Process Design and Comparison of Three Innovative Technologies for Biomethane Production and/or Purification and Upgrading from Biomass and Biological Wastes

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SINTEF Industry – Process Technology

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Outlines

1 **Introduction**

Role of biogas in the EU decarbonization strategy

2 **Processes overview**

Processes description and brief overview on modelling strategies

3 **Results**

Main KPIs and other comments

4 **Conclusions**

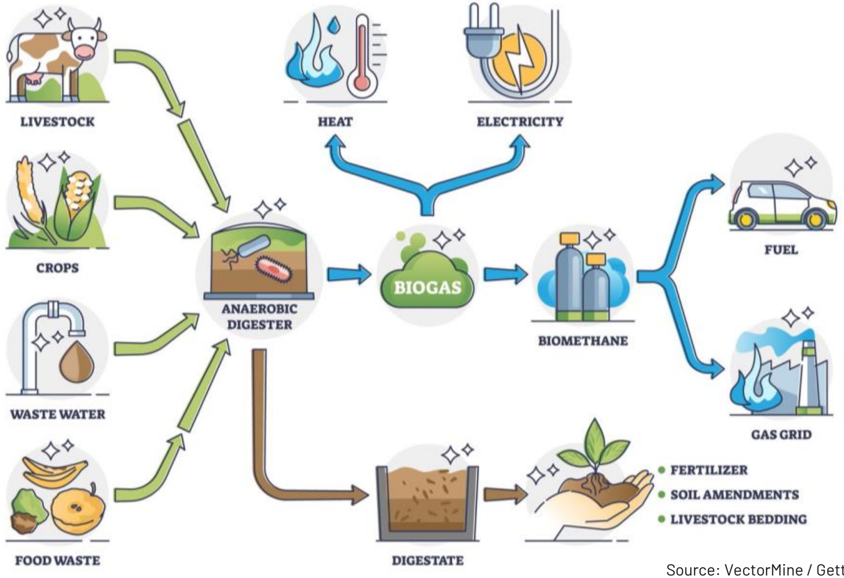
Achievements & future works

1.Introduction

Biogas production

- Mainly produced via **anaerobic digestion**
- **CH_4** content variable from **45 to 75 vol%**
- The remaining is **wet CO_2** with **traces of NH_3 and H_2S**
- **Upgrading** is necessary for applications of bio-CH_4 as **fuel** or **transport** (either gas o liquid)

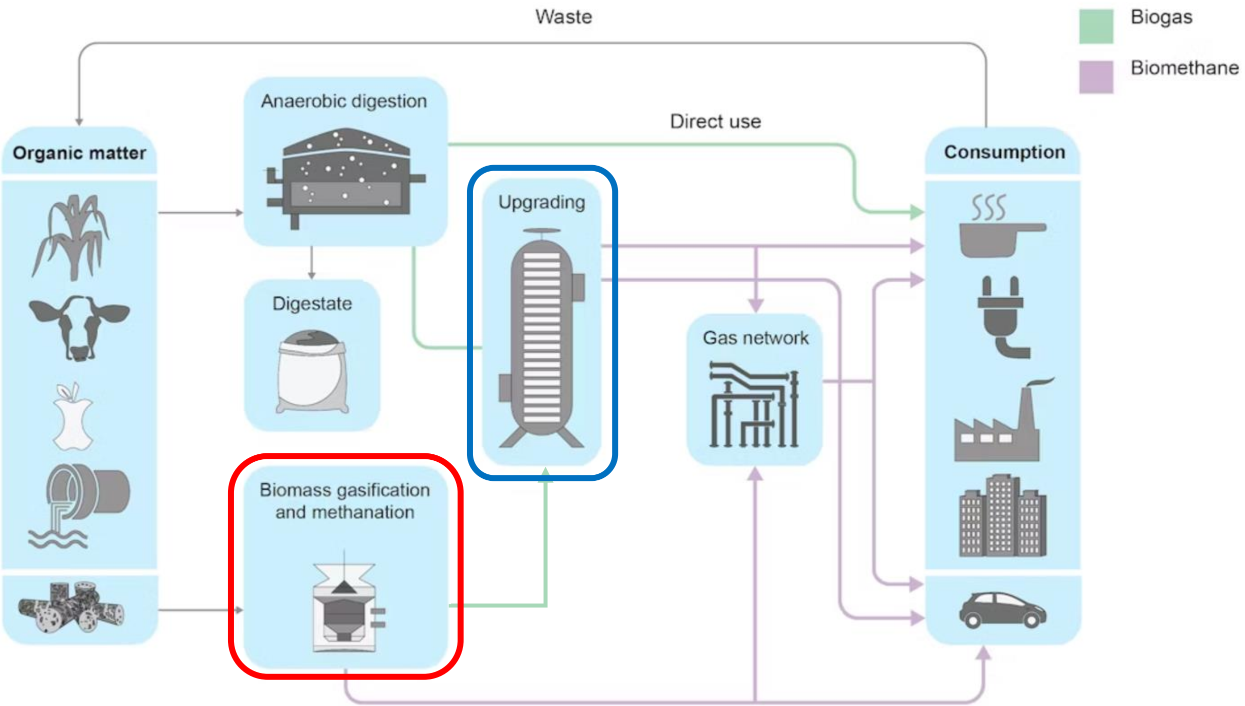
European Biogas Association - https://www.europeanbiogas.eu/
IEA - https://www.iea.org/reports/outlook-for-biogas-and-biomethane-prospects-for-organic-growth/an-introduction-to-biogas-and-biomethane



Source: VectorMine / Getty Images

Biogas production

- Upgrading is crucial to meet **specs for transport in the NG grid**
- Upgrading is also relevant for **liquefaction** and delivery (supply chain)



Source: IEA

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SEMPRE-BIO project

- SEMPRE-BIO aims at **demonstrating novel and cost-effective bio-CH_4 production solutions** to support the circular economy and **reduce dependence on fossil fuels**
- Biomethane production tested in **3 demo plants** across Europe accounting for **different feedstocks**

CETAQUA WATER TECHNOLOGY CENTRE
Biogas-E platform voor anaerobe vergisting
Naturgy
Cryo Inox
inveniam Opening up technology pathways
UNIVERSITEIT GENT
terrawatt
Aigües de Barcelona
Innolab Lab 4 Biomass
DBFZ
NV De Zwanebloem
Beta UVIC UNIVERSITAT DE VIC UNIVERSITAT CENTRAL DE CATALUNYA
TMB
ProPuls
DTU
SINTEF
BIOTHANE VEOLIA

SEMPRE-BIO

SEcuring doMestic PRoduction of cost-Effective BIOmethane

Total funding € 9 926 450

HORIZON-IA

7 AFFORDABLE AND CLEAN ENERGY
9 INDUSTRY, INNOVATION AND INFRASTRUCTURE
12 RESPONSIBLE CONSUMPTION AND PRODUCTION
13 CLIMATE ACTION

Case studies

Aigües de Barcelona, Barcelona, Spain

Terrawatt, Marmagne, France

Direct biomethanation of bio-gas/syngas

De zwanebloem, De Panne, Belgium

Biogas upgrade and bio-CH_4 Liquefaction

Source: SEMPRE-BIO webpage

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2.Processes

CSI

Aigües de Barcelona, Barcelona, Spain

Direct biomethanation of biogas

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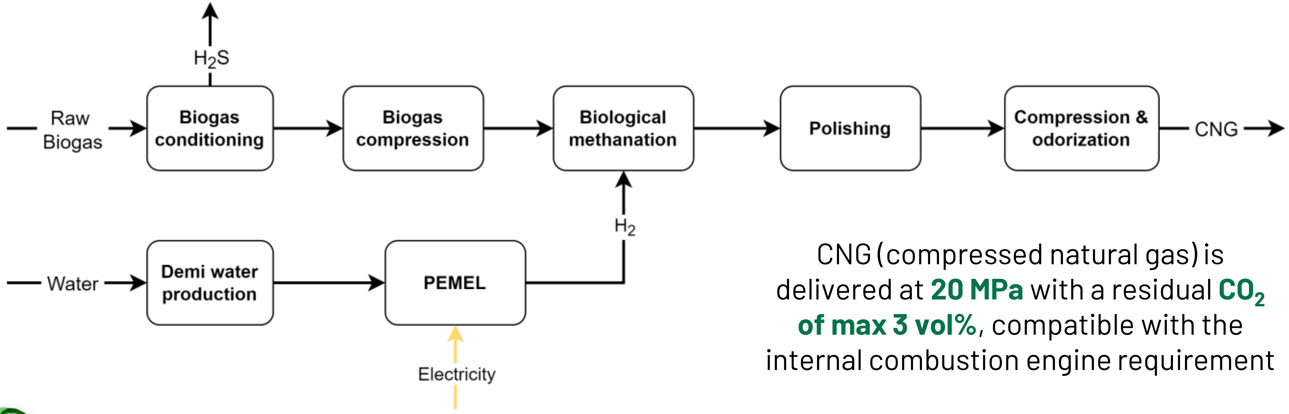
Block Flow Diagram CSI

- **Direct biomethanation of biogas** to bio-CH_4
- Application for transport engines burning bio-CH_4
- Simulation in **COFE V3.6**, license-free simulation software by AmsterChem



CNG (compressed natural gas) is delivered at **20 MPa** with a residual **CO_2 of max 3 vol%**, compatible with the internal combustion engine requirement

Technology provider: CETAQUA WATER TECHNOLOGY CENTRE

CS2

Terrawatt, Marmagne, France

Bio-syngas biomethanation

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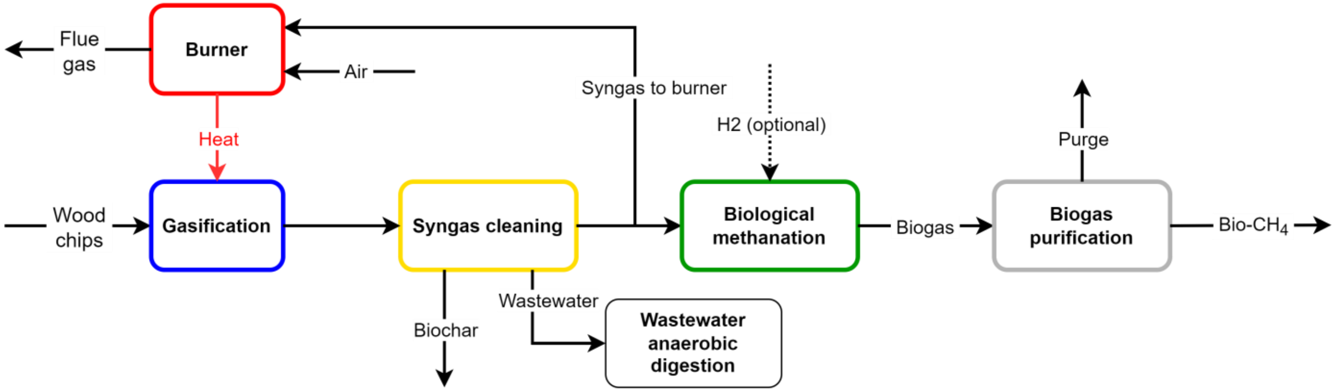
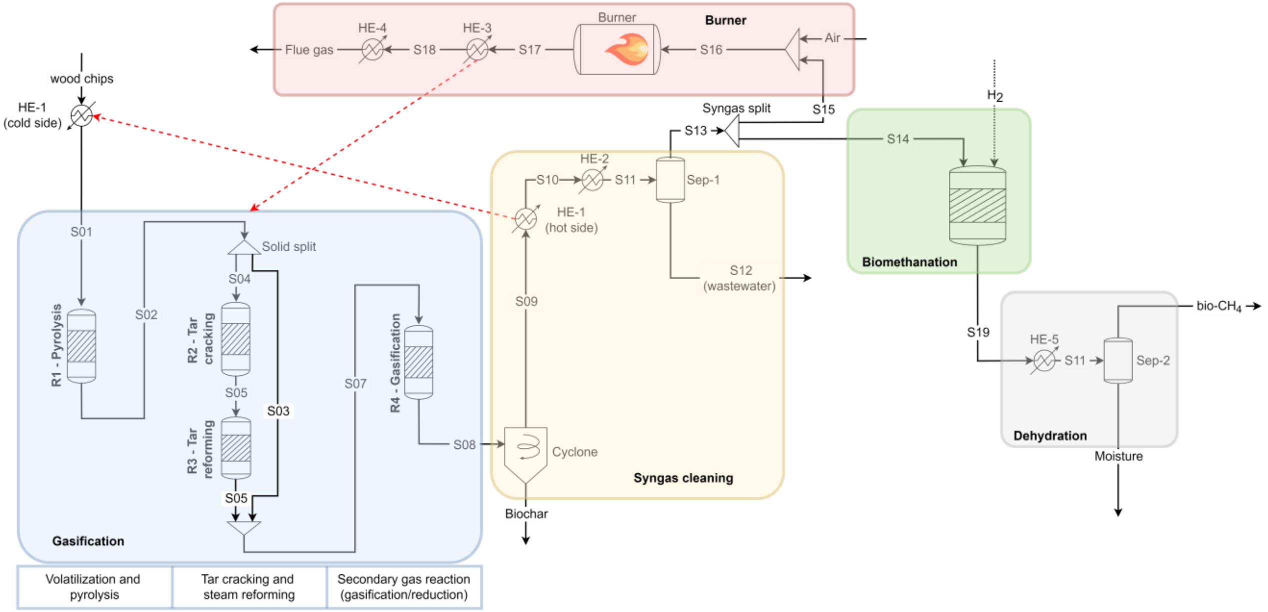
Block Flow Diagram CS2

- **Biomass gasification** followed by **biomethanation** of syngas
- Simulation in **COFE V3.6**, license-free simulation software by AmsterChem

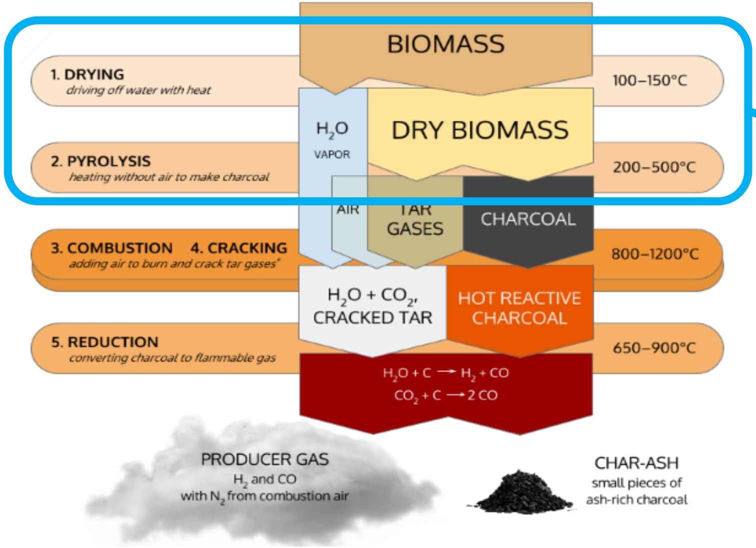


Technology provider: terrawatt

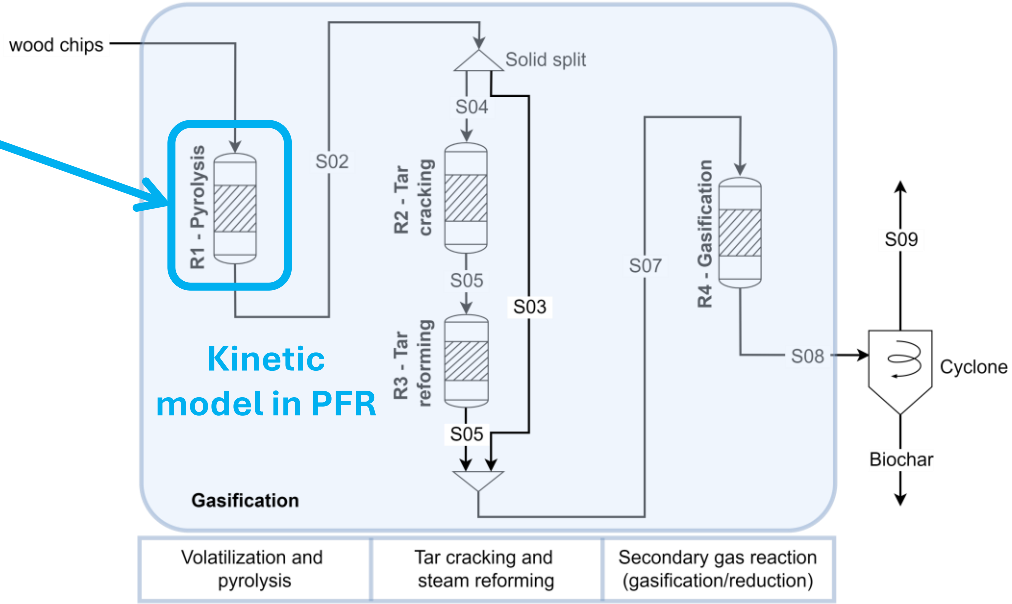
Process Flow Diagram



Biomass gasification



Ranzi et al, 2017. ACS Sustainable Chemistry & Engineering 5, 4, 2867–2881



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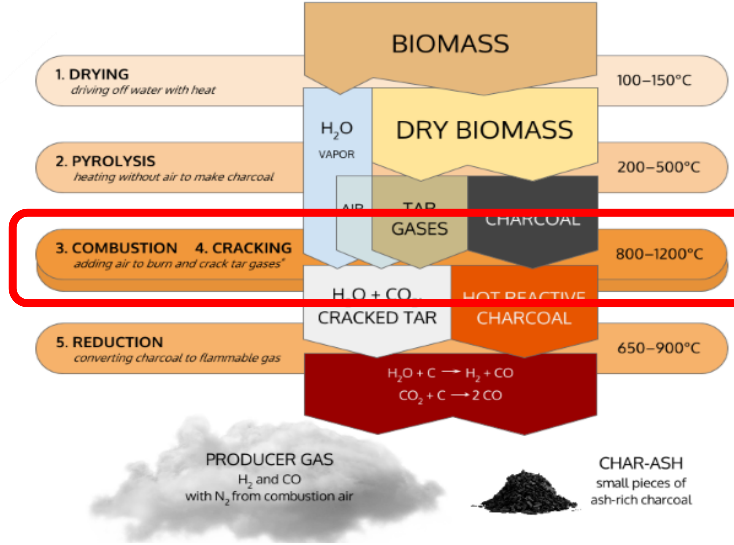
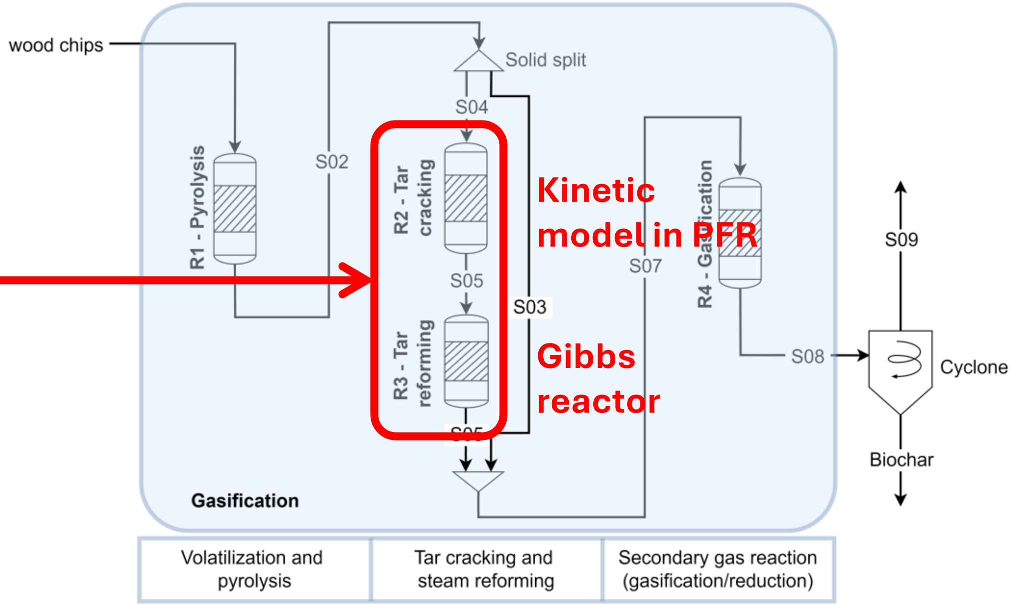
Biomass gasification





Chen et al., 2021. Chemical Engineering Journal, 417, 127923
Chaurasia, A., 2016. Energy, 116, 1, 1065-1076.

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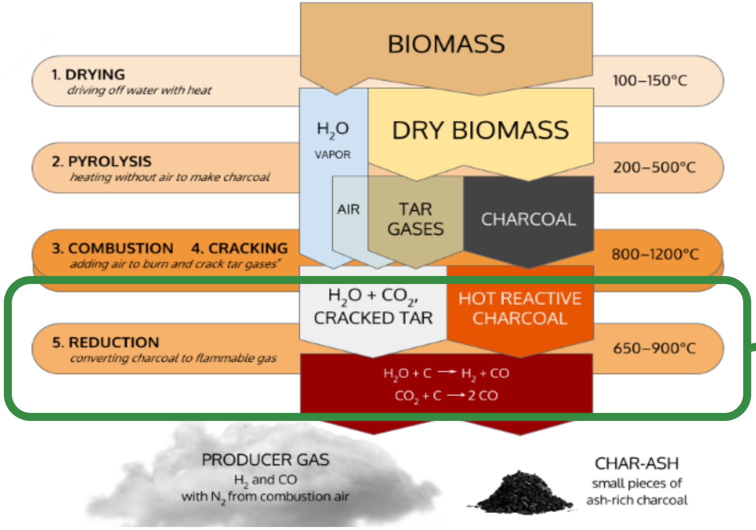
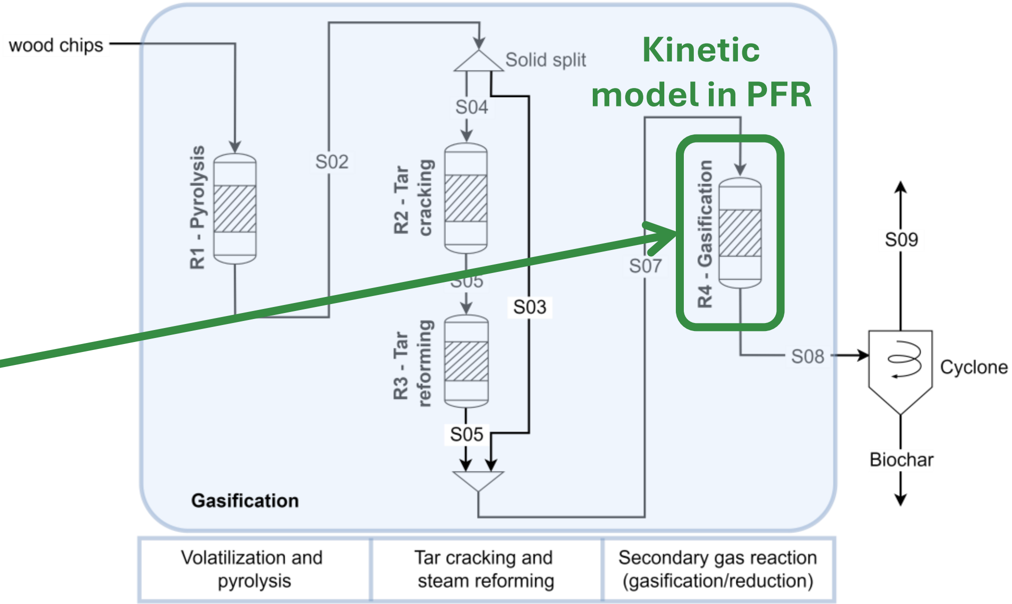
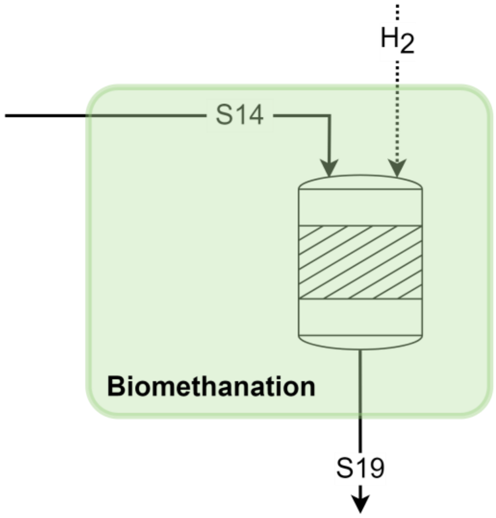
Biomass gasification





Chaurasia, A., 2016. Energy, 116, 1, 1065-1076.
Groeneveld, M.J., van Swaaij, W.P.M., 1980. Chemical Engineering Science, 35, 1-2, 307-313.
Gómez-Barea, A., Leckner, B., 2010. Progress in Energy and Combustion Science, 36, 4, 444-509.

Biomethanation



Li et al., 2020. Biosource Technology, 314, 123739

- Two **cases**: CS2A with extra H2 and CS2B without addition

- **Modelled as a data-driven black box** with conversion and yield for thermophilic bacteria retrieved from the literature

$$CO + 3\ H_2 \rightarrow CH_4 + H_2O$$
$$CO_4 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$$
$$4\ CO + 2\ H_2O \rightarrow CH_3COOH + 2\ CO_2$$

- **Reaction extent (stoichiometric reactor)** is tuned to meet the
  1. observed complete depletion of CO
  2. bio-CH_4 yield and purity
  3. acetic acid production

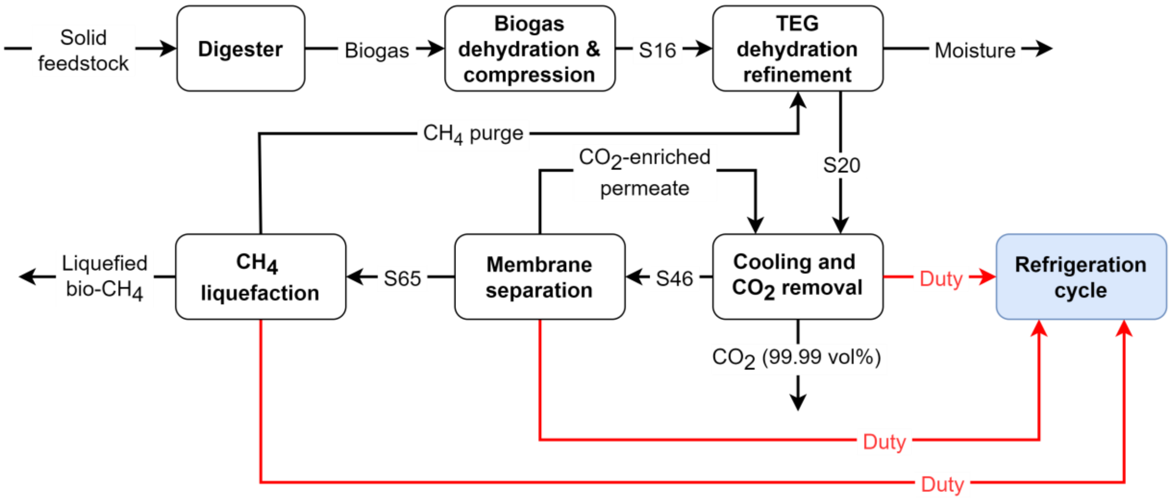
CS3

De zwanebloem, De Panne, Belgium

Biogas upgrade and bio-CH_4 Liquefaction

Block Flow Diagram CS3

- **Upgrading** and **liquefaction** of bio-CH_4
- Application for transport of bio-CH_4 delivery in the absence of surrounding infrastructure (e.g., farms and remote biogas sites)
- Simulation in **COFE V3.6**, license-free simulation software by AmsterChem



Technology provider: Cryo Inox

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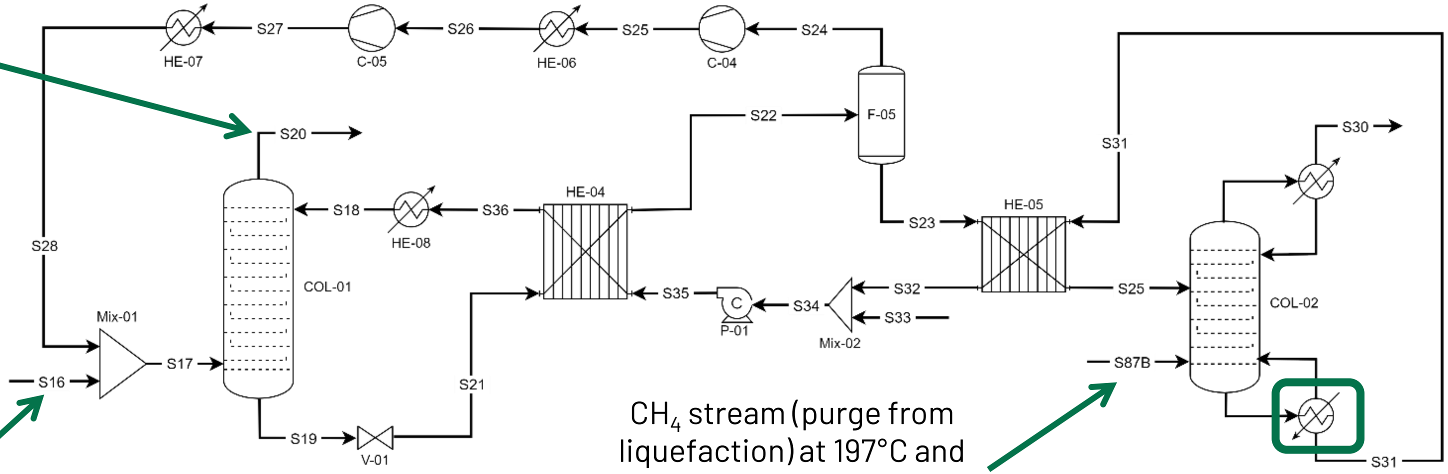
TEG dehydration

Residue moisture in biogas **< 3 ppmv**

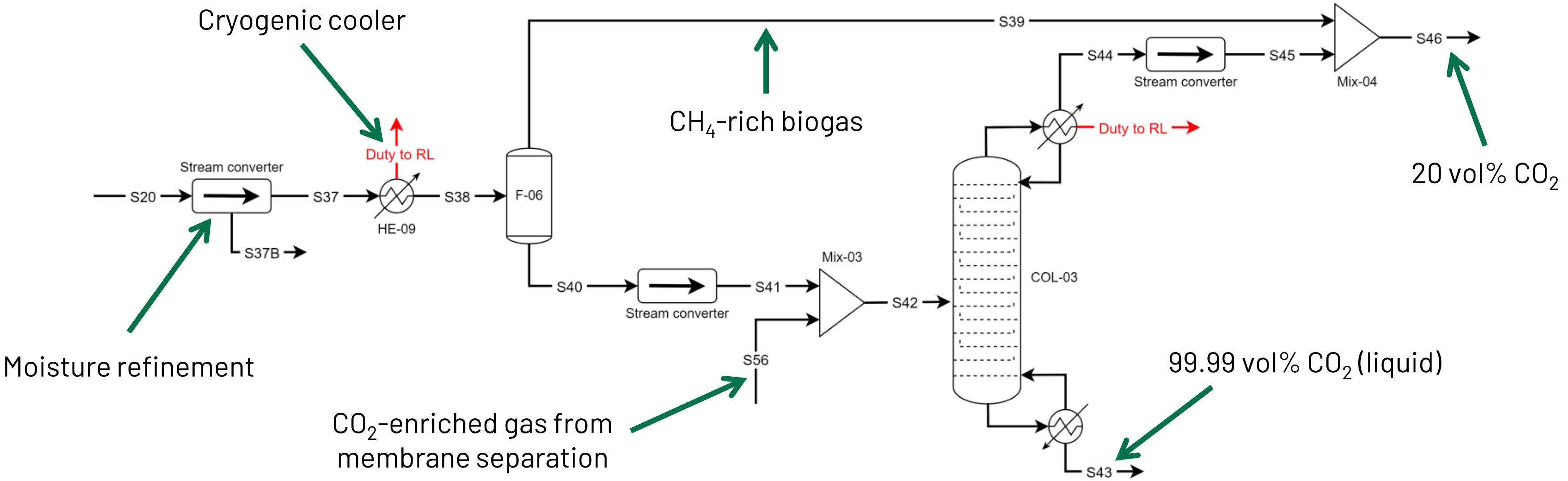


Compressed and purified biogas

CH_4 stream (purge from liquefaction) at 197°C and 5 bar as **stripping gas to lower the duty**

T < 210°C to prevent TEG degradation

CO_2 removal



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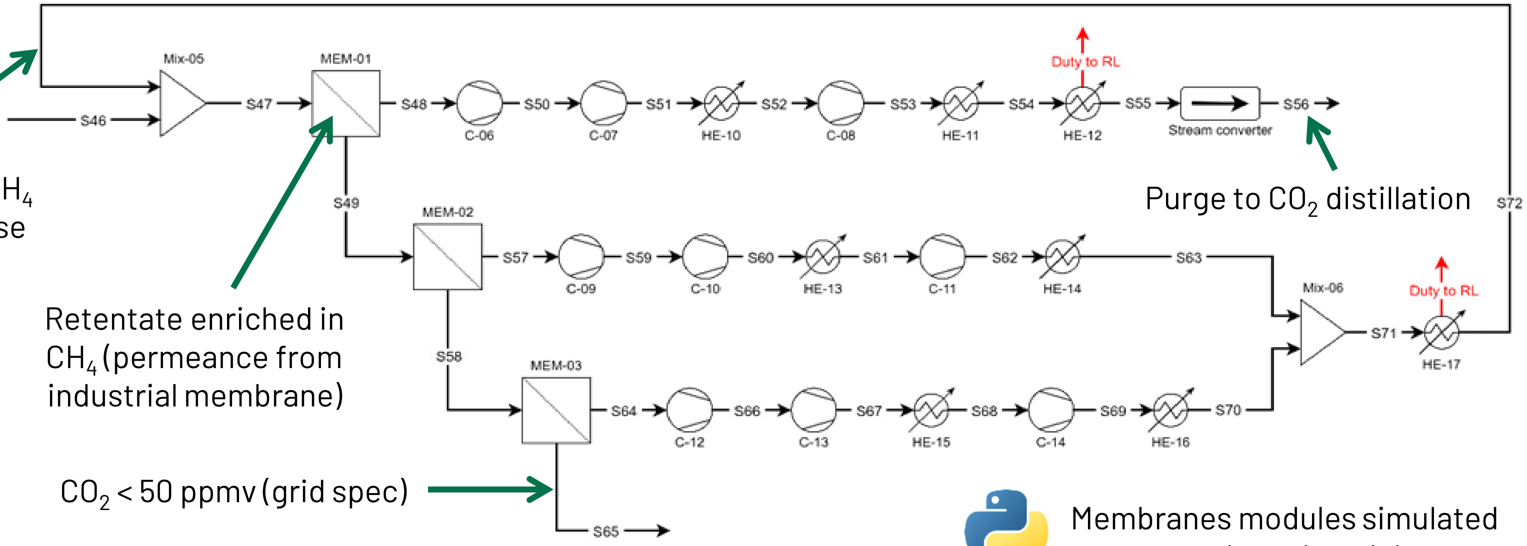
CO_2 refinement



Recycle: reduce CH_4 purity, but increase recovery

Retentate enriched in CH_4 (permeance from industrial membrane)

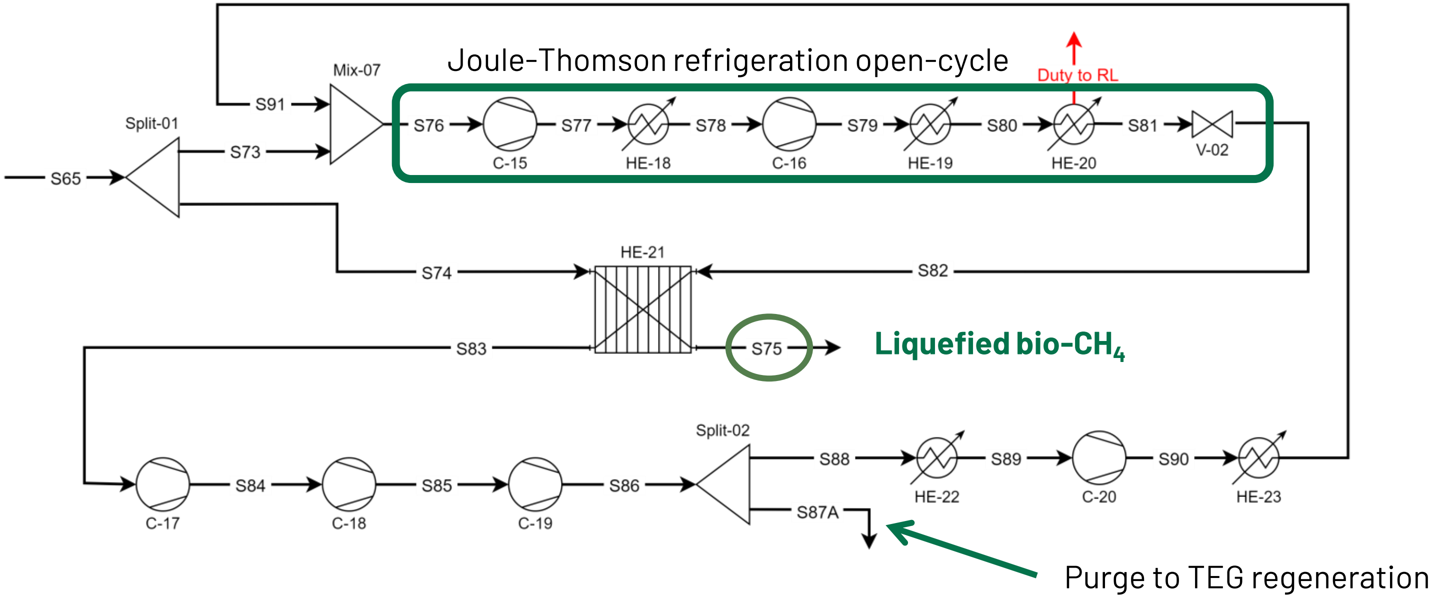
CO_2 < 50 ppmv (grid spec)

Purge to CO_2 distillation

Membranes modules simulated as custom-based modules

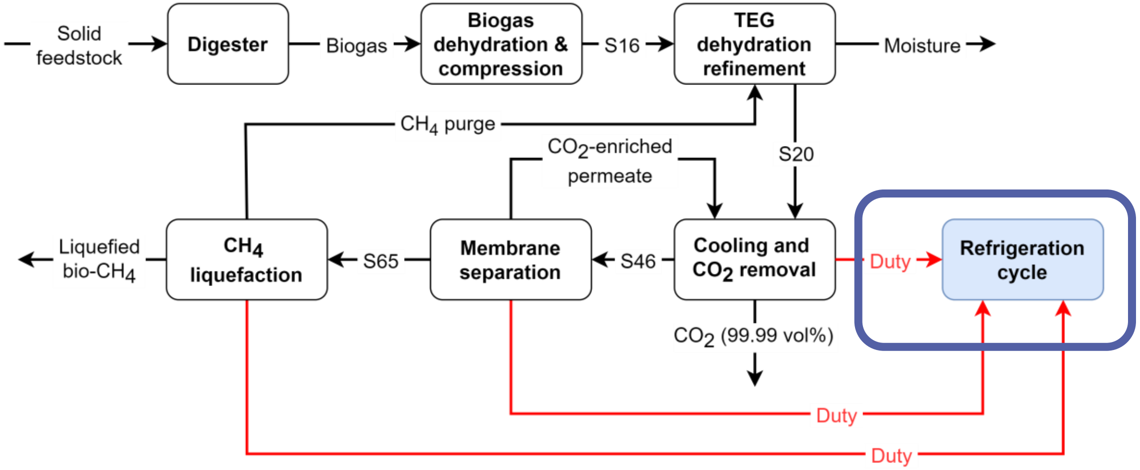
Nobandegani et al., Chemical Engineering Journal, 446, 4, 137223

CH_4 liquefaction



Cold box

- Cold box temperature is kept through an **external refrigeration loop** based on a **Joule-Thompson cycle**
- Working fluid is a mixture of C_2:C_3 hydrocarbon at 92:8 on a mass basis
- Pressure drop across the lamination valve is 45 bar



3.1 Results

Processes KPIs

	CS1 (ES)	CS2A (FR)	CS2B (FR)	CS3 (BE)
Solid feedstock	Wastewater sludge	Lignocellulosic biomass		Manure
Bio-CH_4 productivity ($kg_{bio-CH4}/ton_{dry\ feedstock}$)	9.20	220	107	12.1
Bio-CH_4 purity (vol%)	97.2	96.5	50.7	99.99+
Impurities (vol%)	N_2 – O_2 (1.5 – 0.4%) H_2 (0.4%) CO_2 (0.4%)	CO_2 (3.2%) CO (30 ppm_v) C_{2+} (0.2%)	CO_2 (35.8%) CO (13.5%)	CO_2 (42 ppm_v)

Processes KPIs

	CS1 (ES)	CS2A (FR)	CS2B (FR)	CS3 (BE)
Cool water demand ($kg/kg_{bio\text{-}CH4\ delivered}$)	Wastewater sludge	Lignocellulosic biomass		Manure
Steam ($kg/kg_{bio\text{-}CH4\ delivered}$)	-	Gasification consumes moisture vaporised from biomass		0.76
Electricity ($kWh/kg_{bio\text{-}CH4\ delivered}$)	10.8	12.7	Negligible	3.10
H_2 demand* ($kg/kg_{bio\text{-}CH4\ delivered}$)	0.18	0.24	NA	NA

* H_2 from a PEM electrolyser, consuming on average 53 kWh/kg_{H2}

3.2 Bio-CH_4 upgrading

What are the advantages of CS3 compared to the conventional carbon capture option?

Input data

- Manure is the solid feedstock
- Produced biogas is a sensitive info
- Biogas composition (used for the simulation)

CH_4	57.5 vol%
CO_2	39.5 vol%
Moisture	~ 3.0 vol%
H_2S/NH_3	~ 200 ppmv

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Utilities

Electricity
Compressors
Pumps
Refrigeration loop
Air cooler

Cooling water
Heat exchanger
(interstage cooling)
Top condenser chiller
Reboiler of CO_2 distillation

Heat (steam)
TEG regeneration

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Results CS3 (KPIs)

Key Performance Indicator	Value	Note
CH_4 recovery (before liquefaction)	96.0%	Basis: mass flow bio-CH_4 in biogas from anaerobic digester Purity 99.99+ vol%
CH_4 liquefied	91.2%	After liquefaction cycle
CO_2 recovery	80.6%	Basis: bio-CO_2 in biogas from anaerobic digestor As liquid at 99.99 vol% purity

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CS3 KPIs

Key Performance Indicator	Value	Note
Electricity demand	3.10 $kWh_{el}/kg_{CH4\ liq}$ 1.19 kWh_{el}/Nm^3_{biogas}	Normal condition: 1 bar and 0°C Include refrigeration, compressions and others
Heat demand	0.38 $kWh_{th}/kg_{CH4\ liq}$ 0.15 kWh_{th}/Nm^3_{biogas}	Mainly steam
Steam demand	0.76 $kg/kg_{CH4\ liq}$ 0.29 kg/Nm^3_{biogas}	Saturated steam at 225°C (25 bar)
Cooling water demand	196.2 $kg/kg_{CH4\ liq}$ 75.6 kg/Nm^3_{biogas}	Assuming CW at 20°C and max discharge temperature 30°C

Comparison

KPI	Study work (no liquefaction)	MDEA 50 wt%	Optimised MDEA
CH_4 purity	99.99+ vol%	98 vol%	98 vol%
CO_2 purity	99.99 vol%	Off specs	Off specs
Pressure (bar)	Sensitive	2	2
Impurities in CH_4 and CO_2	Negligible	Moisture Amine (above limit 10 mg/Nm^3)	Moisture Amine (above limit 10 mg/Nm^3)
Electricity demand	0.80 kWh_{el}/Nm^3_{biogas}	0.10 kWh_{el}/Nm^3_{biogas}	0.10 kWh_{el}/Nm^3_{biogas}
Heat demand	0.15 kWh_{th}/Nm^3_{biogas}	0.30 kWh_{th}/Nm^3_{biogas}	0.26 kWh_{th}/Nm^3_{biogas}

MDEA 50 wt%: Pellegrini et al., Chemical Engineering Transaction, 43, 409-414 Optimised MDEA: Capra et al., Energy Procedia, 148, 970-977

Comments

- Cryogenic process delivers far purer CH_4 and CO_2 without moisture and potential corrosive amines
- Amine scrubbing studies limit their analysis to CO_2 and acid gas removal, but **further purification is disregarded**
- **Energy demand exponentially increases** as purity specs becomes strict and imposes limitations on which pollutants (and how much is tolerated)

KPI	Study work	MDEA 50 wt%	Optimised MDEA
CH_4 purity	99.99+ vol%	98 vol%	98 vol%
CO_2 purity	99.99 vol%	Off specs	Off specs
Impurities in CH_4 and CO_2	Negligible	Moisture Volatile amine	Moisture Volatile amine
Electricity demand (kWh_{el}/Nm^3_{biogas})	0.80	0.10	0.10
Heat demand (kWh_{th}/Nm^3_{biogas})	0.15	0.30	0.26

Comments

Amine scrubbing studies limit their analysis to CO_2 and acid gas removal, but further **post-processing is disregarded**

- Compression of bio-CH_4
- Amine and moisture removal
- CO_2 purification and compression

KPI	Study work	MDEA 50 wt%	Optimised MDEA
CH_4 purity	99.99+ vol%	98 vol%	98 vol%
CO_2 purity	99.99 vol%	Off specs	Off specs
Impurities in CH_4 and CO_2	Negligible	Moisture Volatile amine	Moisture Volatile amine
Electricity demand (kWh_{el}/Nm^3_{biogas})	0.80	0.10	0.10
Heat demand (kWh_{th}/Nm^3_{biogas})	0.15	0.30	0.26

To wrap up CS3

- Biogas upgrading is a necessary step to **meet specs for biomethane transport** as liquid or in the natural gas grid
- Liquefaction (**cryogenic process**) is an alternative to **valorise biogas whenever the direct injection into the NG grid is not possible**
- Cryogenic purification has significant electricity consumption; however, delivers **both pure CO_2 and CH_4** (and pressurized)

4.Conclusions

To wrap up

- SEMPRE-BIO identified **three innovative routes** to deliver biomethane starting from solid feedstocks

- The technologies deliver bio-CH_4 at **different purities** according to **different downstream uses and needs**

- The technologies found applications in **different locations and sectors**

- Technologies show good KPIs, and **validation is still ongoing**

Next steps

- **Upscale the technologies (CS1 and CS2)** to a significant scale, i.e., realistic for large-scale applications. CS3 is constrained to the digestor capacity and feedstock availability – **FINALISING!**
- For CS2, identify in silico the **best operation point** to reduce residue tar/C_{2+} and avoid expensive bio-syngas purification
- **Optimise** the processes based on end-user requests and/or needs to deliver bio-CH_4
- Proposing **effective strategies for bio-CH_4 upgrading** downstream to biomethanation for more stringent specs
- Results of the **upscaled plants** will be used for **TEA** and **LCA** (not in charge of SINTEF)

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Thank you for your kind attention!

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