Carbon capture and re-use: technological and other challenges

Grégoire LEONARD June 23, 2021

2nd Edition of The International Congress of Chemical Engineering Science and technology Faculty of Settat,

• CUEM Morocco





University of Liège - ULiège

- Liège: 3rd urban area in Belgium
 ~750 000 inh.
- ULiège, a pluralist university
 - 11 faculties, 23 000+ students, 122 Nationalities
 - 38 bachelor study lines, more than 200 master study lines







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Outline

- 1. How big is the CO₂ challenge?
- 2. Carbon Capture

3. Storage and/or re-use?

4. Perspectives

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The energy transition is on-going... revolution



It has to address 2 objectives in contradiction:

Limit GHG emissions

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Meet the worldwide increasing energy demand!





Meeting the increasing demand is already a challenge in itself!





CO₂ Budget

Budget by 2050 for having 80% chances to stay below 2°C



At european level...

The EU Green Deal

- Carbon neutrality by 2050
- 55% CO₂ by 2030



Cooling it

EU, progress on greenhouse gas targets Emissions, gigatonnes of CO₂ equivalent per year*



The Economist





CCUS forecasts

CCUS = Carbon Capture, Utilization and Storage









CO₂ capture

It's a question of fluid separation!

- Sources usually contain CO_2 , N_2 , H_2O , H_2 , CH_4 , O_2 ...
- CO₂ concentration varies between 0.04% and almost 100%
- Mature (exist for >50 years) & flexible, but costly!







CO₂ separation technologies

- Avoid fluid mixtures
- Absorption
 - PhysicalChemical
- Adsorption
- Membranes
- Cryogenic separation
- Others...





Partial Pressure

Threshold value ~15 vol-% in flue gas, or 4 bar of P_CO2





CO₂ capture benchmark – Power sector

	Ultra-superc	riti cal coal-fired	power plant	Natural-gas	combined-cycle power plant		
	W/O PCC	MEA	DZ/AMP	W/OFCC	MEA	PZ/AMP	
Technical performance							
Gross power output (MW)	900	900	900	890	890	890	
Auxiliary power (MW)	83	266.1	215.6	12	161.8	128.2	
Net power output (MW)	817	633.9	684.4	878	728.2	761.9	
Net plant higher heating value efficiency (%)	42.5	32.97	35.59	52. 66	43.91	45.94	
Net plant lower heating value efficiency (%)	44.4	34.48	37.23	58.25	48.57	50.82	
CO ₂ generation (t/h)	604	604	603.3	310	310	310	
CO ₂ emission (t/h)	604	61	59.1	310	31	31	
CO2 emission (t/MWh)	0.739	0.095	0.084	0.353	0.042	0.040	
CO ₂ capture (t/h)	0	543	544	0	279	279	
Equivalent energy consumption (MWh/tCO ₂)	_	0.337	0.244	-	0.506	0.423	
Economic performance							
Total capital requirement (million €)	1342.8	1681.1	1659.5	835.7	1172.8	1166.3	
Specific capital requirement (€/kW)	1647	2654	2424	939	1611	1531	
Fixed operations & maintenance (O&M) (million €)	37.7	46.3	45.9	29.2	39.7	39.5	
Variable O&M (million €)	7.54	20.1	17.8	3.41	11.9	9.1	
LCOE (€/MWh)	51.6	87.0	79.5	52.9	77.6	73.8	
CO ₂ avoided cost (€/tCO ₂)	-	55.0	42.8	-	79.3	67.1	

W/O PCC = without post-combustion capture

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IEAGHG, 2019. Further assessment of emerging CO_2 capture technologies for the power sector and their potential to reduce costs 13



- Modeling and optimization of processes
- Stability of chemical solvents



OPEX: viscosity, altered properties...

Léonard et al., 2014&2015. DOI:10.1021/ie5036572, DOI: 10.1016/j.compchemeng.2015.05.003





Objective: Representativity of accelerated degradation versus industrial degradation



IC.AL



=> 21% MEA loss after 7 days vs. 4% loss in 45 days

Léonard et al., 2014. Int. J. Greenhouse Gas Control 30, 171. DOI: 10.1016/j.ijggc.2014.09.014



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Leads to a kinetic model of solvent degradation:

=> 2 main degradation mechanisms
 => Equations balanced based on the observed proportion of degradation products

Dxidative degradation

$$r = 5.35 \ 10^5. \ e^{-\frac{41\ 730}{8.314\ T}}. \ [O_2]^{1.46}$$

 \downarrow
0,6 NH₃ + 0,1 HEI + 0,1 HEPO + 0,1 HCOOH + 0,8 CO₂ + 1,5 H₂O

Thermal degradation with CO_2 MEA + 0,5 $CO_2 \rightarrow 0,5$ HEIA + H₂O

 $r = 6.27.10^{11} \cdot e^{-\frac{143\,106}{8.314\,T}} \cdot [CO_2]^{0.9}$

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Léonard et al., 2014. DOI 10.1016/j.ijggc.2014.09.014



- Include degradation model included into process model
 - Steady-state simulation, closed solvent loop
 - Additional equations in the column rate-based models
 - => predicts degradation in the capture process (80 vs 300 g MEA/tCO₂)



- Further work on amine degradation
 - Experimental study of other solvents (MDEA)
 - Kinetic modeling of mass-transfer
 - SO₂-induced degradation



CHEMICAL Benkoussas et al., 2018. SO2 effect on oxidative
 ENGINEERING degradation of monoethanolamine for post combustion 18
 CO2 capture. GHGT-14



Pre-combustion capture

Remove C from the fuel => Natural gas sweetening

- Conventional process: absorption with solvents
- From 80 to 2 vol%; down to 50 ppm if liquefaction



- Current PhD thesis running: Multi-objective optimization of sour natural gas sweetening processes (MDEA/DEA)
 - M. Berchiche, cotutelle with Algerian industry

Picture: Berchiche M. (2017).

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Pre-combustion capture

- Process multi-objective optimization
 - CO₂ capture for Natural gas sweetening operations
 - Energy integration (Pinch + ORC)
 - BTEX emissions + LCA



CALBerchiche et al., 2020. Energy reduction potential in natural
gas processing through heat and process integration.20EERINGComputer aided chemical engineering 48, 67-72.



Recovery ratio

PROCURA ETF: Decision support tool



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Decision-support tool

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	WEL	COME!	
The purpose of this Decision Supp I main categories in CO2 capture	ort Tool (DST) is to provide a consisten processes:	t and robust selection approach to CO2 ca	pture technologies. There are
OXY-COMBUSTION	PRE-COMBUSTION	POST-COMBUSTION	DIRECT AIR CAPTURE (DAC)
f you are a returning user, please nalfunctioning of this model. It is	remember that prior to using the DST, also good practice to save each DST as e DST, please click the START button at	please first save it onto your computer as sessment as a new file to have a clean ter the bottom of this page. Otherwise, pleas	a .xism file to avoid any nplate to work with each time. we access the User Guide
Owecombustion	CO ₂ CAPTURE	TECHNOLOGY	Direct Air Canture
Oxy-combustion	CO ₂ CAPTURE	TECHNOLOGY Pos-tcombustion	Direct Air Capture
Oxy-combustion	CO2 CAPTURE Pre-combustion 1. Flue gas characteristics: 1.1 Percentage of CO2	TECHNOLOGY Pos-tcombustion I. Flue gas characteristics: I.1 Percentage of CO2	Direct Air Capture
Oxy-combustion 1. Applied in the steel and glass industry	CO2 CAPTURE Pre-combustion I. Flue gas characteristics: 1.1 Percentage of CO2 [Vol %]: 20-40%.	TECHNOLOGY Pos-tcombustion I. Flue gas characteristics: 1.1 Percentage of CO2 [Vol %] 4-15%.	Direct Air Capture
Oxy-combustion 1. Applied in the steel and glass industry 2. Suitable for fuels with low heating power	CO ₂ CAPTURE Pre-combustion 1. Flue gas characteristics: 1.1 Percentage of CO2 [Vol %]: 20-40%. 1.2 Typical operating pressure: 10-80 har.	TECHNOLOGY Pos-tcombustion I. Flue gas characteristics: I.1 Percentage of CO2 [Vol %] 4-15%. I.2 Typical operating pressure: 1 har.	Direct Air Capture
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Oxy-combustion 1. Applied in the steel and glass industry 2. Suitable for fuels with low heating power 3. Retrofit and repowering option	CO ₂ CAPTURE Pre-combustion 1. Flue gas characteristics: 1.1 Percentage of CO2 [Vol %]: 20-40%. 1.2 Typical operating pressure: 10-80 bar. 2. Work with a gasification system	TECHNOLOGY Pos-tcombustion 1. Flue gas characteristics: 1. Percentage of CO2 [Vol %] 4-15%. 1.2 Typical operating pressure: 1 bar. 2. suitable for retrofitting 3. Applicable to the	Direct Air Capture 1. Manage emissions from distributed sources 2. Treats percentage of CO2 in volume around 0.04% 3. Can be installed
Oxy-combustion 1. Applied in the steel and glass industry 2. Suitable for fuels with low heating power 3. Retrofit and repowering option 4. Small scale application only at the	CO ₂ CAPTURE Pre-combustion 1. Flue gas characteristics: 1.1 Percentage of CO2 [Vol %]: 20-40%. 1.2 Typical operating pressure: 10-80 bar. 2. Work with a gasification system	TECHNOLOGY Pos-tcombustion 1. Flue gas characteristics: 1. Percentage of CO2 [Vol %] 4-15%. 1.2 Typical operating pressure: 1 bar. 2. suitable for retrofitting 3. Applicable to the majority of existing coal- fired nower plants	Direct Air Capture 1. Manage emissions from distributed sources 2. Treats percentage of CO2 in volume around 0.04% 3. Can be installed almost everywhere but large volume are
Oxy-combustion 1. Applied in the steel and glass industry 2. Suitable for fuels with low heating power 3. Retrofit and repowering option 4. Small scale application only at the moment, but applicable	CO ₂ CAPTURE Pre-combustion 1. Flue gas characteristics: 1.1 Percentage of CO2 [Vol %]: 20-40%. 1.2 Typical operating pressure: 10-80 bar. 2. Work with a gasification system	TECHNOLOGY Pos-tcombustion 1. Flue gas characteristics: 1.1 Percentage of CO2 [Vol 35] 4–155. 1.2 Typical operating pressure: 1 bar. 2. suitable for retrofitting 3. Applicable to the majority of existing coal- fired power plants	Direct Air Capture 1. Manage emissions from distributed sources 2. Treats percentage of CO2 in volume around 0.04% 3. Can be installed almost everywhere but large volume are needed

The decision support tool (DST) assesses and compares widely available CO2 capture technologies in terms of three main criteria: ENGINEERING, ECONOMICS, and ENVIRONMENT. There are various key performance indicators (KPIs) under each criterion which play important roles. Then, you can express your preferences in terms of a score system (1 to 9) in two points. First, inserting which criteria, economic, engineering, or environment is preferable with respect to others. your preferences will be used to calculate and provide the first set of weights to each criterion. Inside each criterion, there are KPI factors that must be evaluated by you following the same procedure to obtain the second set of weights of each KPI. In this way you will show your preferences in two phases of the process and based on that, the suitability of each technology will be analyzed. A database associated with each KPI is built and used to score each technology accordingly. Lastly, CO2 capture technology options are evaluated and ranked to screen and recommend suitable possibilities considering all important criteria

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START

Decision-support tool

Following the Analytical Hierarchy Process

4. Analytical Hierarchy Process - KPIs for Environment criteria

Table 4.1	
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Environment																		
Please rate importances of these KPIs																		
(j - k)																		
Criterion j	Very Very Extreme Strong Strongly Slightly Slightly Strongly Strong Extreme favors favors								Criterion k									
(LCA score	09	08	07	06	05	04	Q3	Q 2	01	02	۵3	04	05	06	07	08	09	- Safety Issue)
(LCA score	09	08	07	06	05	04	03	O 2	1	02	Q3	04	O 5	06	07	08	09	 Public acceptance)
(Safety Issue	09	08	07	06	05	04	03	Q 2	01	02	03	04	05	06	07	08	09	 Public acceptance)

Table 4.2	
KPIs	KPIs Weight
LCA score	0.210
Safety Issue	0.550
Public acceptance	0.240
Inconsistency	0.016
Total Inconsistency	0.074

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If you are satisfied with the criteria weights and KPI weights of each criterion, please click the 'Go to Results' button to display analyzed results. If you wish to re-evaluate your preferences, please click the 'Back to Top' button to scroll up and you may repeat the rating process.

As explained in the AHP theory page, Pairwise matrices can be displayed when you click the 'Show Pairwise Matrix' button provided below.







Decision-support tool

Results display



If you are **NOT** satisfied with the recommendations, kindly go back to the AHP step by clicking the **'Back to AHP**' button below. If you wish to look at the appendix of this analysis, please click **'Appendix**' button at the end of this page.



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Direct Air Capture (DAC)

Negative CO₂ emissions BECCS or DAC





Elon Musk promet 100 millions de dollars à celui qui pourra l'aider à résoudre ce problème





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 K.S. Lackner, CNCE ASU, 2017.
 https://www.nytimes.com/2019/02/12/magazine/climeworksbusiness-climate-change.html?smid=em-share



Direct Air Capture

Motivations



- Address non-concentrated CO₂ emissions (410 ppm in the air)
- Close the carbon cycle of synthetic fuels
- Reduce the need for transporting CO₂
 - No Nimby effect, you can go wherever you want, incl. close to use or storage sites
- Long-term considerations: remove C from the atmosphere
- Adsorption / Absorption
- Temperature-swing, moisture-swing
 - Sorbent regeneration has similar cost whatever the CO₂ concentration in the gas stream
- Expected costs vary between 100 and 800 \$/ton



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Cost of CO₂ capture

Estimated cost for different industries

Opex ~75% of the cost







CO₂ market

IGINEE

- European Emissions Trading System (ETS)
- CO_2 price now reaches > 50 $\in/t!$



https://ember-climate.org/data/carbon-price-viewer/



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3. Storage and/or re-use of CO₂?

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Storage is state-of-the-art

- Potential for storage exceeds by far the needs
 - □ 5000 25 000 GtCO₂ vs. ~ 40 GtCO₂/y
 - Pure storage: ~ 5 Mtpa
 - Capture and EOR: ~ 30 Mtpa in 2016
- Storage costs ~2-15 USD/t, large infrastructure costs needed!





Global CCS Institute 2017 doi: 10.3389/fclim.2019.00009



Northern lights

Norway, off-shore field, saline aquifer
 Up to 5 Mt CO₂/y
 A ship based solution means access for CO2 emitters across Europe



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https://northernlightsccs.eu/en



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Porthos

- Rotterdam, off-shore depleted gas field
- 2.5 Mt CO₂/y



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Antwerp@C

No storage capacity offshore of Belgium

- Antwerp@C studies the infrastructure for connection to Norway and The Netherlands
- > Pipelines, intermediate storage, liquefaction unit...



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CO₂, waste or feedstock?

- Sequestration or re-use?
 - Consider CO₂ as a resource in a Carbon-based society, not as waste



Main uses of CO2 (Mtpa)

- CO_2 re-use potential up to ~ 4 18 Gtpa
- So far, sources for CO₂ are high-purity ones
 - Industrial (Ethanol, Ammonia, Ethylene, Natural gas...)
 - Natural (Dome)

Global CCS Institute. Global Status of CCS 2016: Summary Report. Koytsumpa et al, 2016. https://doi.org/10.1016/j.supflu.2017.07.02934



Main CO₂ re-use pathways

- Direct use, no transformation
- Biological transformation
- Chemical transformation
 - To lower energy state
 - Carbonatation
 - To higher energy state
 - Fuels
 - Chemicals
 - • •



=> At large scale, need to make sure that energy comes from renewables!
• CHEMICAL Frenzel et al, 2014. Doi:10.3390/polym6020327
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Perspective ULiège: FRITCO₂T platform

Federation of Researchers in Innovative Technologies for CO₂ Transformation **Pharmaceutics Synthetic Fuels Chemical Transformation** Physical Use & Cosmetology **Direct CO**₂ use **Monomers &** (solvent, **Polymers** CO, foaming...) Sourcing **Capture & Purification** Transversa **Process Mineralization** sustainability (LCA and economics)

•••• CHEMICAL www.chemeng.uliege.be/fritco2t



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- Our society is currently based on fossil carbon
 - Need to find replacement sources: Biomass and atm. CO₂
- C is a fantastic support for energy storage, but also a great atom for materials !



Power-to-fuel

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- Long-term energy storage
- => addresses time imbalance generation consumption





Process integration

Models for electrolysis, CO₂ capture and fuel synthesis







- Heat integration and intensification
 - Heat integration to improve LHV conversion efficiency
 - Design of a heat exchanger network
 - ε increases from 40.1 to 53.0% !



CO₂ reduction lab under construction
 Intensification of synthesis reactor for CO₂ reduction
 Flexibility towards input and load



4. Conclusions and perspectives

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State of technology CCUS

- Capture of CO₂
 - Mature but limited application yet
- Storage
 - Commercially applied (mostly EOR)
- Re-use
 - Maturity depends on technology, from TRL 1 to 9
- Big acceleration due to Paris COP21 agreement and environmental urgency
 - European Green Deal

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Perspective

- We live in a carbon-based society, with very good reasons for that !
- A CO₂ neutral future is in sight with passionating (and huge) challenges for engineers!



CHEMICAL Martens et al., (2017) The Chemical Route to a CO₂-neutral world, ChemSusChem Saeys (2015), De chemische weg naar een CO₂-neutrale wereld, Standpunt KVAB
 FNGINFFRING



Thank you for your attention!

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Process design for power-to-industry

- Feasibility study for green H₂ industry
 - Master's students work 2019-2020
 - Low carbon ammonia production in Europe



CHEMICAL
 Source: Hoxha J.-L., Caspar M., Donceel A., Fraselle J., Philippart de Foy
 N., Poncelet R., Léonard G., 2020. Feasibility study of low-carbon ammonia
 and steel production in Europe. Eceee Industrial Summer Study



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CHEMICAL
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 N., Poncelet R., Léonard G., 2020. Feasibility study of low-carbon ammonia
 and steel production in Europe. Eceee Industrial Summer Study



Process design for power-to-industry

- Assuming 85% efficiency, the H₂ needs in green industry would be:
 - For a typical ammonia plant (540 kt NH₃/year) => 700 MW power
 - For a typical steel making plant (1 Mt steel/year) => 400 MW power
 - Break-even costs (left: ammonia; right: steelmaking)



Further process modeling work

Process dynamic modeling

Applied to CO2 capture



Further process modeling work

Data treatment

- Application of data processing and machine learning techniques for the improvement of a phosphoric acid production process
- PhD thesis in coll. with Prayon



Further process modeling work

- LCA & TEA
 - Pulsatec project
 - Development of a methodology for techno-economic and life-cycle assessment of innovative technologies: case of functionalized coatings by pulsed plasma



CHEMMericA. and Leonard G., 2020. Development of a framework integrating TEA and LCA : advances and challenges. Oral presentation at Cape Forum 2020. 51

Recent initiatives

Projects recently submitted

- Direct air capture
 - Design of DAC systems based on existing gas treatment infrastructures
 - Recruitement of PhD student in progress
- Carbonation of mineral wastes
 - Accepted, start in August 2021
- CO₂ conversion to jet fuels
 - CO₂ based Fischer-Tropsch reactor design
 - Dynamic modeling





PROCURA ETF: Decision support tool

- We are convinced that CO₂ capture will play a role in future industrial systems
- But many technologies are available, and the right choice depends on many variables
 - Techno-economics and environmental footprint
 - Required purity of CO₂; presence of flue gas contaminants

• ...

- In the framework of the PROCURA project, we develop a decision support tool for helping local companies in their choice
 - Tool is currently at version 1.0, based on literature data
 - Next steps will refine the selection criteria, based on in-house process models (including TEA & LCA)
 - Tool will be demonstrated with Belgian case studies



