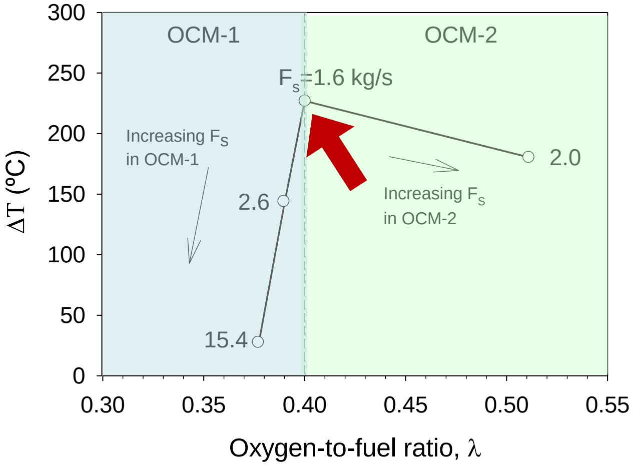


OCM-2

BY VARYING SOLIDS CIRCULATION RATE

- Produces big changes in temperature
- Dilution of oxygen carrier is possible.

Lines correspond to autothermal conditions



Lines correspond to autothermal conditions

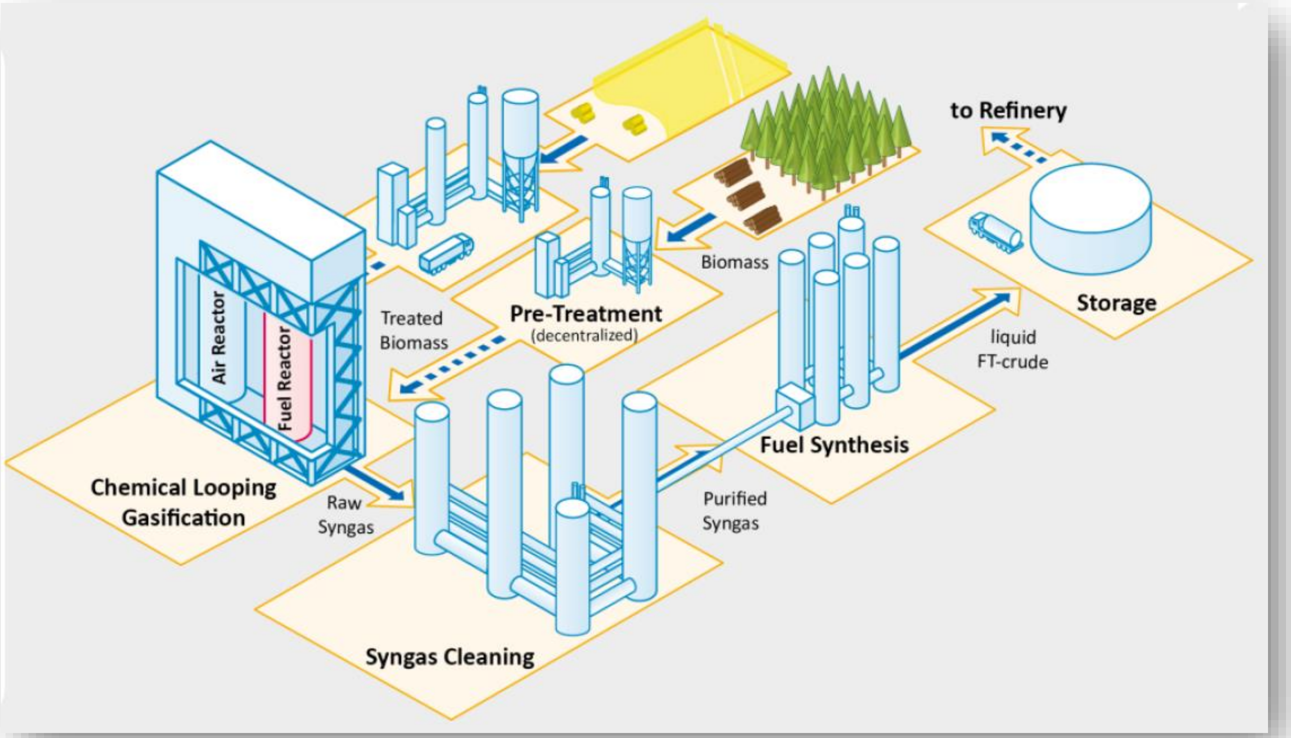
Samprón et al. Energy 226 (2021) 120317

CLara

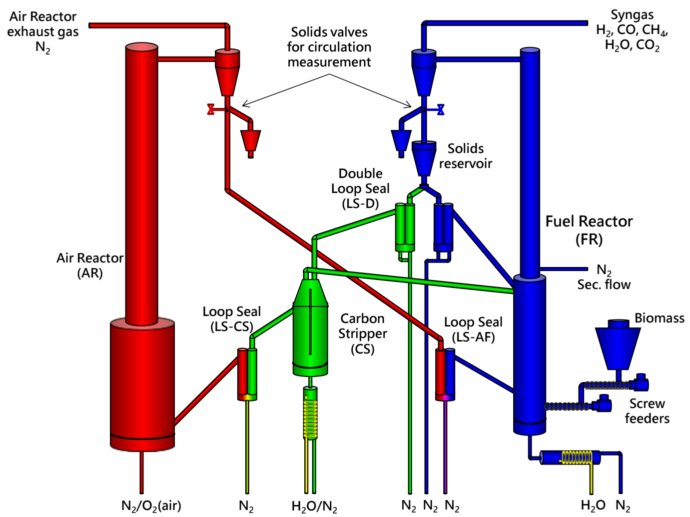
H2020-No. 817841

Nov 2018 – April 2023
https://clara-h2020.eu/

Chemical Looping Gasification for Sustainable Production of Biofuels



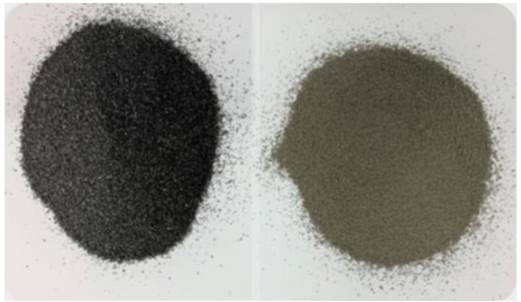
The aim of CLARA was to develop a new concept for the production of **biofuels** based on **chemical looping gasification** of biogenic residues, through a Fischer-Tropsch process.



50 kW$_{th}$ Chemical Looping Gasification unit at CSIC

- To select the oxygen carrier for TUDA tests (ilmenite)
- To test several biomasses
- To demonstrate a new method for control the oxygen used in gasification
  (By controlling the oxygen introduced in AR to produce almost pure N_2 at the AR outlet)

Ilmenite in CLC (active phases)		
Oxidized		Reduced
Fe_2TiO_5	⟷	$FeTiO_3$
Fe_2O_3	⟷	Fe_3O_4



Ilmenite
Option 1

LD Slag
Option 2

Operating conditions	
T= 980 ºC	
λ= 0.3	
S/B= 0.7	
Gas composition (vol%)	
CO_2	27.4
CO	23.3
H_2	38.3
CH_4	9.8
C2-C3	1.3
Syngas yield, Y	0.61

CLara

Chemical Looping Gasification for Sustainable Production of Biofuels

H2020-No. 817841
Nov 2018 – April 2023
https://clara-h2020.eu/

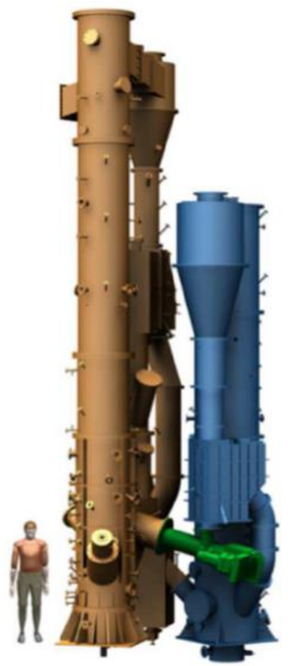
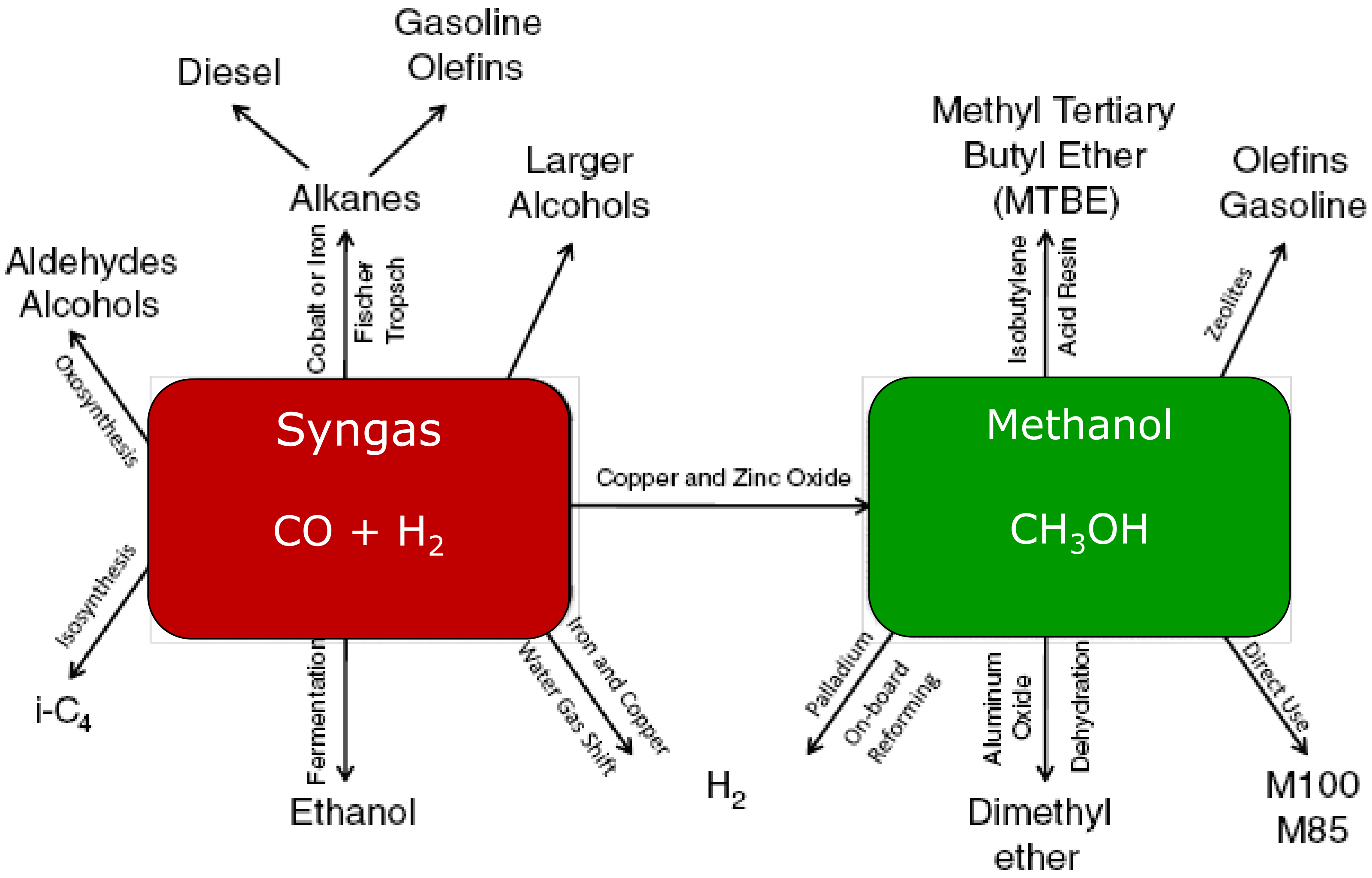


Figure 8 Drawing of TUDA 1 MW_{th} pilot plant

- **BCLG technology demonstrated** at 1 MW_{th} scale in TUDA (Germany) during summer 2022
- More than 130 h of autothermal operation
- More than 75 tn of biomass used
- 3 biomasses: IWP, PFR, WSP
- Increased from TRL4 to TRL5-TRL6

NEW PRODUCTS



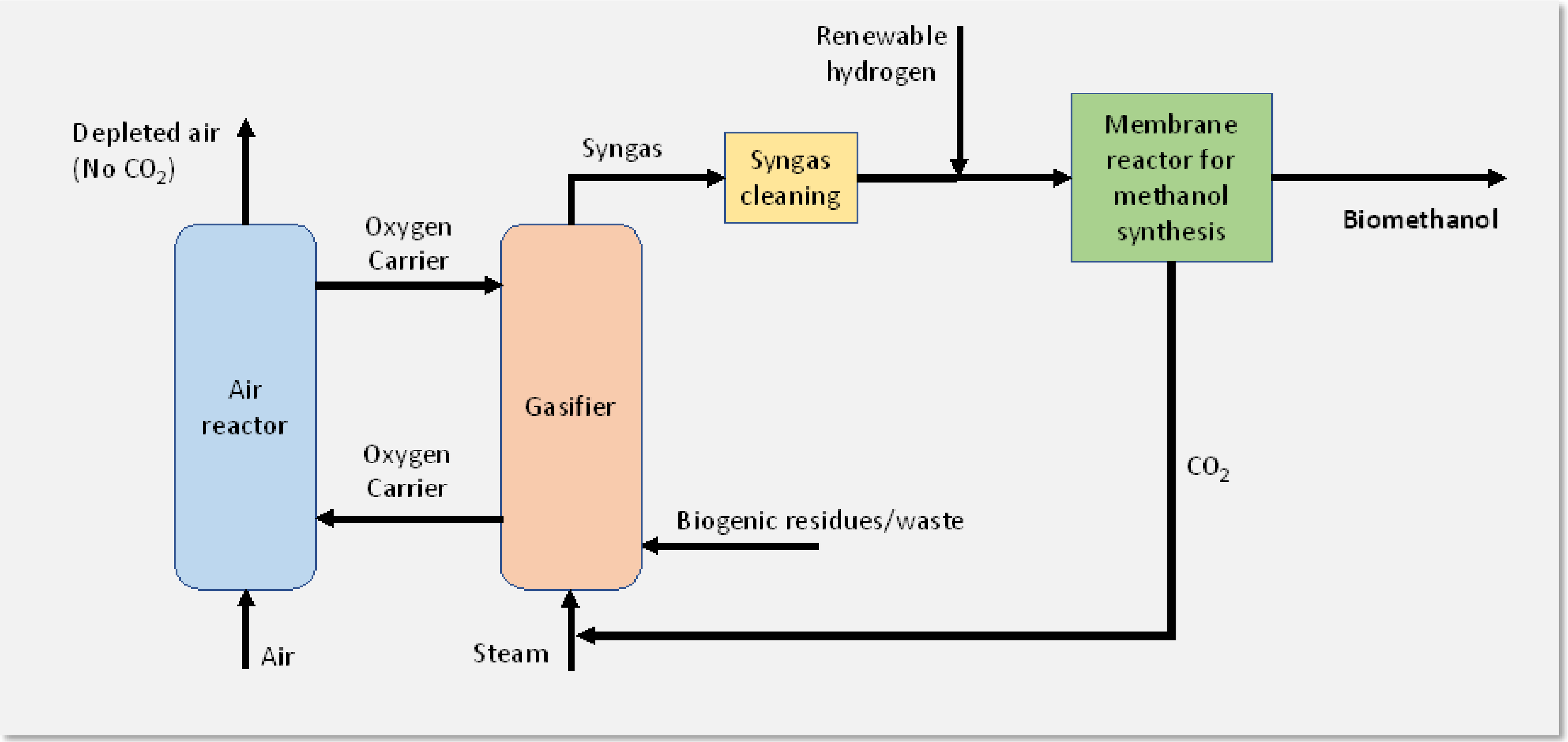
Spath and Dayton, 2003

Funded by the European Union
HORIZON-No. 101147737
Sep 2024 – Aug 2028
https://www.biomegafuelproject.eu/

BioMeGaFuel

Bio Methanol Production via Chemical Looping Gasification Coupled with Membrane Reactors

The aim is to develop a novel efficient, and scalable process to convert low-value biogenic residues and organic waste to biomethanol through chemical looping gasification coupled with membrane reactors by using renewable H_2



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The aim is to develop a novel efficient, and scalable process to convert low-value biogenic residues and organic waste to biomethanol through chemical looping gasification coupled with membrane reactors by using renewable H_2

CHEMICAL LOOPING GASIFICATION OF SOLID FUELS

Funded by the European Union

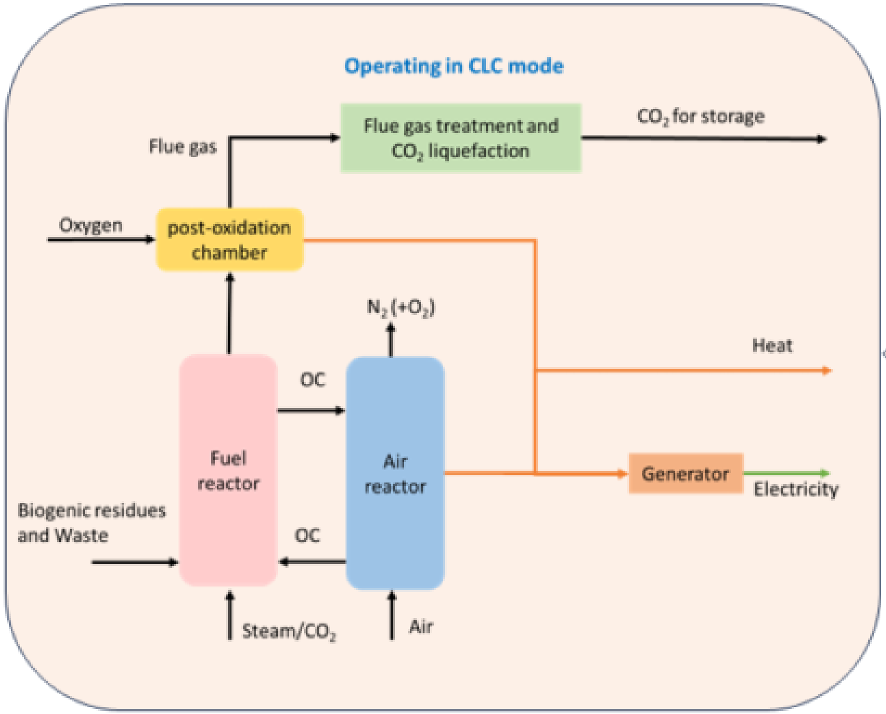
HORIZON-No. 101147904

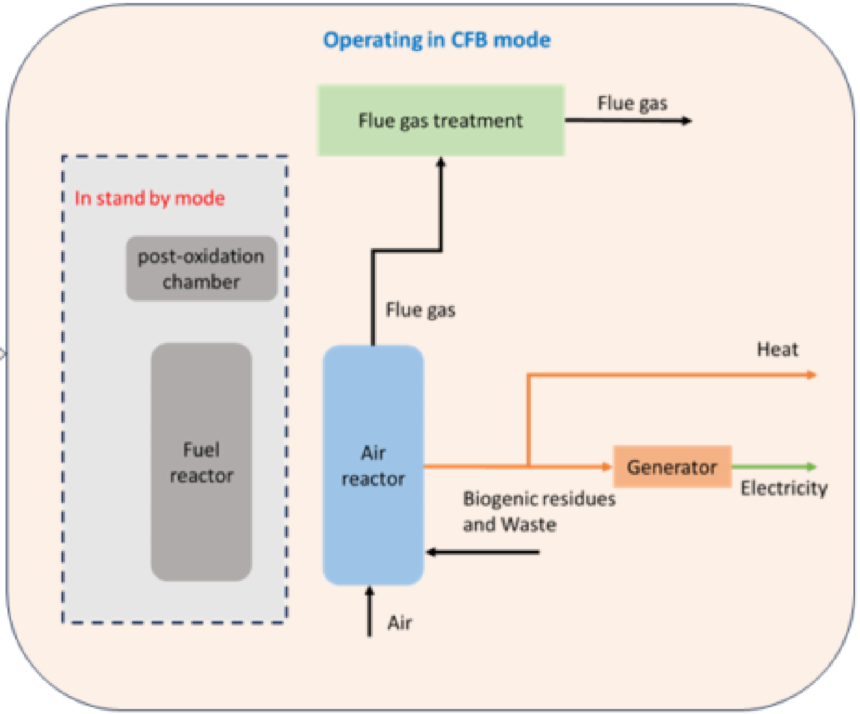
June 2024 – june 2028
https://www.bioflexclcproject.eu/

Bio-Flex CLC

Flexible chemical looping combustion for combined heat and power production from biogenic residues with negative emission (Bioflex-CLC)

- The concept is based on dual Circulating Fluidized Bed (CFB) reactors, which can operate in Chemical Looping Combustion (CLC) mode while both reactors are in use or switch to conventional CFB operation when only one reactor is in use.
- Operating in CLC mode enables CHP production with negative emissions at low-cost while the concept is flexible to switch to CFB boiler mode to produce CHP with net-zero emissions.



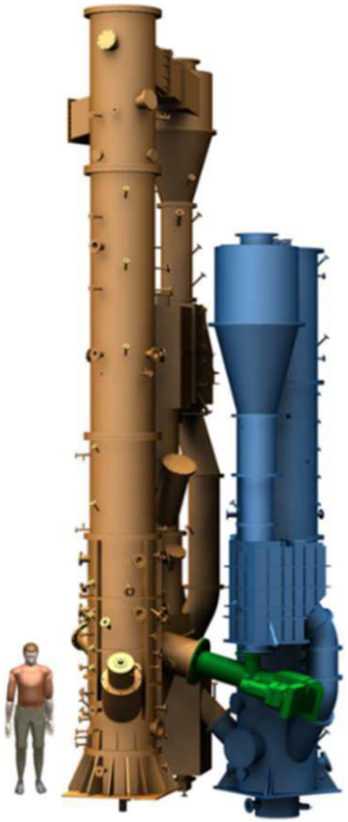


Funded by
the European Union

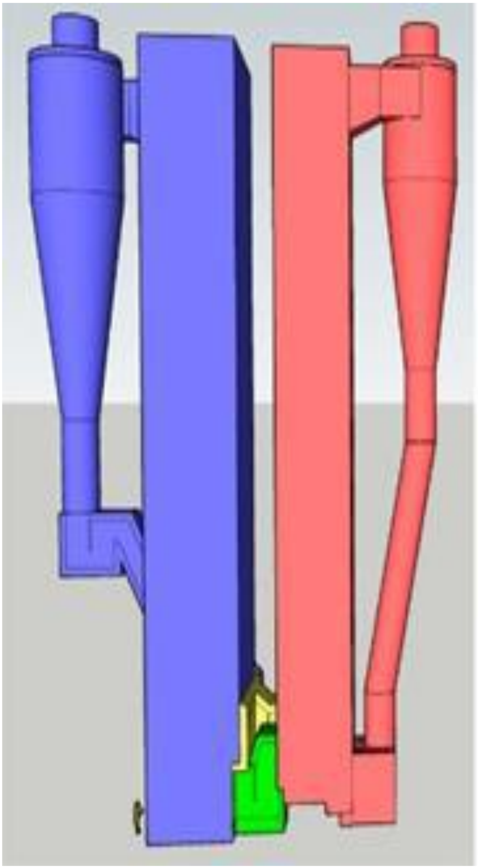
HORIZON-No. 101147904

June 2024 – june 2028
https://www.bioflexclcproject.eu/

Flexible chemical looping combustion for combined heat and power production from biogenic residues with negative emission (Bioflex-CLC)



1 MW TUDA



Model 100 MW commercial scale Bio-FlexCLC

Use of Iron for Energy Storage

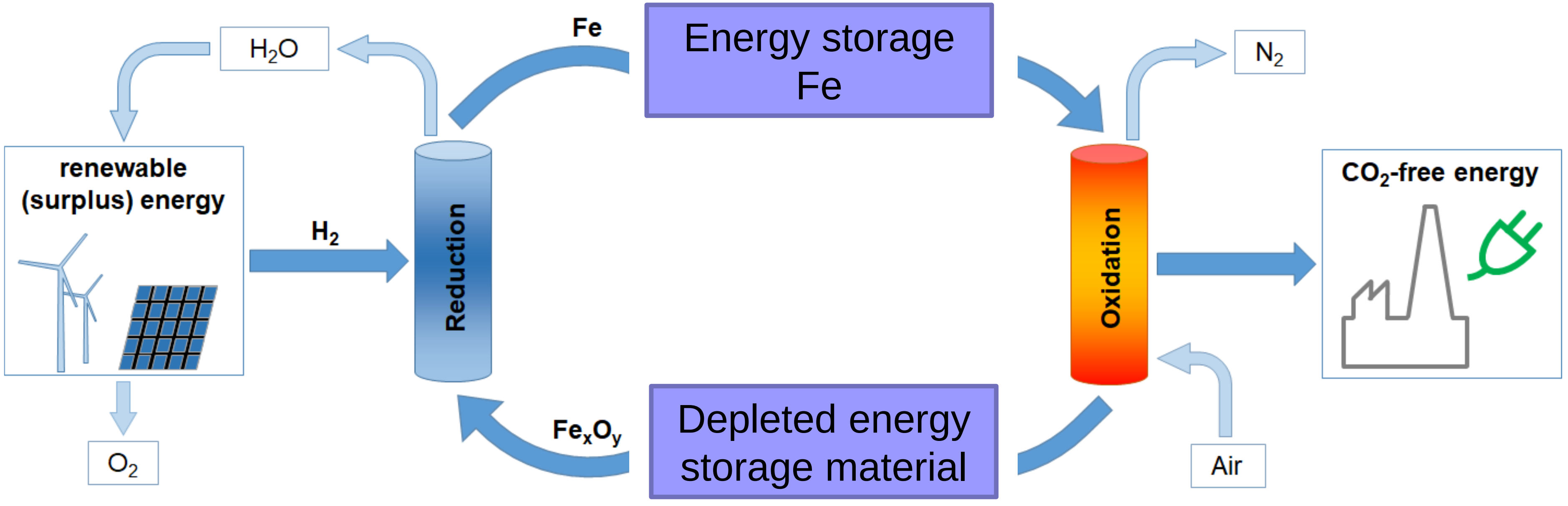
Funded by the European Union

Research Fund for Coal and Steel (RFCS)

Sep 2024 – Sep 2028

The Combustion of Rechargeable Metal Fuels in Fluidized Bed Boilers project *(CORAL project)*

The cyclic reduction/oxidation of metal oxide/metal is a promising approach for energy storage and flexible CO_2-free provision of heat and power.
The project explores a novel concept of metal oxidation utilizing retrofitted coal-fired fluidized bed power plants.



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Funded by the European Union

Research Fund for Coal and Steel (RFCS)

Sep 2024 – Sep 2028

The Combustion of Rechargeable Metal Fuels in Fluidized Bed Boilers project *(CORAL project)*

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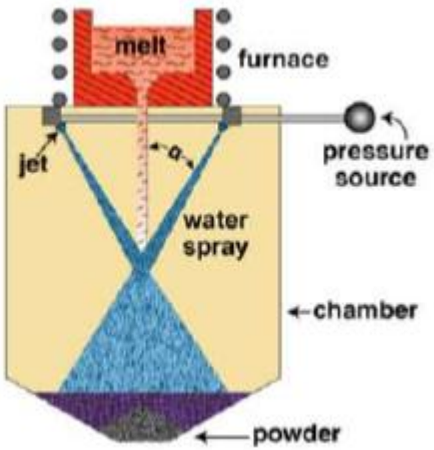

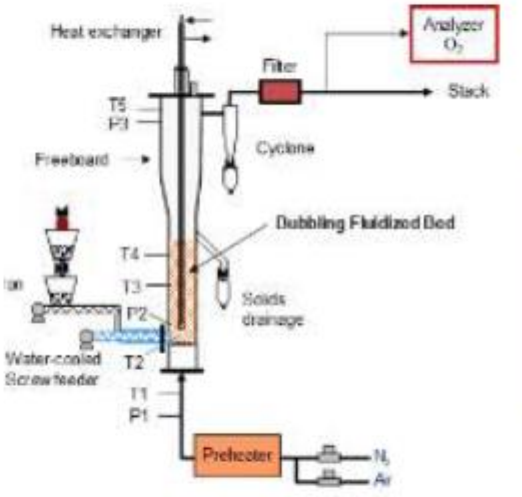

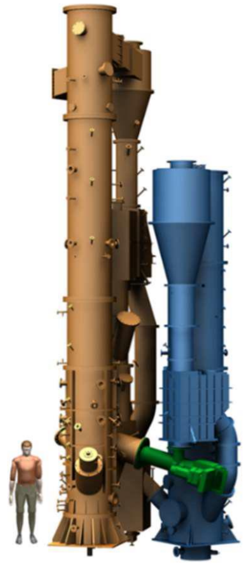

1 MW TUDA

PARTNERS

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ENERGY IS US

Thanks

Questions

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非常感謝您的關注

問題？

Pilot plants

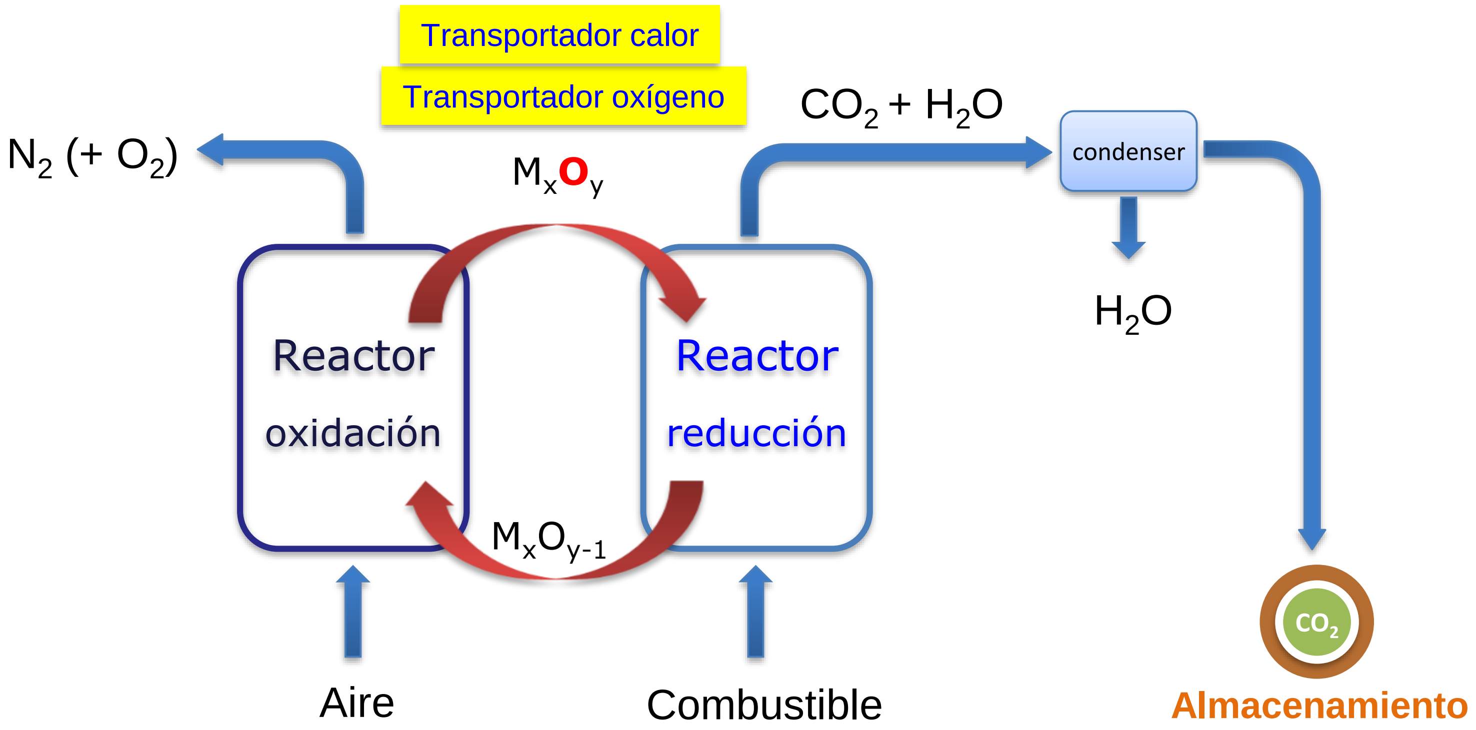
CLC - 500 W
Natural gas

CLC - 10 kW
Natural gas

CLC – 50 kW
Carbón/biomasa

Oxicombustión – 3 kW
coal

Chemical Looping Combustion



Reducción	$CH_4 + 4\ M_xO_y$	$\longrightarrow$	$4\ M_xO_{y-1} + CO_2 + 2\ H_2O$	ΔH_r
Oxidación	$2\ O_2 + 4\ M_xO_{y-1}$	$\longrightarrow$	$4\ M_xO_y$	ΔH_o
Global	$CH_4 + 2\ O_2$	$\longrightarrow$	$CO_2 + 2\ H_2O$	$\Delta H_c = \Delta H_r + \Delta H_o$

Chemical Looping Combustion

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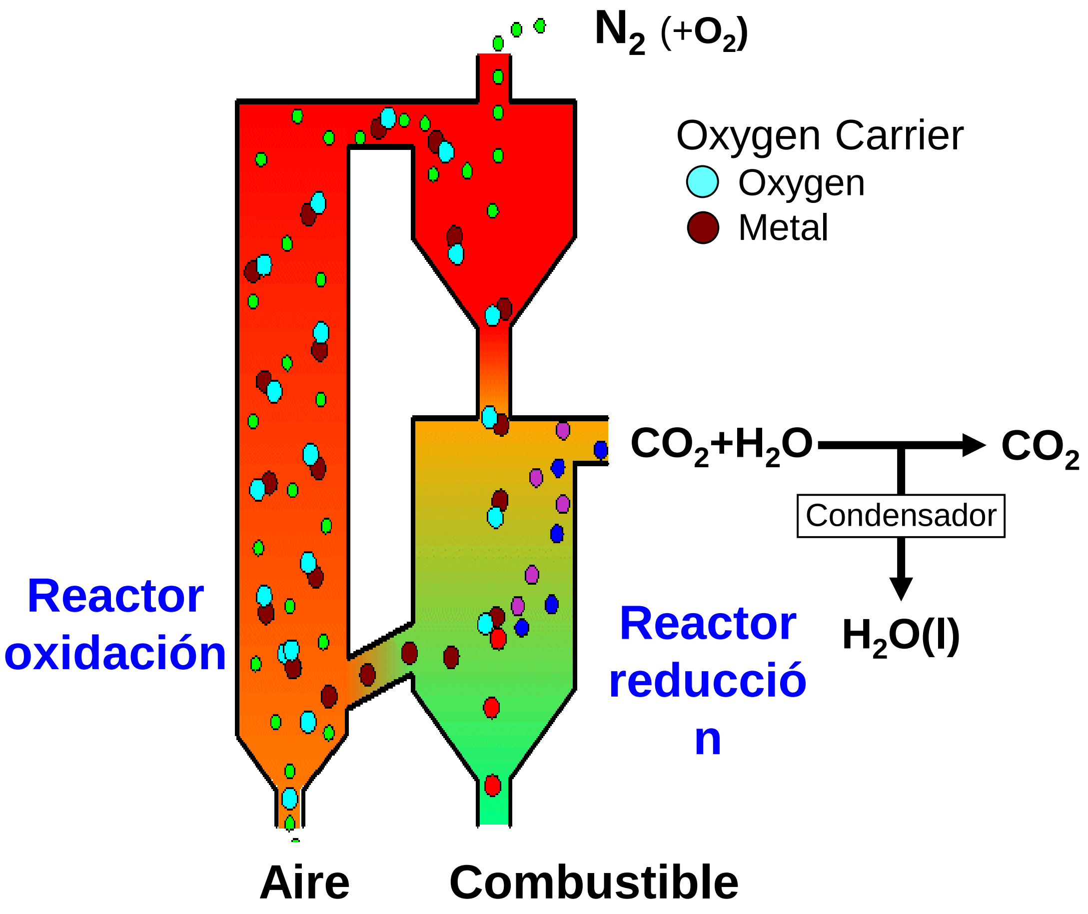
Grupo de Combustión y Gasificación



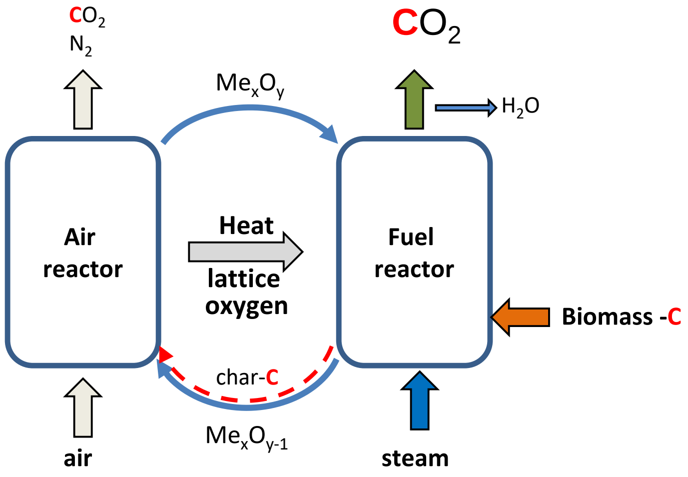
Oxígeno se transfiere del aire al combustible por medio de óxidos metálicos (**Transportadores de oxígeno**) utilizando la tecnología de los lechos fluidizados.

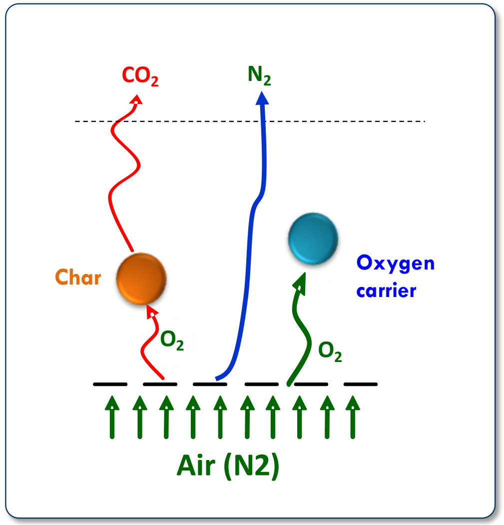
Captura inherente de CO_2

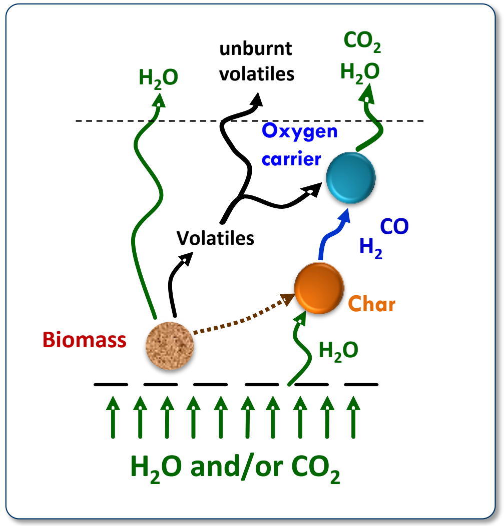
- Aire y combustible nunca se mezclan
- No existen etapas de separación de gas
- Se evitan los costes económicos/ energéticos de dichas etapas
- Se basa en la tecnología de lechos fluidizados disponible comercialmente
- Bajas emisiones de NOx

Chemical Looping Combustion

In situ gasification CLC







- Drying and devolatilization:

  Biomass $\rightarrow$ H_2O + Volatiles + Char

- Char gasification:

  Char + H_2O $\rightarrow$ H_2 + CO

  Char + CO_2 $\rightarrow$ 2 CO

- Volatiles oxidation with the oxygen carrier

  Volatiles / H_2 + CO + Me_xO_y $\rightarrow$ Me_xO_{y-1} + H_2O + CO_2

- Water-Gas Shift

  CO + H_2O $\leftrightarrow$ CO_2 + H_2

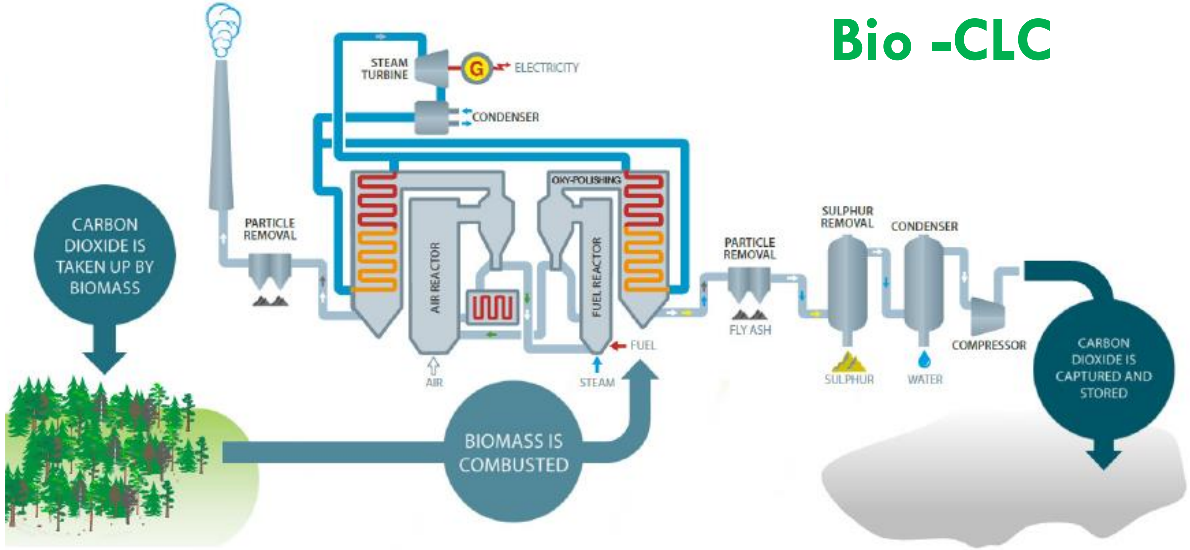
- Oxygen carrier oxidation:

  Me_xO_{y-1} + O_2 $\rightarrow$ Me_xO_y

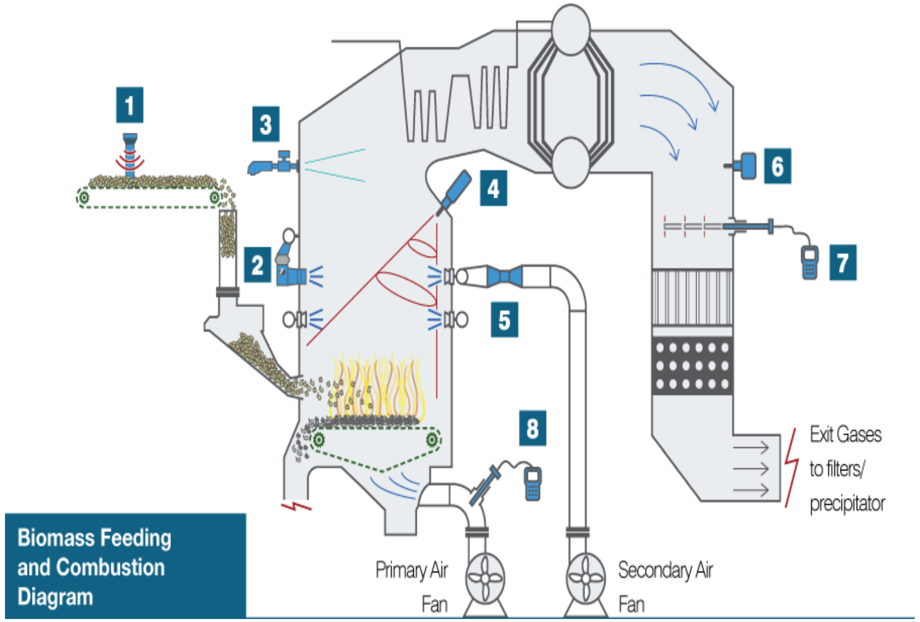
- Char combustion:

  C + O_2 $\rightarrow$ CO_2

Chemical Looping Combustion



Bio -CLC



Advantages of bio-CLC versus conventional biomass combustion:

- ❑ Lower corrosion and longer life of components (heat extracted in AR where no alkalis components are present)
- ❑ Higher thermal efficiency
- ❑ NO_x formation reduction
- ❑ Negative CO_2 balance achievable