

Turning industrial waste gases into valuable polyurethanes

European research collaboration between steel and chemical industry

Marseille/Fos, 20th March 2019

Dr. Liv Adler Covestro Deutschland AG Sylvain Pichon Port de Marseille Fos Prof. Mark Saeys Universiteit Gent

CHALLENGES: Saving our fossil resources Reducing the greenhouse effect



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 768919

20th March 19 | Carbon4PUR

Mission





Generate value from the entire carbon from CO/CO₂-containing waste streams Making carbon productive and the resulting PUR products more sustainable



Carbon4PUR



Turning industrial waste gases (mixed CO/CO_2 streams) into intermediates for polyurethane plastics for rigid foams / building insulation and coatings



Responding to call: H2020-SPIRE-8-2017

Contributing to

- Circular economy
- Industrial symbiosis
- Carbon productivity
- Renewable materials

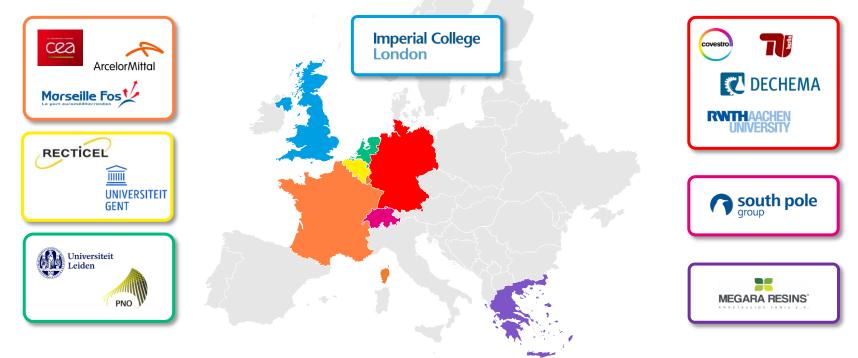
EC contribution: 7.75 mln. € Duration: Oct. 2017 – Sept. 2020



Consortium



14 Partners from 7 countries – interdisciplinary and across sector



Leading experts teaming up for an excellent consortium



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Collaboration Open Innovation





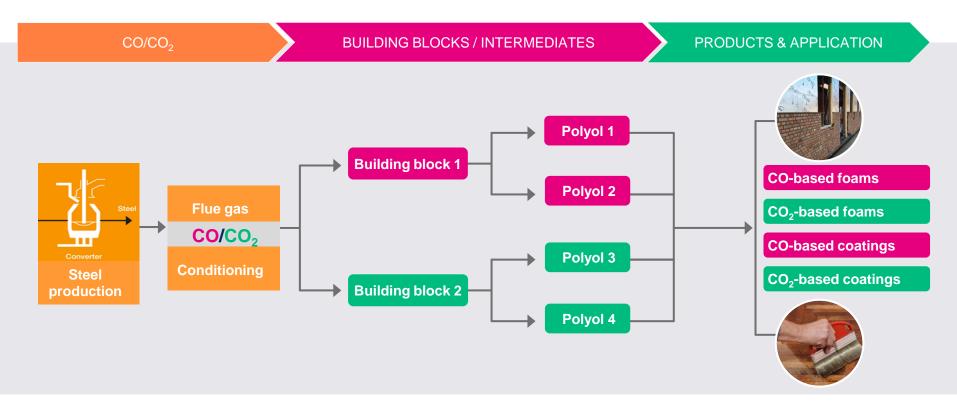
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Methodology







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Ambition



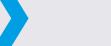
CO/CO₂

BUILDING BLOCKS / INTERMEDIATES

PRODUCTS & APPLICATION



- **Demonstration** taking into account all variables at the same time:
 - Steel plant flue gases characteristics
 - Material and process parameters
 - End product market requirements
- Small **piloting** of the new process (20t/y)
- Adaptable to products for existing large-scale markets



Full value chain



Methodology



CO/CO ₂	BUILDING BLOCK					
Steel industry			Polymer industry			
Steel Flue gas treatment						
ArcelorMittal	Covestro RNTHAACHEN UNVERSITY	covestro RWTHAACHEN	RECTICEL Insubition Covestro MEGARA RESINS			
Industrial symbiosis analysis	LCA and economic analysis Extended LCA Economic evaluation Societal impacts Oniversiteit Implementation Societal pole		Exploitation – Replication – Dissemination			

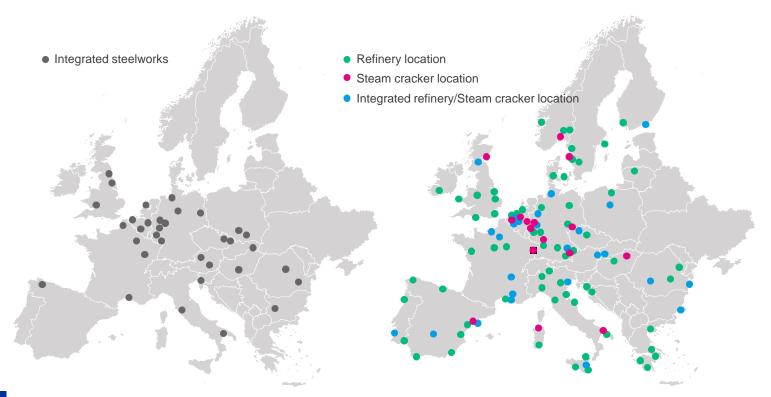


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Replication potential



Geographical distribution of integrated steelworks and refineries in Europe



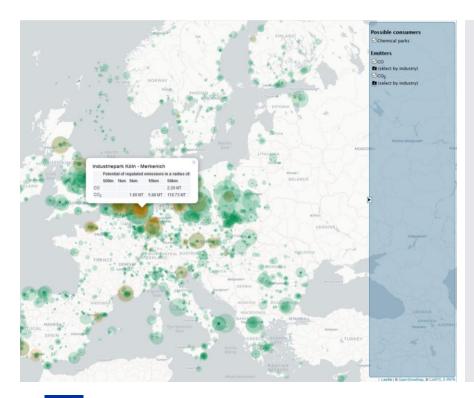


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Replication potential

Mapping activities



Modifications to previous mapping of CO/CO_2 availability based on E-PRTR:

- Limited distance to next chemical plant
- Gas composition based on production process for a list of compatible processes

The output will identify the best replication sites for chemical plants in Europe



Methodology



CO/CO ₂	BUILDING BLOCKS / INT	PRODUCTS & APPLICATION			
Steel industry	Chemical – Polyol industry		Polymer industry		
Steel production Flue gas treatment	Catalyst Process design design	Upscaling	Insulation boards & Coatings		
Arcelor/Mittal	COVESTIG RWTHAACHEN UNIVERSITY		RECTICEL insudition Covestro MEGARA RESINS		
	Accompanyin	q			
Industrial symbiosis analysis			Exploitation – Replication – Dissemination		
	Extended LCA Economic evaluation	Economic evaluation Societal impacts			



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CARBON4PUR Présentation du projet - *Project presentation*

Sylvain PICHON - Energy transition lead - Port of Marseille Fos







Industrial symbiosis





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WP7 – Objectives > industrial symbiosis preparation



- Evaluation of the technical and economic feasibility of a process implementation in Fos, as prime industrial symbiosis case investigated in Carbon4PUR; this includes feasibility assessment of connecting the infrastructure (distance, potential pipeline length, investments, legal requirement, safety) to lay the foundation for future detailed studies.
- To develop a best practice case for industrial symbiosis for replications or learnings for other industrial sites and CO2/CO recycling projects in Europe
- □ To assess the potential for replication of the investigated case to other sites in Europe via mapping of sources and industrial infrastructures and identification of preferable locations which would offer promising conditions for industrial symbiosis



□ To anticipate and implement a mix of industrial waste gases and CO2 recycling solutions

on the industrial port zone (>12MT CO2 emission) in addition to current experimentations : Jupiter 1000 (methanation), VASCO (algae bioremediation),

□ To develop industrial symbiosis profitable to our actual and future industrial customers,

- □ To create sustainability, acceptance towards industrial developments and commercial attractiveness, in an increasing carbon price context,
- □ To market the port of Marseille Fos as a "port of the future" deeply involved in the ecology and energy transition
- Green port in a blue economy

Port of Marseille main role in the project



WP7 Lead beneficiary "Industrial symbiosis preparation"

Partners = ICL, DECHEMA, ARCELOR MITTAL, COVESTRO, PNO

The Port of Marseille role will be mainly to facilitate the connection between Arcelor Mittal and Covestro, taking part of the development of an industrial symbiosis within the industrial port zone.

The main tasks to carry out will be :

- Task 7.1 Definition of gas specifications
- Task 7.2: Definition of the future activity size,
- Task 7.3: Concept for gas treatment on site before transport
- Task 7.4 Evaluation of the technical and economic feasibility of a gas pipeline in Fos
- Task 7.5: Mapping of industrial sites for CO/CO₂ recycling
- Task 7.6: Replication of Carbon4PUR to other industrial sites



CARBON4PUR Présentation du projet - *Project presentation*

Jean-Philippe GENDARME – President of PIICTO



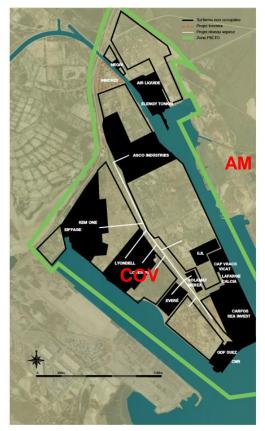




PliCTO Platform for Industry and Innovation at Caban Tonkin



A Cutting Edge Industrial Port Zone



Piero FOS Berender Be

Key Figures:

- > 1,200 ha site located in the industrial port area of Fos
- ≻ 3,000 jobs
- > 17 plants
- > 5 million tons of maritime throughput
- > More than 600 ha still to commercialize

A Multimodal Platform and Diverse Energy Hub:

- ➢ Electricity (225 kV)
- Natural Gas and Frigories (2 LNG Terminal)
- Coal, Biomass
- Wind and Solar Power
- > Hydrogen, Ethylene, Propylene, Nitrogen, etc.



The PIICTO Association

A collective dynamic that unites diverse economic and institutional stakeholders and is in accord with local and regional economic development policies

Governance:

- President: Jean-Philippe Gendarme (Kem One)
- Vice President: Christine Cabau-Woehrel (GPMM)
- Vice President: Mathieu Stortz (Elengy)
- Treasurer: Corinne Ramombordes (Solamat Merex)
- Secretary: Patrick Grimaldi (Kem One)

Two main objectives:1: Strengthen industrial competitiveness2: Enhance economic appeal of port area

Tools: > Industrial ecosystem: exchange of material and energy flows, cooperation between actors, mutualized services and facilities, etc.

> Innovation: energy transition, green industry, pilot projects, etc.



6 Operational Working Groups and several projects already launched or implemented A Circular Economy creating synergies

Green

Industry

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Promotio

Steam Network

Governa

nce

between industries (valorization of ferrous metals, recovery of sludge, etc.) Steam network projects, a strategic investment in the port area to create synergies between consumers and

Circular econom y

Innovati

on

Fostering dynamic innovation (INNOVEX) 4 Key Areas: Energy Storage / Circular Economy / Smart Grid / Safety

+ 60M€ private investments for industrial demonstrators



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Marketing and building of a Plug & Play approach

PROVENCE

Multi-Platform Approach: A metropolitan-

including Berre, La Mède, and PIICTO tackling major issues such as microalgae, bio-plastics,

scale approach to industrial innovation

and biofuels. Launching of *Provence Industry'Nov* industrial innovation hub.

PLUG > START > SHARE

INDUSTRY'NOV

PIICTO is one of the major pillars of both the Industry of the Future and the Energy of Tomorrow economic development plans developed by the PACA region. PIICTO's innovative projects are generating more interest in international partnerships







PIICTO Today

A dynamic industrial ecosystem featuring:

Key synergies between industrial plants already implemented or in the process of being implemented (exchanges of material or energy flows, cooperation between actors, mutualized services or facilities, etc.)

> An array of industrial opportunities including:

- Over €300 million in cumulative potential investment
- Current and future creation of hundreds of jobs
- Systematic search for potential integrations and synergies with existing industry members on the platform





And an innovative platform with:

- Pioneering projects:
 - ➤ ~60M€ already engaged
 - > More than 20 projects in progress (from start-ups to large corporations)



> A Commitment to the energy and environmental transition:

- > Power-to-Gas Power-to-Power Power-to-Liquids Solar Energy Wind Power etc.
- Recycling of CO2 and waste flows: microalgae, sludge, biofuels, etc.



For more information, feel free to contact:

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Methodology



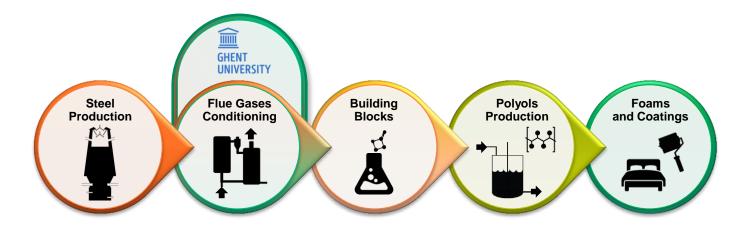
C	O/CO ₂	BUILDING BLOCKS / INTERMEDIATES			PRODUCTS & APPLICATION			
Steel	industry		Chemical – Polyol industry			Polymer industry		
Steel production	Flue gas treatment	Catalyst Process design design		Ups	caling	Insulation boards & Coatings		& Coatings
ArcelorMittal	UNIVERSITEIT GENT	Construction Conversion		covestro	RWITH AACHEN UNIVERSITY	RECTICEL	covestro	MEGARA RESINS







How is UGent involved in Carbon4PUR?





Overview of our work Aims, Objectives & Partners

Aim

Reduce H₂ concentration in steel mill flue gas stream to less than 0.1% by volume

Objectives

Analyze, select, pretreat, and sample industrial flue gases from a steel mill for conditioning Develop an economical chemical process to reduce H₂ content in a CO/CO₂-rich waste stream

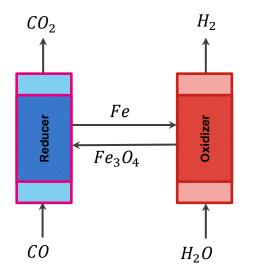




Chemical Looping

Chemical intermediates are used in a reaction-regeneration to

1) Decompose one target reaction into two or more sub-reactions. First commercial steam-iron process (Howard Lane, 1904)



Reducer: $Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2$

Oxidizer:
$$3 Fe + 4 H_2 O \rightarrow 4 H_2 + Fe_3 O_4$$

et reaction:
$$CO + H_2O \rightarrow CO_2 + H_2$$

ooping medium: $Fe_3O_4 \leftrightarrow Fe$

Benefits:

- 1) WGSR equilibrium avoided
- 2) Combined gas separation

L. S. Fan (2010) Chemical Looping Systems for Fossil Energy Conversions. Hoboken, NJ: American Institute of Chemical Engineers.

R. W. Breault (2018) Handbook of Chemical Looping Technology. Morgantown, WV: Wiley-VCH.

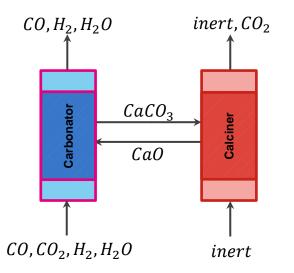


Chemical Looping

Chemical intermediates are used in a reaction-regeneration cycle to:

2) Separate gases.

The CO2 Acceptor Gasification Process (G. P. Curran et al., 1967)



Carbonator:
$$CaO + CO_2 \rightarrow CaCO_3$$

Calciner: $CaCO_3 \rightarrow CaO + CO_2$

Looping medium: $CaO \leftrightarrow CaCO_3$

Benefits:

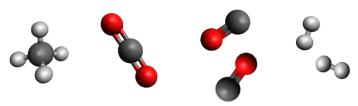
- 1) High temperature sorbents
- 2) High ability of regeneration

R. W. Breault (2018) Handbook of Chemical Looping Technology. Morgantown, WV: Wiley-VCH. F. Schora (1967) Advances in Chemistry. Washington, DC: American Chemical Society.

Dry Reforming of Methane



 $CH_4 + CO_2 \rightarrow 2CO + 2H_2$



Reduces greenhouse gases Produces valuable chemicals

Currently, there are no commercial processes

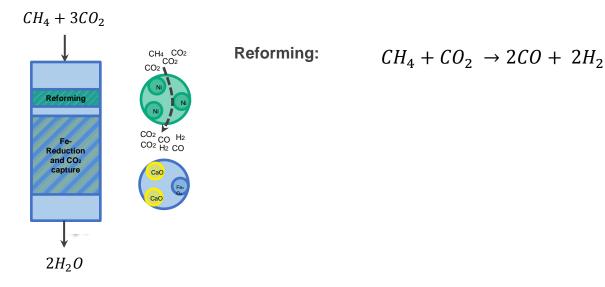
Thermodynamic limitations.

Deactivation of the catalysts due to carbon formation

Disadvantageous spent material disposal



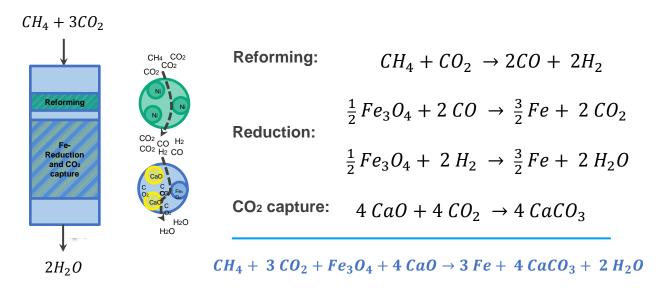
Super-Dry Reforming of Methane $CH_4 + 3 CO_2 \rightarrow 4 CO + 2 H_2O$



Buelens, Galvita et al., Science, 2016, 354 (6311).

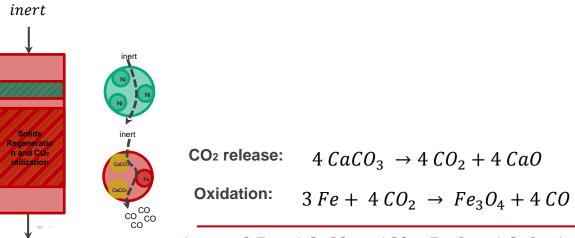


Super-Dry Reforming of Methane $CH_4 + 3 CO_2 \rightarrow 4 CO + 2 H_2O$





Super-Dry Reforming of Methane $CH_4 + 3 CO_2 \rightarrow 4 CO + 2 H_2O$



4 *CO* + *inert*

 $inert + 3 Fe + 4 CaCO_3 \rightarrow 4CO + Fe_3O_4 + 4 CaO + inert$



Super-Dry Reforming of Methane

Single fixed bed

30 T = 1023 K **CH**₄:**CO**₂ He $CH_4:CO_2 = 1:3$ 25 CO 25 cycles STY (mmol s⁻¹ kg_{Fe}⁻¹) 01 21 05 H₂O 5 CO 0 20 0 40 60 Time (s)

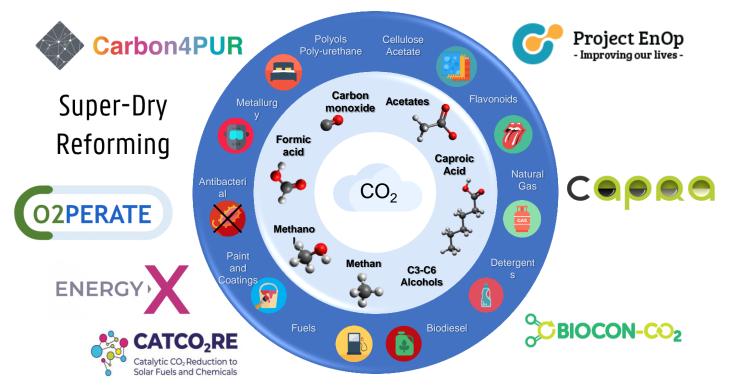


Super-Dry Reforming of Methane

Super-Dry Reforming of Methane	Conventional Dry Reforming of Methane		
$CH_4 + 3 CO_2 \rightarrow 4 CO + 2 H_2O$	$CH_4 + CO_2 \rightarrow 2 CO + 2 H_2$		
ΔH°_{298K} = 110 kJ mol ⁻¹ _{CO2}	ΔH°_{298K} = 250 kJ mol ⁻¹ _{CO2}		
Water-gas shift reaction avoided.	Limited by the water-gas shift reaction.		
Carbon deposition avoided.	Carbon deposition causes deactivation.		
Allows use of Ni-based catalyst at 750 °C.	Requires noble metal catalyst to mitigate carbon formation between 800 to 1000 °C.		
Reduces separation costs.	Separation of gases is required.		
Flexible process where process variables, reactor configurations and materials can be fine-tuned.	Process limited by the water-gas shift reaction.		



CCU Portfolio at UGent

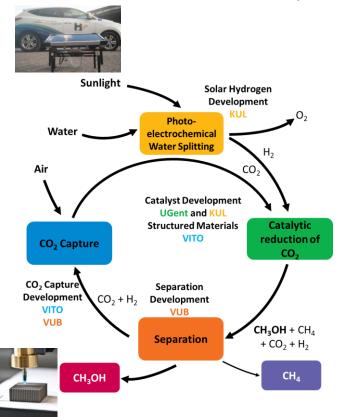






Investigate conversion of CO_2 to solar fuels (methane and methanol), integrating new developments in the production of solar hydrogen, with the design and synthesis of selective catalysts active at milder reaction conditions, and effective CO_2 capture and separation technologies.





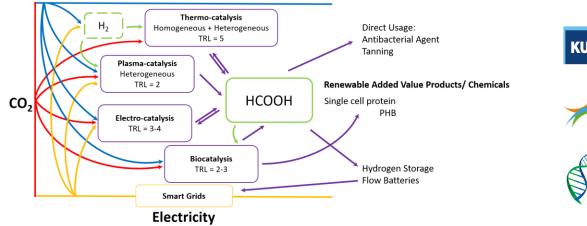




Develop new technologies for the conversion of CO₂ to value-added chemicals using catalysis and renewable energy; benchmark, compare and develop the various technologies starting with Formic Acid



H₂O

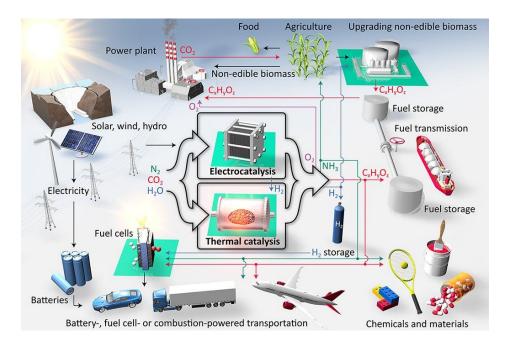


Bio Base Europe

Pilot Plant















Thank you!





- ... You for your attention
- ... The EC for funding
- ... The Port for today's organisation
- ... and all collaboration partners

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