Whole CCU chain 3MWth demo project with detailed NOX measurements

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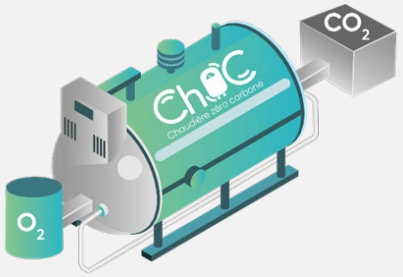
A french decarbonation initiative

- Partners

- Observing members & potential end-users

Ch0C : « Chaudière Oxycombustion bas Carbone »



- Oxycombustion fire-tube boiler
- CO_2 emissions reduction > 90%
- Capacity: $1MW_{th} < P < 25MW_{th}$

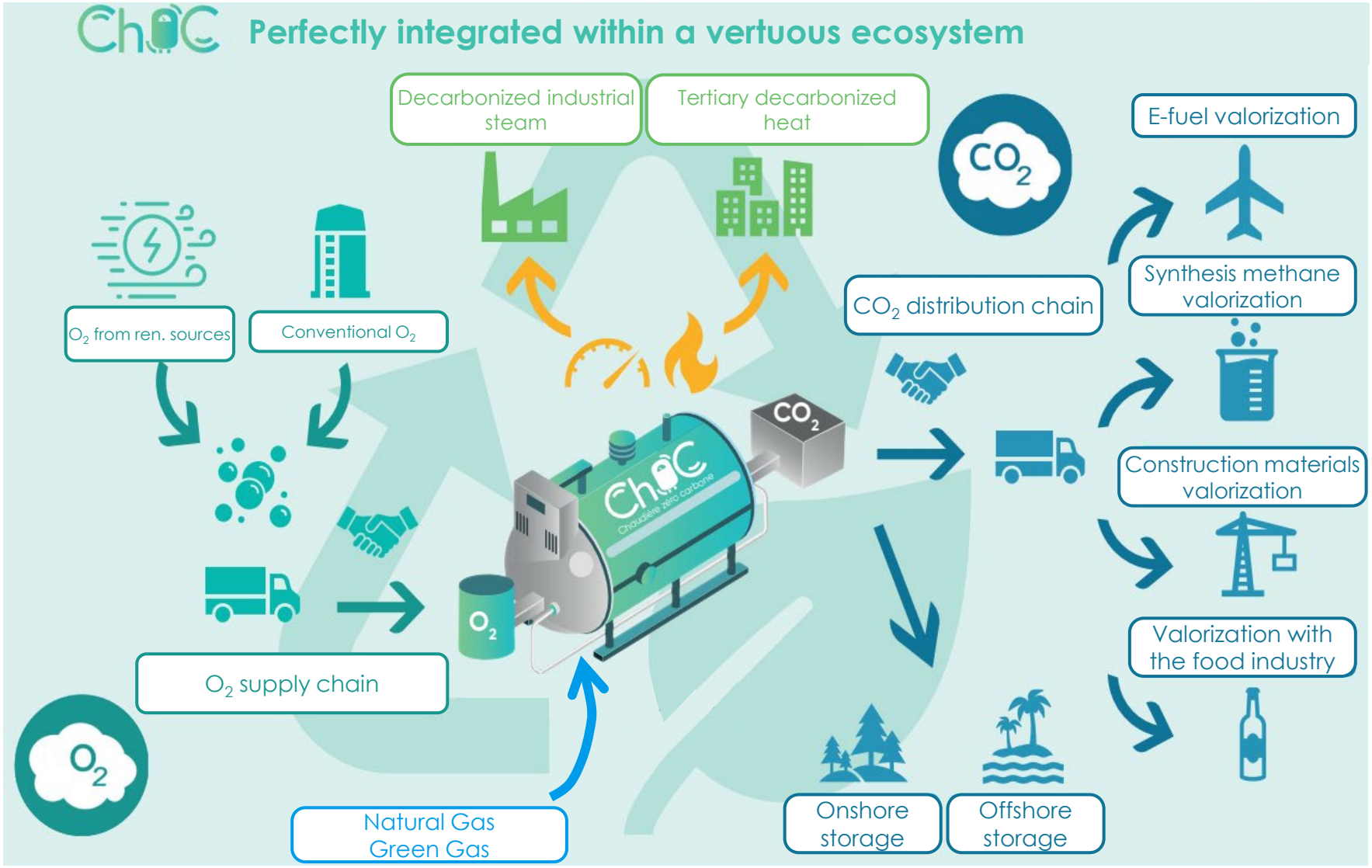
Objectives

- Design, manufacturing & testing of a $3MW_{th}$ oxycombustion boiler on an industrial site (Villers-Saint-Paul)

Technical challenges

- Low-NO_x oxyburner
- NO_x in purification unit

A virtuous ecosystem



The demonstration project

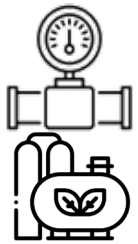
Electricity

CO_2 Purification Unit **(CPU)**

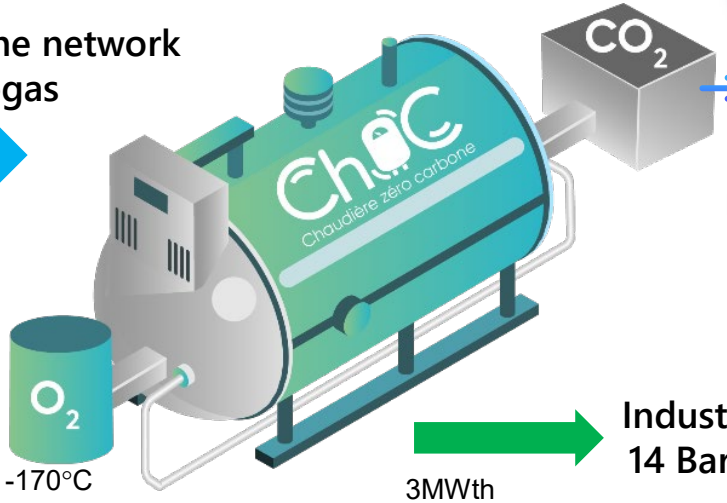
Off-gas

-17°C
19b

5000 tpa food grade
15 tpd,



Gas from the network
On-site biogas



Dehydratation
Liquefaction CO_2
Condensation
Compression
Purge treatment unit
H_2O

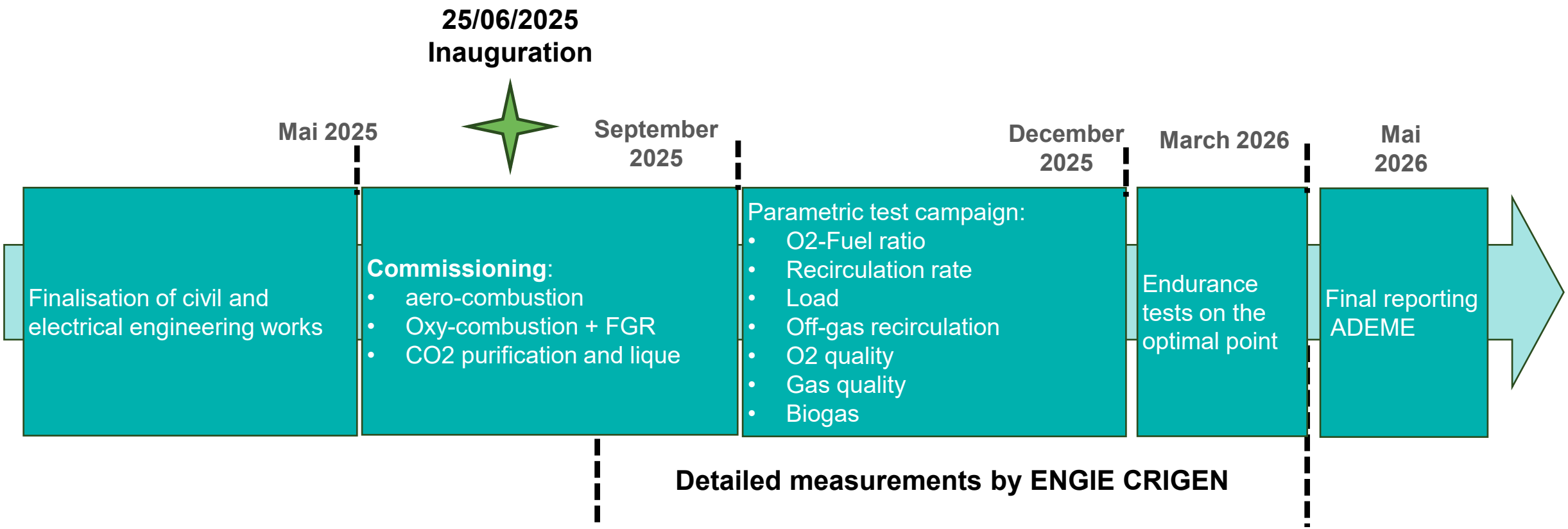
O_2 supply

-170°C
5b

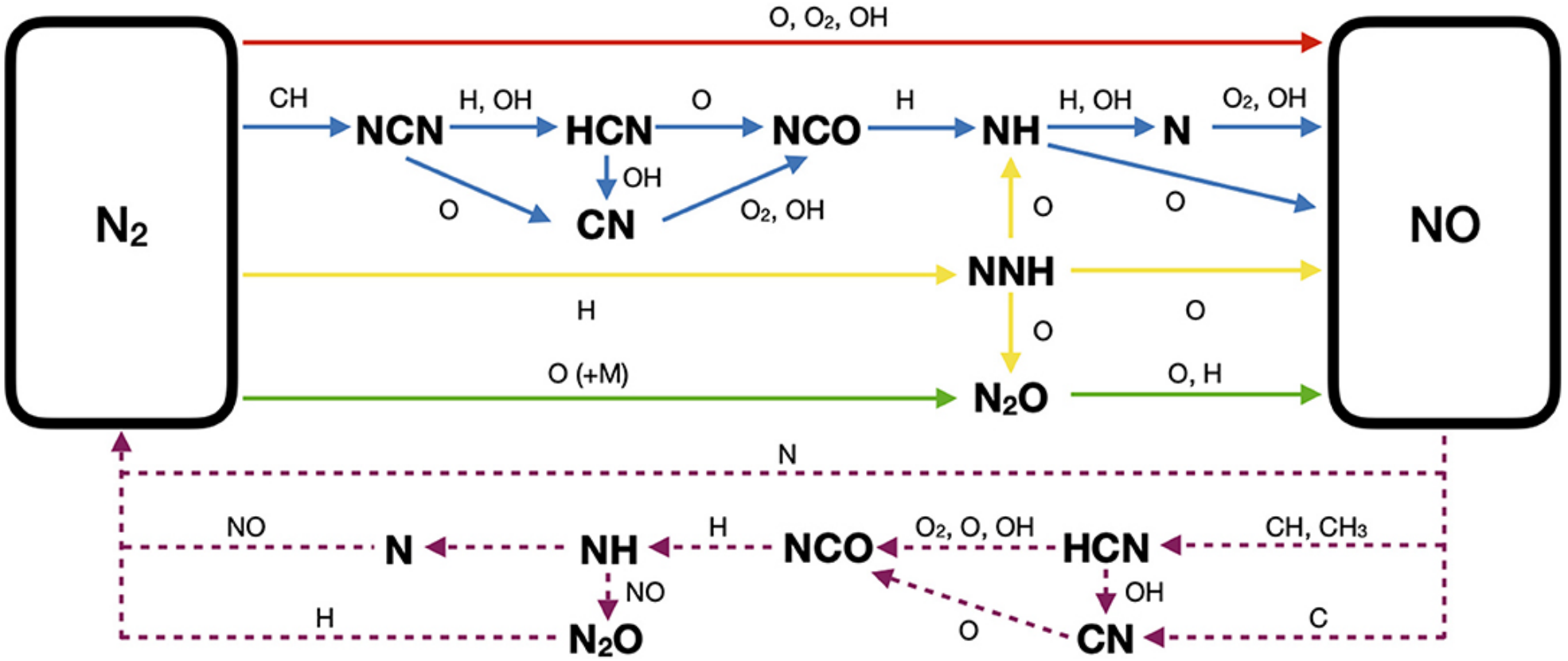
3MWth

Industrial steam
14 Bar / 250°C :

Project progress & planning



NOX complex formation



Légende :

Thermal NOx

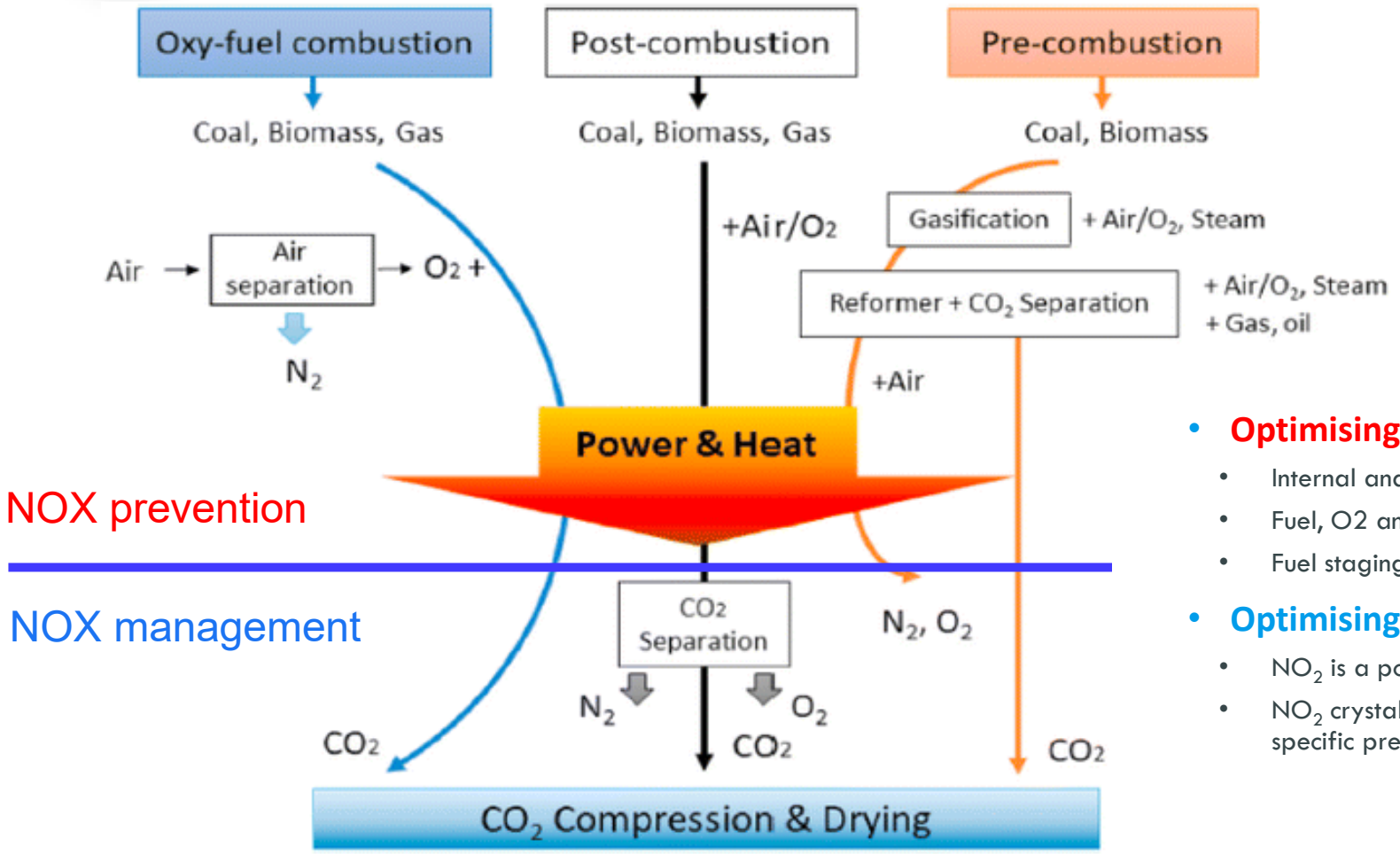
Prompt NOx

NOx fuel

N2O intermediate

Reburning

In all Combustion types



- **Optimising combustion**
  - Internal and External recirculation
  - Fuel, O2 and FGR premixing
  - Fuel staging
- **Optimising CO_2 capture process**
  - NO_2 is a poison for amine and leads to an increase in amine consumption
  - NO_2 crystalizes at higher temperature (-11°C) than CO_2 liquefaction and requires specific pre-treatment for cryogenic CO_2 separation processes
- **Ultra low NOx requirement for CO_2 transportation and storage**

  It corrodes drastically compressors / piping and drastic limitation are given for transportation/storage :
  Example: 1.5 ppm NOx v in Northlight CO_2 capture project.

A challenge for the CCUS value chain

		Northen Ligths		
		2022	2024	2025
		Liquide	Liquide	Liquide
CO_2	%v.		> 99.81	> 99.81
H_2O	ppm mol	≤ 30 ppm mol	≤ 30 ppm mol	≤ 30 ppm mol
H_2	ppm mol	≤ 50	≤ 50	≤ 50
N_2	ppm mol	-	≤ 50	≤ 50
Ar	ppm mol	-	≤ 100	≤ 100
CH_4	ppm mol	-	≤ 100	≤ 100
CO	ppm mol	≤ 100	≤ 100	≤ 100
O_2	ppm mol	≤ 10	≤ 10	≤ 10
H_2S	ppm mol	≤ 9	≤ 9	≤ 1
SO_x	ppm mol	≤ 10	≤ 10	≤ 10
NO_x	ppm mol	≤ 10	≤ 1.5	≤ 1.5
NH_3	ppm mol	10	≤ 10	≤ 10
Amines	ppm mol	≤ 10	≤ 10	≤ 10
Méthanol	ppm mol	-	≤ 30	≤ 30
Ethanol	ppm mol	-	≤ 1	≤ 1
Total VOC	ppm mol	-	≤ 10	≤ 10
Glycol	ppm mol	-	TEG pas acceptable MEG ≤ 0.005 ppm mol	MEG < 0.2 TEG < 0.2
Ethylene	ppm mol		≤ 0.5	≤ 50
Ethane	ppm mol		≤ 75	≤ 75
Aliphatic (C3+)	ppm mol	-	≤ 1100	≤ 1100
BTEX	ppm mol	-	≤ 0.5	≤ 0.5
Total aldéhydes	ppm mol	Formaldehyde ≤ 20 Acetaldehyde ≤ 20	Formaldehyde ≤ 20 Acetaldehyde ≤ 20	Formaldehyde ≤ 20 Acetaldehyde ≤ 20
HCN	ppm mol	-	<100	<100
Hg	ppm mol	≤ 0.03	≤ 0.0003	≤ 0.0003
Cadmium + Thallium	ppm mol	≤ 0.03	moved to solids	-
Particule size	um	-	≤ 1	≤ 1

Food spec.:

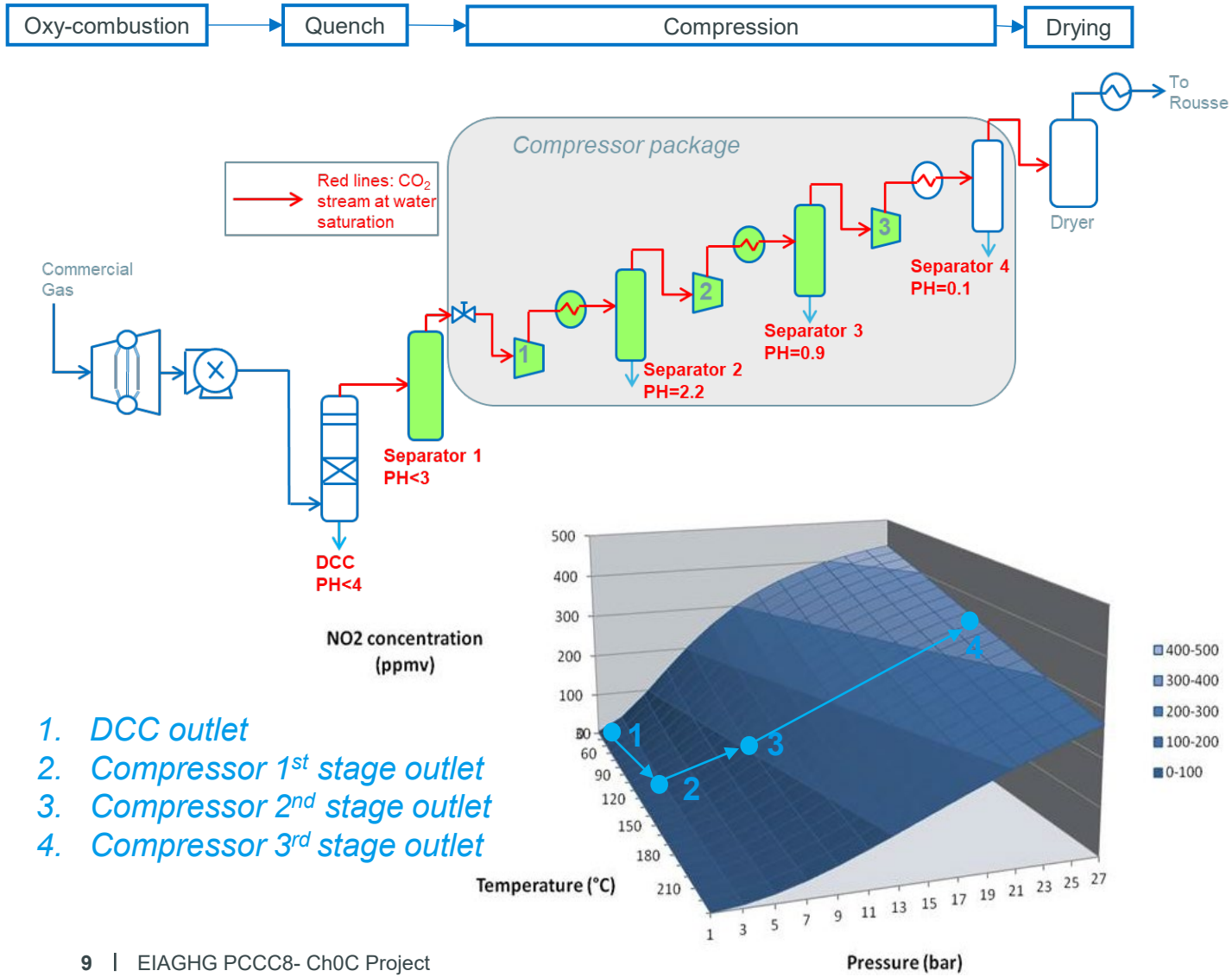
▷ TABLEAU 1 : CRITÈRES DE CONCENTRATION POUR LA NORME EIGA (CO_2 LIQUIDE)

Composé	Concentration
CO_2	▸ 99.9% v/v min.
Humidité	▸ 20 ppm v/v max
Ammoniac	▸ 2.5 ppm v/v max.
Oxygène	▸ 30 ppm v/v max.
Oxydes d'azote (NO/NO_2)	▸ 2.5 ppm v/v max. de chaque
Particules	▸ 10 ppm m/m max.
Résidus organiques non volatils (huiles)	▸ 5 ppm m/m max.
Total des hydrocarbures volatils (correspondance méthane)	▸ 50 ppm v/v max. dont 20 ppm v/v max d'hydrocarbures non-méthaniques.
Acétaldéhyde	▸ 0.2 ppm v/v max.
Hydrocarbures aromatiques	▸ 0.02 ppm v/v max.
Monoxyde de carbone	▸ 10 ppm v/v max.
Méthanol	▸ 10 ppm v/v max.

Les critères de la qualité technique (pour usage en froid ou chimie) varient selon les procédés.

Standardization efforts are underway within **CEN/TC 474's WG1 group** to establish a **European specification for CO_2 quality**.

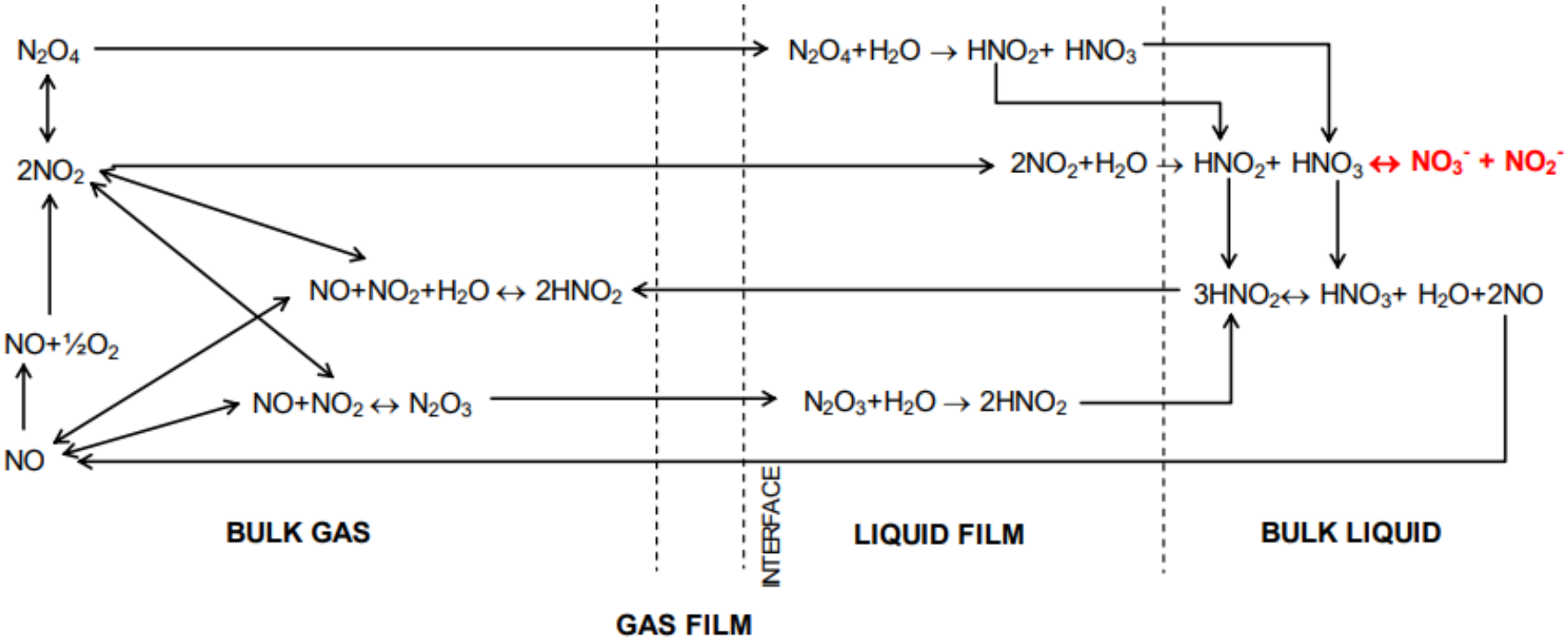
Lacq experience



1. *DCC outlet*
2. *Compressor 1st stage outlet*
3. *Compressor 2nd stage outlet*
4. *Compressor 3rd stage outlet*

3nd stage compressor (14/01/2010)

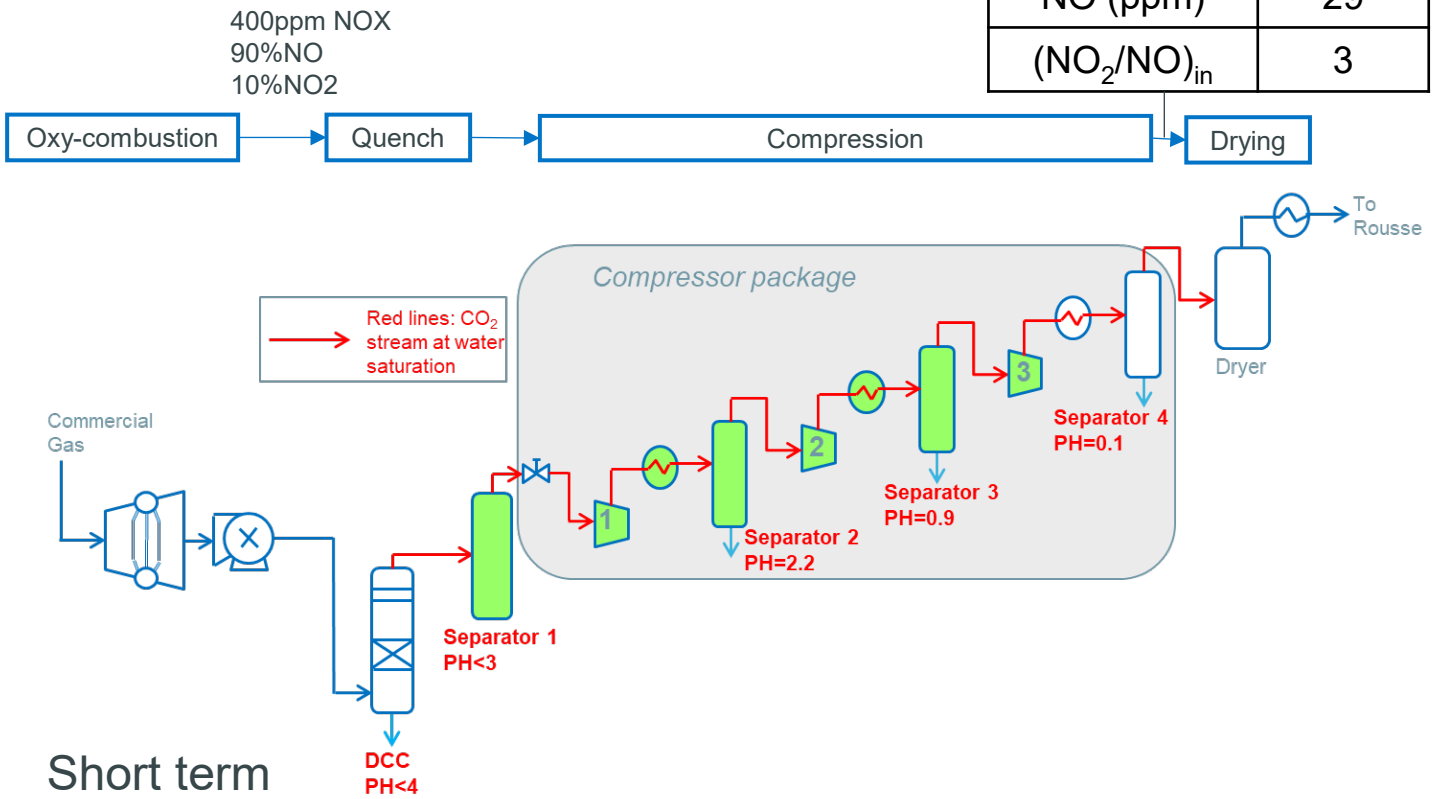
Lacq experience



NO oxydation into corrosive products

Lacq experience

NO_x (ppm)	113
NO_2 (ppm)	84
NO (ppm)	29
$(NO_2/NO)_{in}$	3



Short term

- Reduce liquid carry over from DCC
- To stay always above dew point

Long term

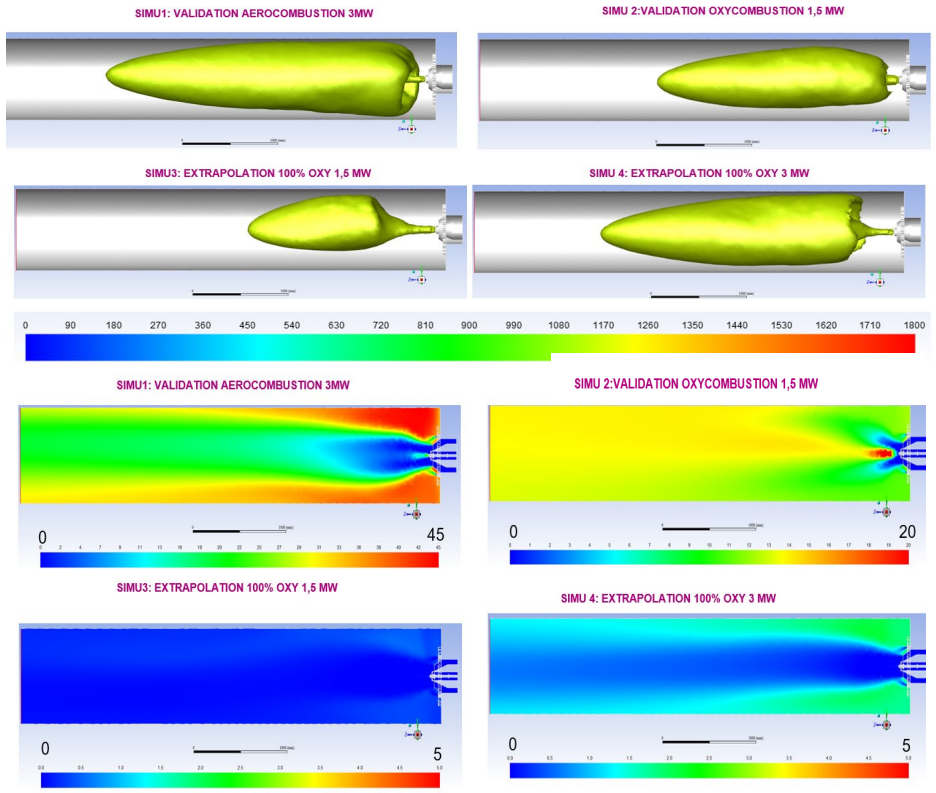
- To select the right metallurgy for compressor
- **To encourage ultra low NOX burner dev.**

Ch0C

- **CFD**

17 equations EDC model - NOx in post treatment (thermal, prompt: NO/NO_2)

ISO TEMPERATURE =1200 °C



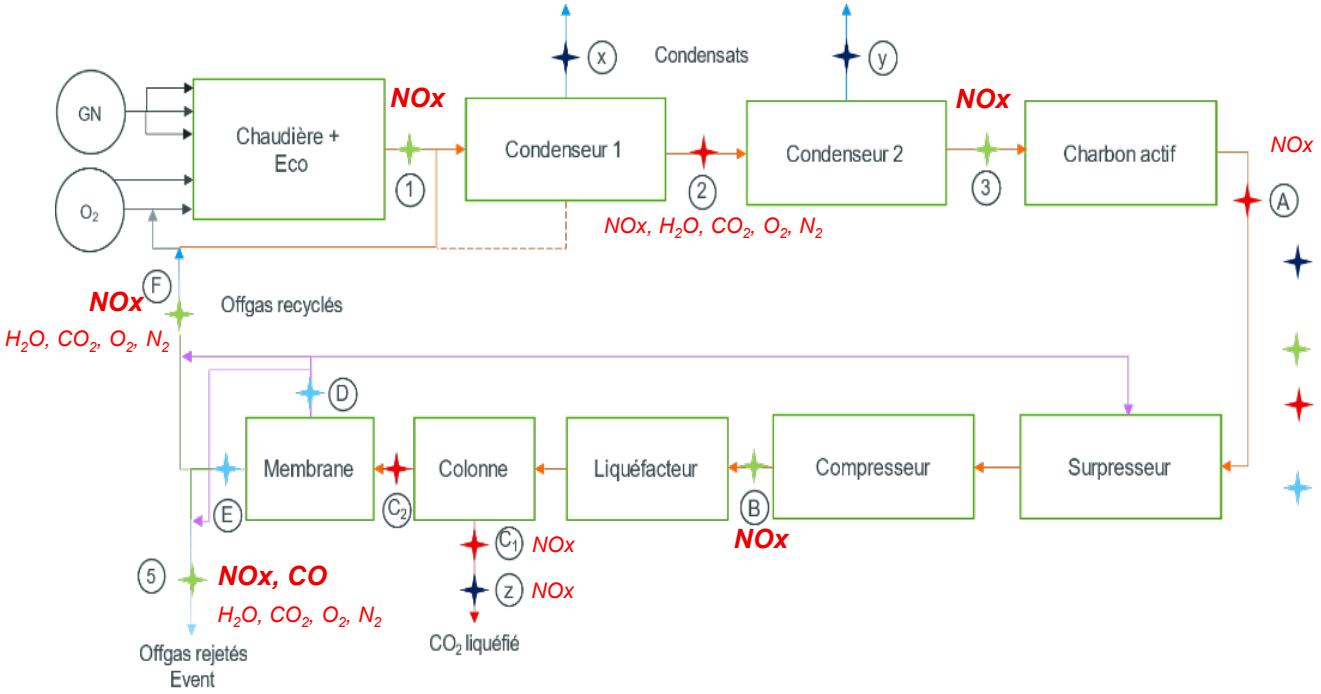
SIMULATION	NOx (ppm) mesure	NOx (ppm) CFD
SIMU 1: base case aerocombustion 3 MW	25	29
SIMU 2: base case oxycombustion 50% 1.5 MW	16.5	14
SIMU 3: extrapolation oxycombustion 100% 1.5 MW	NA	1
SIMU 4: extrapolation oxycombustion 100% 3 MW	NA	2

- **N_2 variation in oxygen and natural gas**

Ch0C pilot includes N_2 injection for testing various composition in natural gas (0 to 8%) and in oxygen (0 to 5%)

- **NOx measuring campaign**

A specific N_2 / NO / NO_2 measurement chain will be implemented to validate NOx formation/ reduction on each of the process phases.



11 points throughout the entire process

TotalEnergies

CH0C boiler project : Operating conditions, gas type matrices and expected NOx contents												
Measurement identification		**1**	**2**	**3**	**A**	**B**	**C1**	**C2**	**D**	**E**	**F**	**5**
Location of the measuring spots		**Outlet BW economizer**	**Outlet BW economizer**	**Outlet VMB condenser**	VMB **post activated carbon bed**	VMB **Downstream compressor**	Process VMB (4) **Liquified CO2 from column**	**Gas from column's outlet**	**Membrane outlet**	**Membrane outlet**	**Recycling offgas**	**VMB final Event**
Measurement frequency		Permanent	Permanent	Permanent	Occasionally	Permanent	Occasionally	Occasionally	Occasionally	Occasionally	Permanent	Permanent
Piping : DN — Schedule Internal Diameter (mm)		CORTEN steel sheathed tube : diam 300 mm	CORTEN steel sheathed tube : diam 300 mm	existing tapping for measurement with GC (DN15 with 15x21 inox valve)	existing tapping for measurement with GC (DN15 with 15x21 inox valve)	existing tapping for measurement with GC (DN15 with 15x21 inox valve)	existing tapping for measurement with GC (DN15 with 15x21 inox valve)	existing tapping for measurement with GC (DN15 with 15x21 inox valve)	existing tapping for measurement with GC (DN15 with 15x21 inox valve)	existing tapping for measurement with GC (DN15 with 15x21 inox valve)	1 measuring tap for GC to add (DN15 with 15x21 inox valve)	1 measuring tap for GC to add (DN15 with 15x21 inox valve)
Available space		~ 1m above the economizer outlet	Close to internal wall (volume ~ 0,5m each side)	VMB	VMB	VMB	VMB	VMB	VMB	VMB	VMB	VMB
Accessibility		height ~ 2,5 m (Above boiler)	Height ~ 3.5m (possible with	VMB	30 cm from ground	VMB	VMB	VMB	VMB	VMB	VMB	VMB
Support		existing support to use for probe	existing support to use for probe	VMB	VMB	VMB	VMB	VMB	VMB	VMB	VMB	VMB
Temperature (°C)		85 - 105	20 - 70	4	40	40	-25	0	15	15	15	15
Pressure into process (bar)		Patm +/- 10mbar	Patm +/- 10mbar	P_{atm} +/- 10mbar	Patm +/- 10mbar	20 barg	20 barg	20 barg	20 barg	20 barg	Patm +/- 10mbar	Patm +/- 10mbar
Flow measurement ranges expected	kg/h	0 - 5350	0 - 1000	0 - 1000	0 - 1000	0 - 1000	0 - 600	0 - 400	0 - 400	0 - 400	0 - 400	0 - 400
	Nm3/h	0 - 3500	0 - 600	0 - 600	0 - 600	0 - 600	0 - L00	0 - 200	0 - 200	0 - 200	0 - 200	0 - 200
Adaptated Flowmeter to identify				X							X	**X**
Compounds to analyze						Expected raw compositions in % by mass and target measurement ranges in relation to mass flow rates						
H2O	**Expected rate**	11,5% — 42,9%	1,8 - 13%	< Point 2	< Point 2	< Point 2	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	Range considered	0% - 100%	0 - 20%	0 - 20%	0 - 20%	0 - 20%	-	-	-	-	-	-
CO2	**Expected measurement rate**	54,7% — 85,8%	84,1% — 95,2%	> Point 2	> Point 2	> Point 2	99,9% environ	71,8% — 91,9%	81,3% — 95,5%	46,5% — 91,9%	81,3% — 95,5%	46,5% — 91,9%
	Range considered	0% - 100%	0% - 100%	0% - 100%	0% - 100%	0% - 100%	0% - 100%	0% - 100%	0% - 100%	0% - 100%	0% - 100%	0% - 100%
N2	**Expected rate**	0,7% - 7,8%	0,9% — 8,6%	similar than point 2	similar than point 2	similar than point 2	qq ppm	4% — 15,6%	1,8% — 9,2%	0,8% - 43,2%	1,8% - 9,2%	0,8% — 43,2%
	Range considered	0% - 10%	0% - 10%	0% - 10%	0% - 10%	0%- 10%	< 0,1%	0 - 20%	0% - 20%	0% - 50%	0% - 20%	0% - 50%
O2	**Expected rate**	1,2% — 1,8%	1,3% — 2,7%	similar than point 2	similar than point 2	similar than point 2	qq ppm	2,5% — 12,9%	1,7% — 12,9%	1,5% — 26,9%	1,7% — 12,9%	1,5% — 26,9%
	Range considered	0% - 10%	0% - 10%	0% - 10%	0% - 10%	0% - 10%	< 0,1%	0% - 20%	0% - 20%	0% - 30%	0% - 20%	0% - 30%
NOx compounds analysis : (NO, NO2 > NOx)	**Expected rate**	0,0013% - 0,0019%	0,0015% - 0,0031%	similar than point 2	similar than point 2	similar than point 2	qq ppm	0 ,0017% - 0,0834%	0 ,0017% - 0,0834%	0 ,0017% - 0,0834%	0 ,0017% - 0,0834%	0 ,0017% — 0,0834%
	Range considered	0 - 0,01%	0 - 0,01%	0 - 0,01%	0 - 0,01%	0 - 0,01%	<0,1%	0 - 0,1%	0 - 0,1%	0 - 0,1%	0 - 0,1%	0 - 0,1%
SOx analysis	**Expected rate**	To be defined		To be defined	-	To be defined	-	-	-	-		-
	Range considered	To be defined	-	To be defined	-	To be defined					-	-

260m sampling lines
30 measuring devices
5 hubs

Sampling lines: From process (tap) to the analysis systems

sampling rod + heated filter

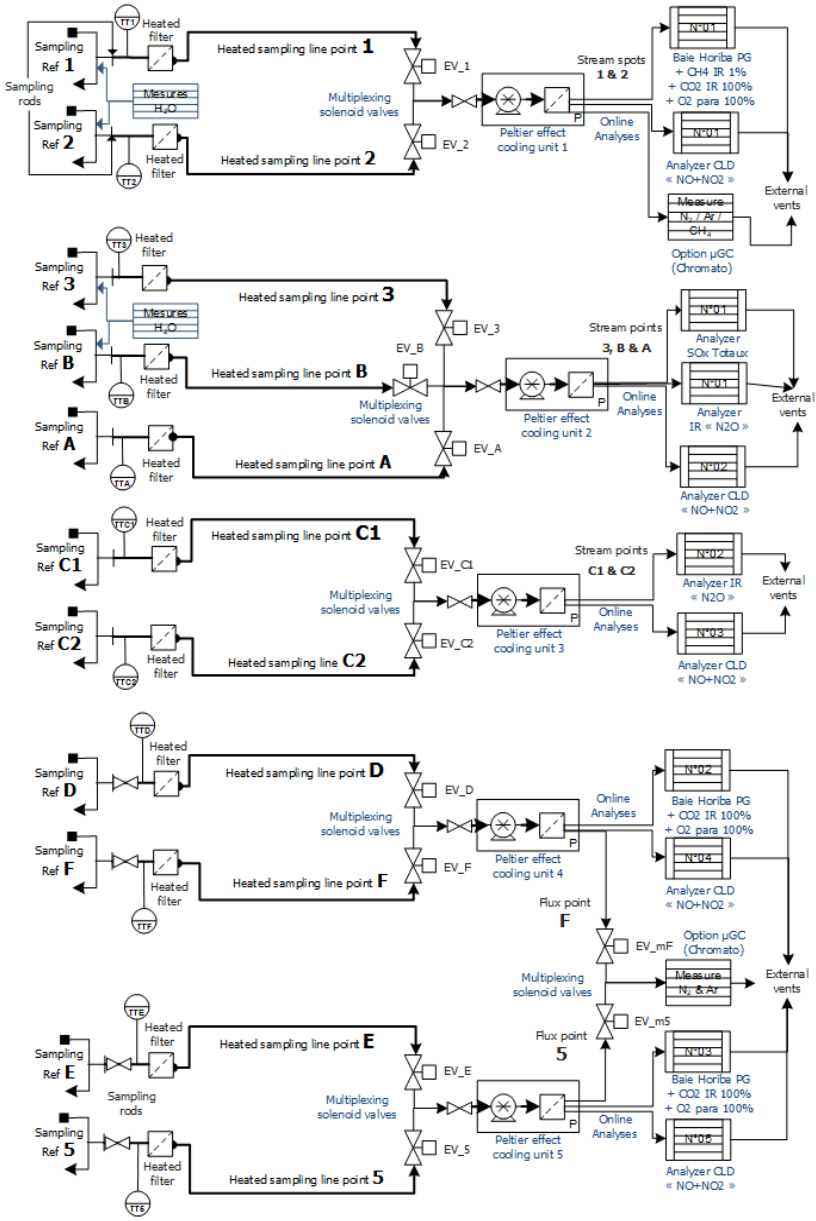
Regulated heated line

Moisture condensation system (cooling unit)

CH0C Project: Multiplexed analytical strategy for reference & detailed campaigns

Measurement systems deployed into the CH0C Project	Brand	Model	Measured Gases	Technologies	Quantity		Additional Equipment	Quantity
	Vaisala	HMS	H2O	Thin-film capacitive	4		Heated filter	4
	Horiba	PG250 (+2 PG350)	O2, CO, CO2, SOX, NOx eq NO	Paramagnetical NDIR, CLD	4		Heated sampling line	19
	EcoPhysics	CLD700	NO, NO2, NOx	Chemiluminescence CLD	6		Sampling Line total lenght	260 m
	Megatec	42i	NO, NO2, NOx	Chemiluminescence CLD	1		Sampling Rod	6
	M&C	GEN-TWO	CO2 (100%)	NDIR	2		Peltier Cooling unit	5
	Siemens	Ultramat 22	CO2 (100%)	NDIR	3		T°K (sensor)	11
	Siemens	Ultramat 22	CH4	NDIR	1		Electrovalves	13
	Servomex	Model 572	O2 (100%)	Paramagnetical	4		Industrial PC	2
	Inficon	Fusion	N2, Ar, CO2	-Gas Chromatograph	1		Webserver	1
	Megatec	42C	N2O	IR Correlation	2		Data acquisition module	2
	Multiplexing carried out on 5 groups: points (1 & 2) ; points (3, A & B) ; points (C1 & C2) ; points (D & F) ; points (5 & E)							

Sampling and analysis strategies for the CH0C Boiler project : Detailed campaigns (V25/03/25)



126 condensate samplings

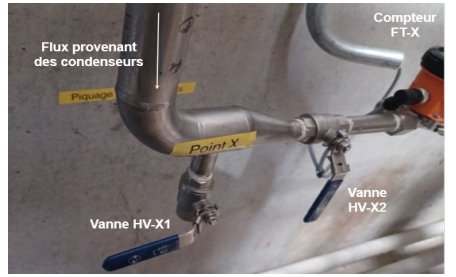
1. Referenced sampling point **X**: 1 measurement created on the condenser collection line, downstream the boiler.
2. Referenced sampling point **Y**: 1 measurement implemented downstream of the VMB activated carbon bed.

Condensates analyses strategy

CH0C Project	Media : Natural Gas																BG
	Essais MSI			Parametrical tests											Essais LD		Essais MSI
	Aéro	Oxy + Liq	Qualif/réception	FA1	FA2	Ox1	GN2	VAP1	VAP2	VAP3	FGR1	Rec1	Liq1	Liq2	Charge fixe	Charge variable	Qualif/réception
M1-A	0																
M1-B		0															
M2-A		0															
M2-B			4x + 4y														
M3-A				3x + 3y	0												
M3-B						3x + 3y	0										
M4-A								2x+2y	1x+1y	1x+1y	0						
M4-B												3x + 3y	0	0			
M5-A															0	0	
M5-B															0	0	
M6-A															0	0	
M6-B															0	0	
M7-A																	4x + 4y
M7-B																	
M8-A																	
M8-B																	

Analyse 1	pH, hardness, conductivity, NO^{2-}, NO^{3-}, NO^{3-N}, NO^{2-N}, HNO_2, HNO_3, CO_3^{2-}, Total Organic Carbon (COT), metals (Cr^{3+}, Ni^{2+}, Al^{3+}, Fe^{3+}), dissolved gases (CO_2, O_2), MES & SO_3^{2-}, SO_4^{2-}, H_2SO_4, only in case of SOx identified into the flue gas
Analyse 2	pH, NO^{2-}, NO^{3-}, NO^{3-N}, NO^{2-N}, HNO_2, HNO_3
Analyse 3	pH, NO^{2-}, NO^{3-}, NO^{3-N}, NO^{2-N}, HNO_2, HNO_3 : only in case of no ability to establish a model within the results from previous tests.

Analyses 1+2+3	
Total : ~ 42 samples	Flacons to be analyzed
Analyses 1 (16)	48
Analyses 2 (12)	36
Analyses 3 (14)	42
TOTAL (3)	126



To provide accurate physico-chemicals measurement, all the aqueous samplings standardly led in the CH0C process are integrating a complemental step by filling all the container dedicated for each species to determine (between 6 & 10 according to the analysis).
All analyses will be achieved by an external specialized laboratory.

Containers dedicated to a full analysis

Photos


PORTIQUE
OXYGÈNE
PORTIQUE
OXYGÈNE
PORTIQUE
CO2
PORTIQUE
AZOTE
AZOTE


VERDEMOBIL
BIOCO2
CRYO
COLLECT
ENGINEERING SOLUTIONS

TotalEnergies

The demo project is open for visit and collaborations. Results will be published

Key take away

-Setting-up a full **NOX measurement along the CCU chain**

- Testing a promising **ultra low NOX burner**

-Agile and Collaborative Team from various companies

Questions ?

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