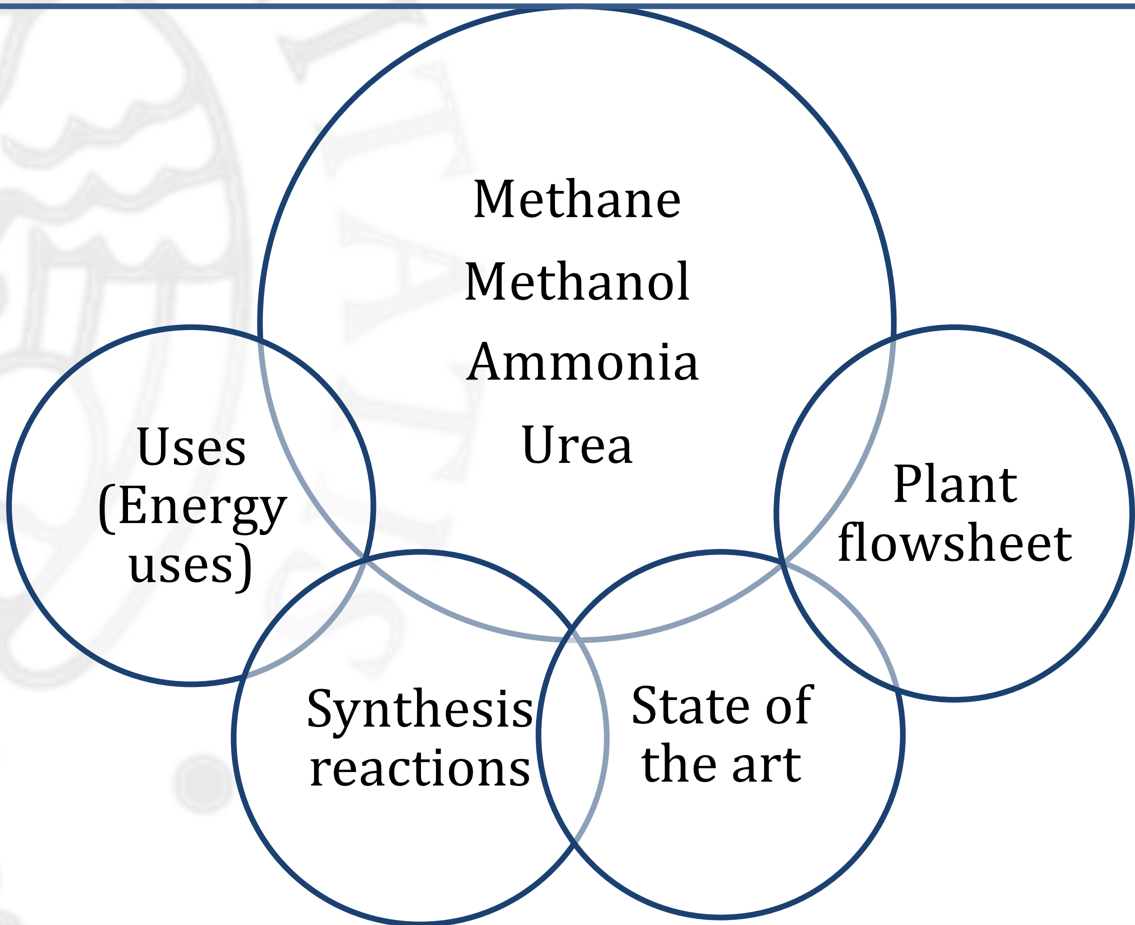
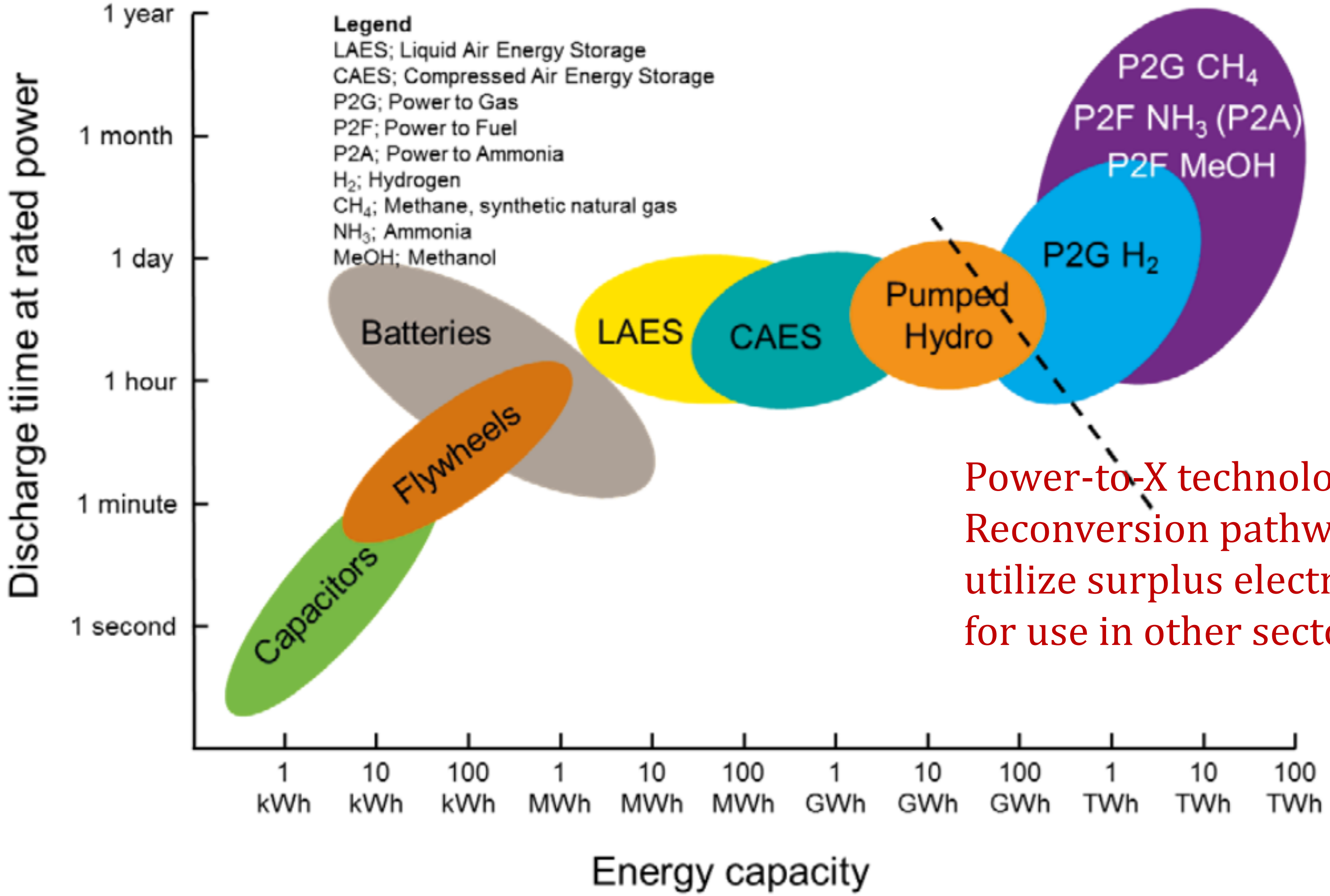
Power - to - Fuel Technologies

Outline

- ➢ Energy storage technologies
- ➢ Hydrogen
- ➢ Power-to-fuel technologies - overview



Energy storage technologies



Power-to-X technologies: Reconversion pathways that utilize surplus electric power for use in other sectors

Hydrogen

- For the last decades, hydrogen has been identified as a **feasible and sustainable energy vector.**

- The challenges that hydrogen has yet to overcome is its **low energy density** at environmental conditions and the construction of a **widespread distribution network.**

Molar Mass	T_{crit}	P_{crit}	Density (15°C, 1 bar)	LHV	Energy density	H_2 content (wt%)
g/mol	°C	bar	kg/m^3	MJ/kg	GJ/m^3	
2.016	-240	12.98	0.085	120.0	14.1	17.6

Hydrogen – Current industrial production

- Although hydrogen is the most common element in the Universe, free molecular hydrogen is extremely hard to find. It is extracted from other elements with energy intensive processes:
  - **Steam reforming** or partial oxidation of light or heavy hydrocarbons
  - Solid fuels **gasification or pyrolysis**
  - **Water electrolysis**

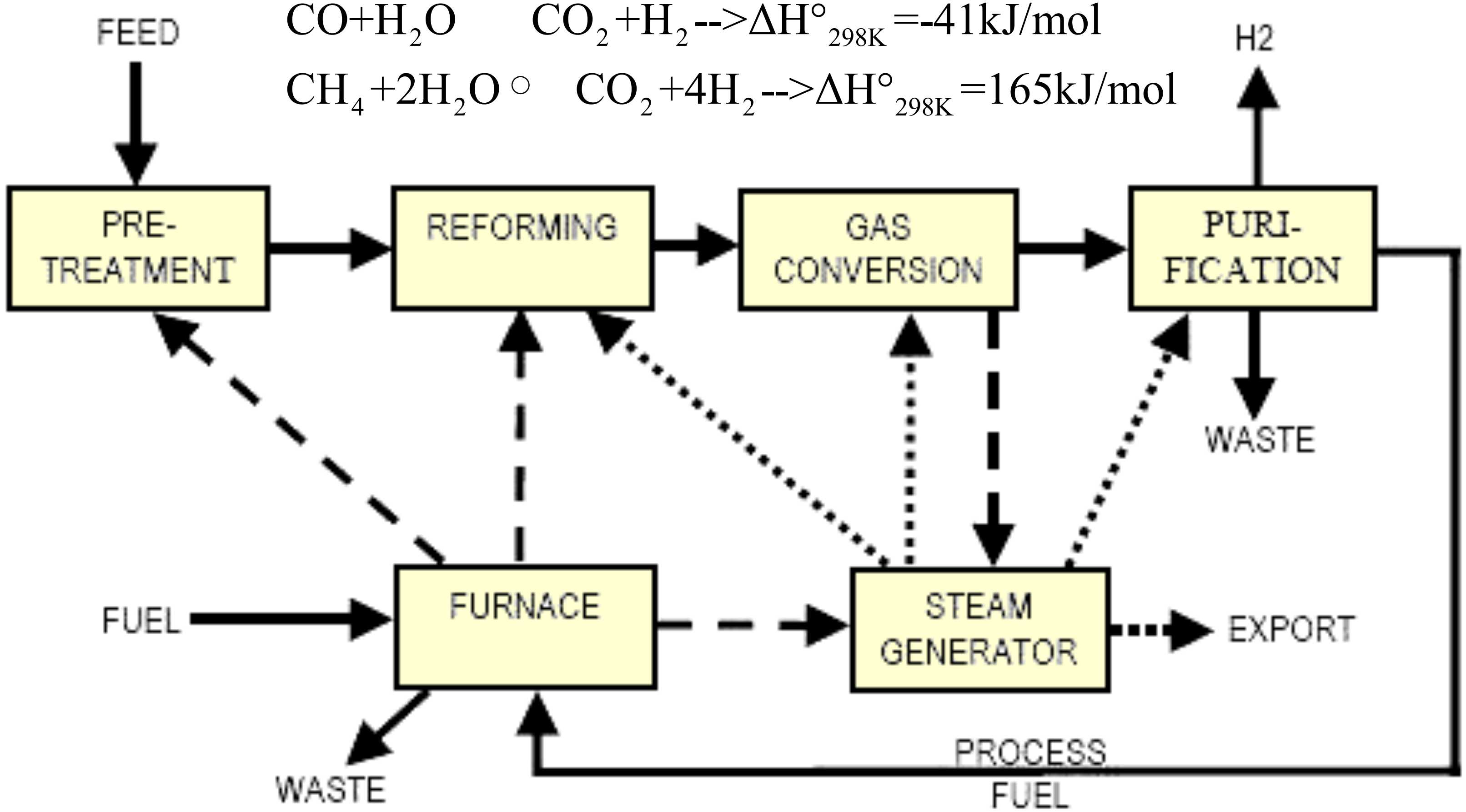
- Current world hydrogen production amounts to 600 billion Nm^3 per year, 95% from fossil sources:
  - 50% from natural gas steam reforming
  - 30% from heavy hydrocarbon cracking
  - 15% from coal gasification

Hydrogen – Production from steam reforming

$CH_4 + H_2O \quad CO + 3H_2 \text{-->} \Delta H^\circ_{298K} = -206 kJ/mol$

$CO + H_2O \quad CO_2 + H_2 \text{-->} \Delta H^\circ_{298K} = -41 kJ/mol$

$CH_4 + 2H_2O \circ \quad CO_2 + 4H_2 \text{-->} \Delta H^\circ_{298K} = 165 kJ/mol$



http://large.stanford.edu/courses/2010/ph240/chen1/

Hydrogen transport in NG grid

The following aspects have been extensively investigated:

- Safety
- Pipeline materials durability

NaturalHY reported the following results:

- Fatigue tests on steel pipelines show no criticality up to 50% H_2-CH_4 mixtures
- Permeability tests on polymeric materials up to 20% H_2 reported gas losses comparable with pure nat.gas
- Fault detection and prevention are equally effective, cracks propagate faster
- Safety tests have no significant differences up to 20% $_{H2}$

Physical aspect	**Impact on risk (H2-n.g.)**
Energy content /m^3	-
Ignition energy	+
Combustible gas/air ratios	+
Combustion velocity	+
Radiation of flames	-
Small leaks	+
Density and diffusivity	-
Total	?

PROBLEMS FOR INDUSTRIAL END-USERS

Power-to-Fuel Technologies

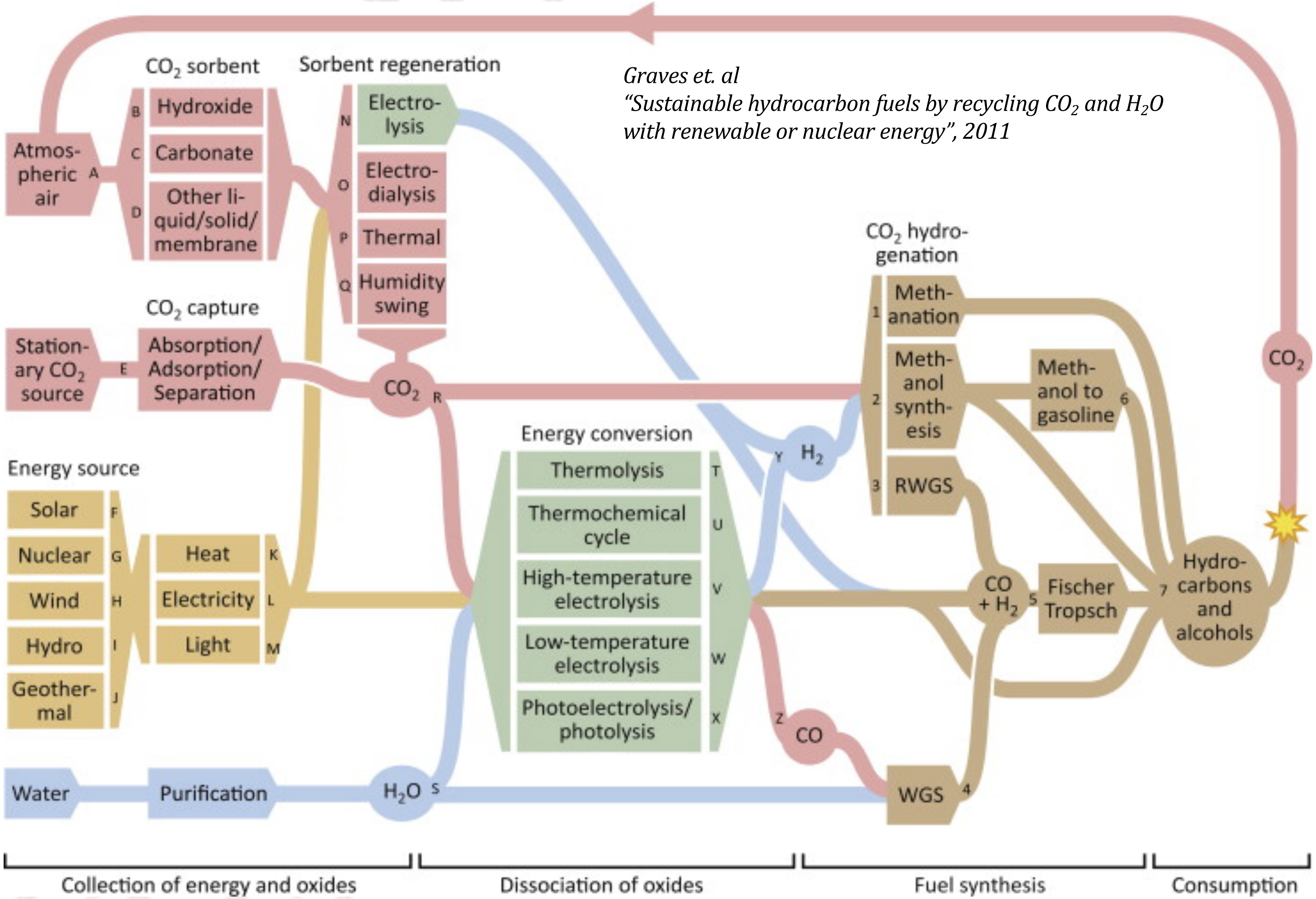
Criticalities and challenges

- Long and energy consuming production chain → relatively low energy efficiency
- Difficulty in producing pure CO_2
- High costs if compared to more mature technologies (batteries)

Advantages

- Long-medium term storage
- High power density (liquid fuels)
- Possibility of maintaining the same infrastructure and know-how
- Carbon neutral fuels (some of them)
- Sectors interconnection

So many different pathways …



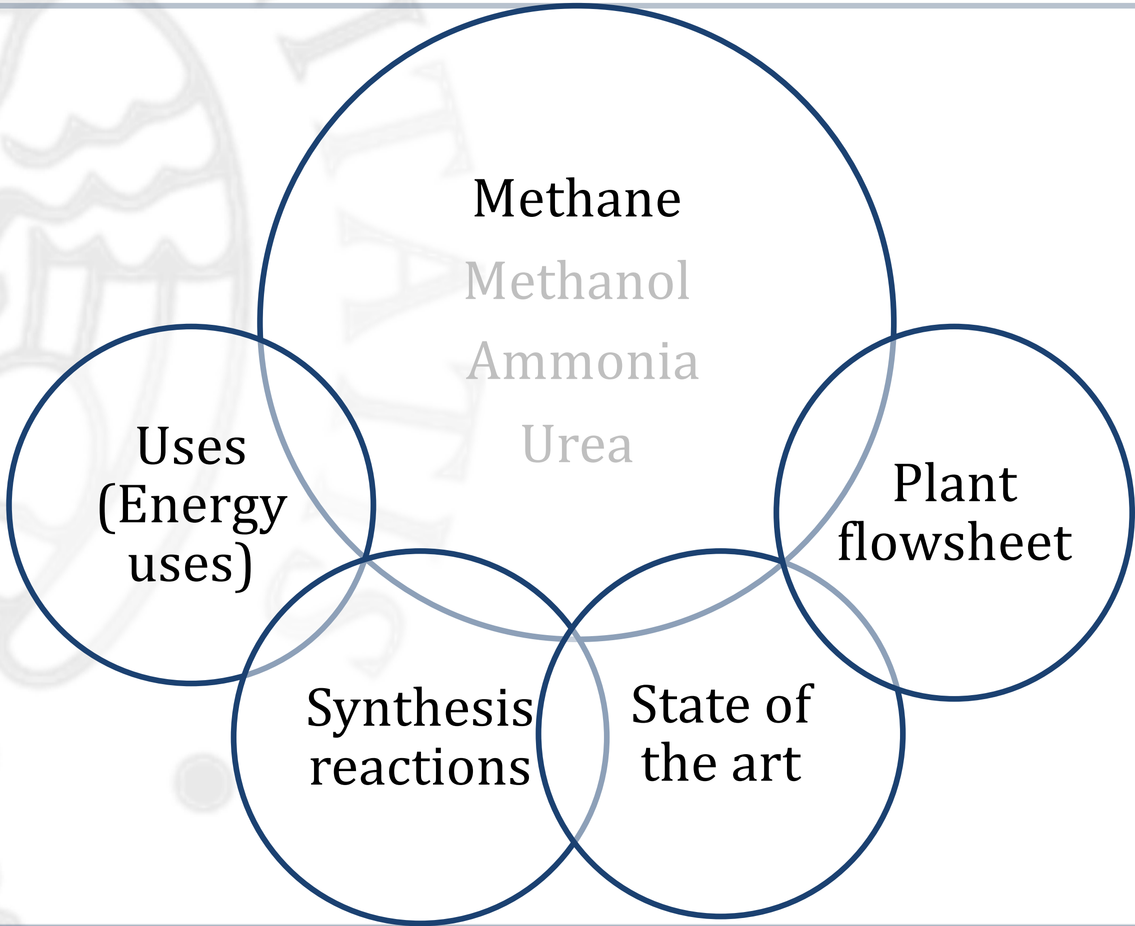
Graves et. al
"Sustainable hydrocarbon fuels by recycling CO_2 and H_2O with renewable or nuclear energy", 2011

- High residual peaks of production due to fluctuating RES
- CO_2 reduction policies

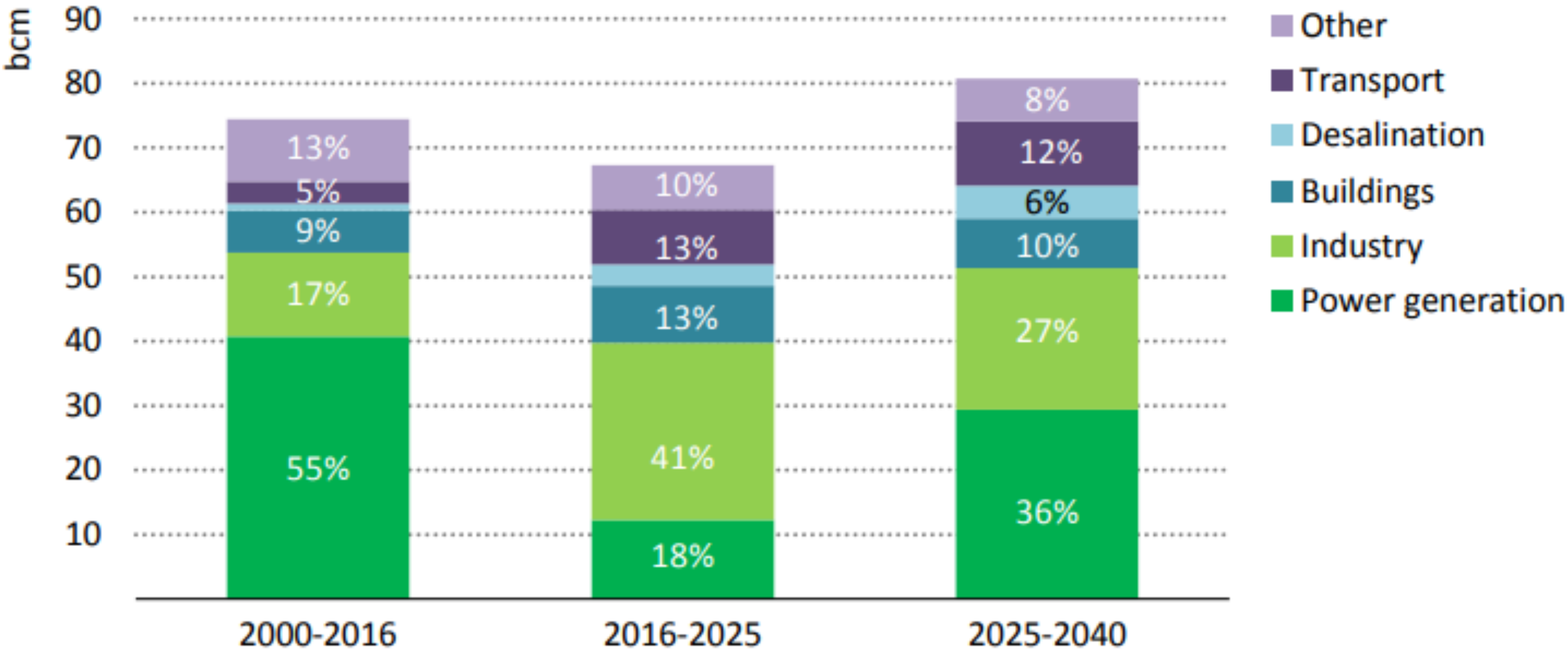
- Need of high power density, carbon neutral energy storage

Outline

- Energy storage technologies
- Hydrogen
- Power-to-fuel technologies - overview



Global natural gas demand by sector



https://www.iea.org/publications/freepublications/publication/WEO2017Excerpt_Outlook_for_Natural_Gas.pdf

Methane

Fuel	Formula	Molar Mass	Density (15°C, 1 bar)	LHV	Energy density	H_2 content (wt%)
Unit		g/mol	kg/m^3	MJ/kg	GJ/m^3	
Methane	CH_4	16.04	0.67×10^{-3}	50.0	33.53×10^{-3}	25.2

- CO methanation

$$4H_2 + CO_2 \Leftrightarrow CH_4 + 2H_2O \dashrightarrow \Delta H°_{298\,K} = -165\frac{kJ}{mol} \text{ (Sabatier reaction)}$$

$$3H_2 + CO \Leftrightarrow CH_4 + 2H_2O \dashrightarrow \Delta H°_{298\,K} = -49.4\frac{kJ}{mol}$$

- CO_2 methanation

$$4H_2 + CO_2 \Leftrightarrow CH_4 + 2H_2O \dashrightarrow \Delta H°_{298\,K} = -165\frac{kJ}{mol} \text{ (Sabatier reaction)}$$

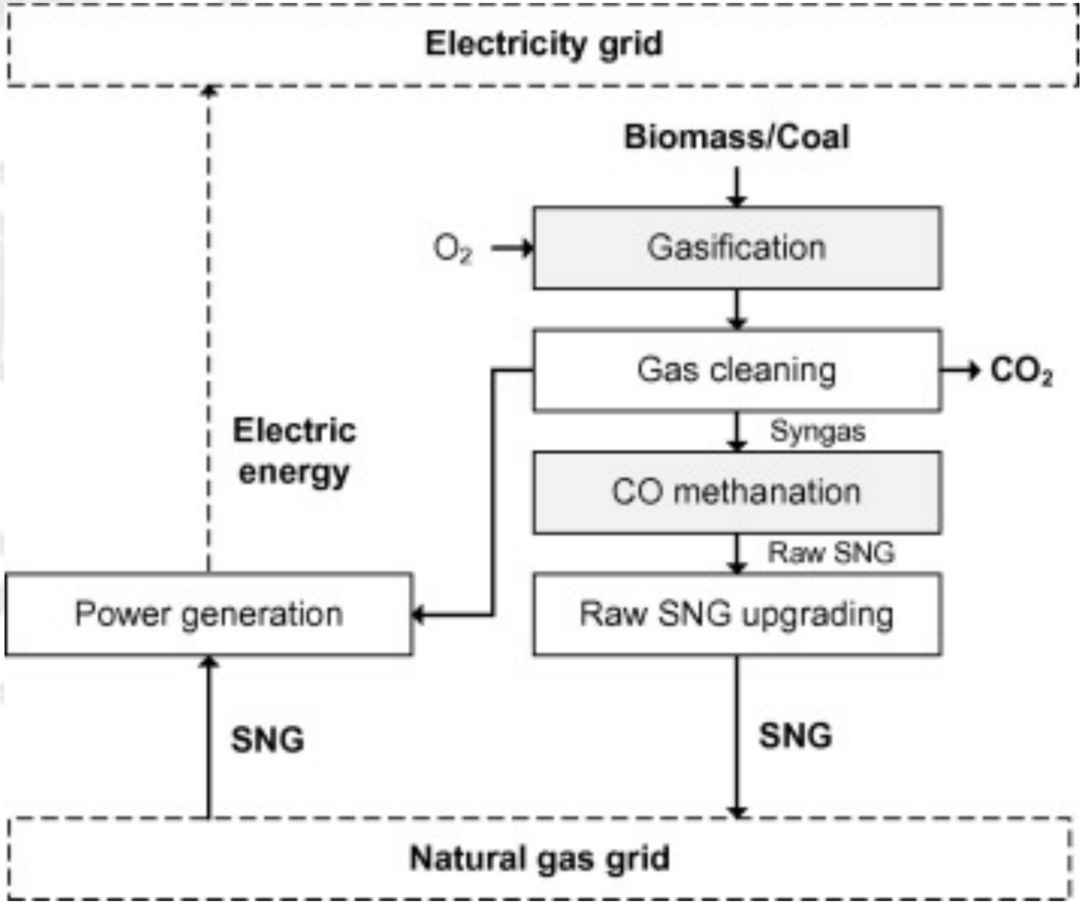
$$3H_2 + CO \Leftrightarrow CH_4 + 2H_2O \dashrightarrow \Delta H°_{298\,K} = -49.4\frac{kJ}{mol}$$

$$H_2 + CO_2 \Leftrightarrow CO + H_2O \dashrightarrow \Delta H°_{298\,K} = 41\frac{kJ}{mol} \text{ (RWGS)}$$

Methane – CO methanation

$$4H_2 + CO_2 \Leftrightarrow CH_4 + 2H_2O \longrightarrow \Delta H^\circ_{298\,K} = -165\frac{kJ}{mol}$$

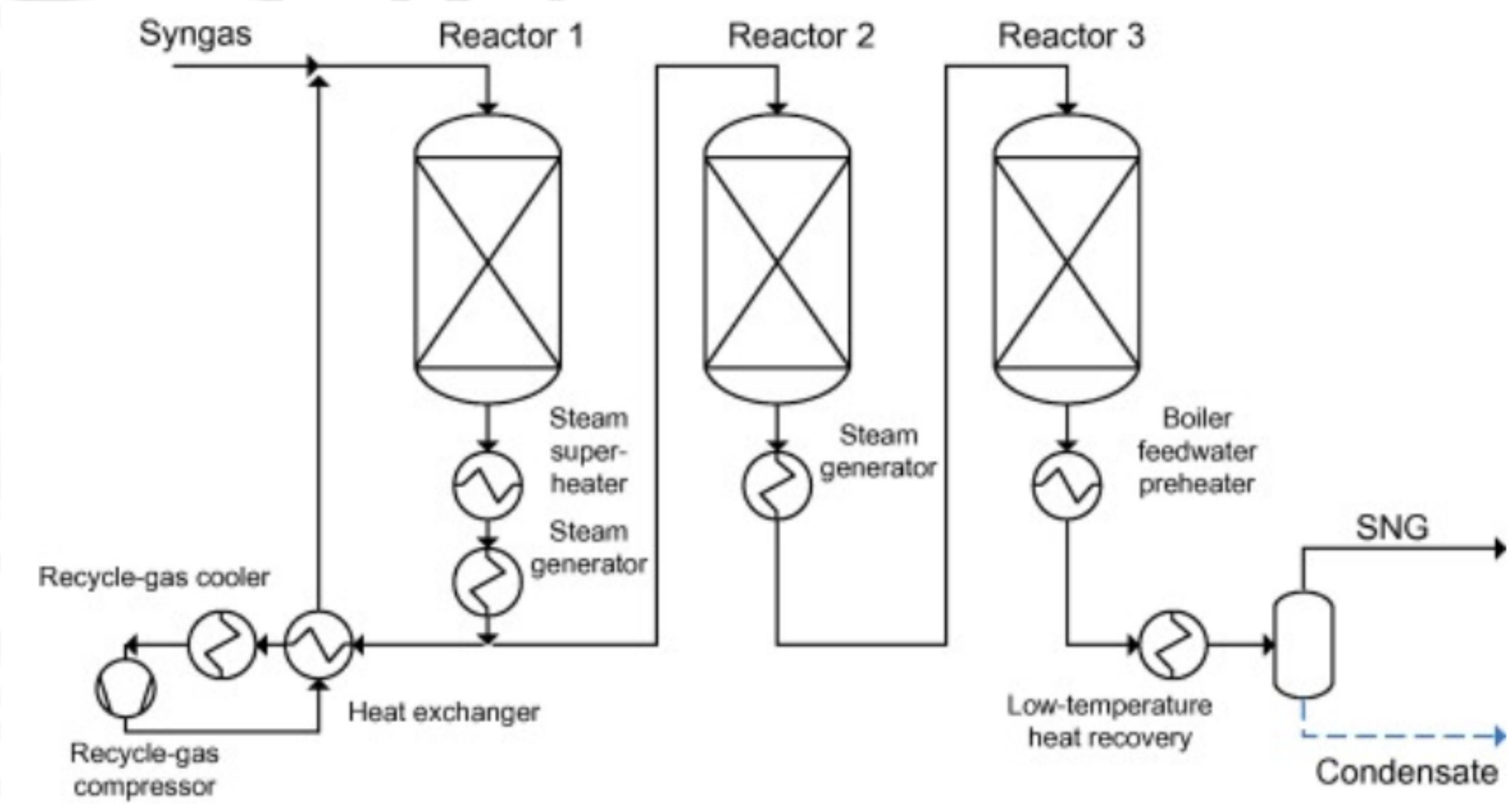
$$3H_2 + CO \Leftrightarrow CH_4 + 2H_2O \longrightarrow \Delta H^\circ_{298\,K} = -49.4\frac{kJ}{mol}$$



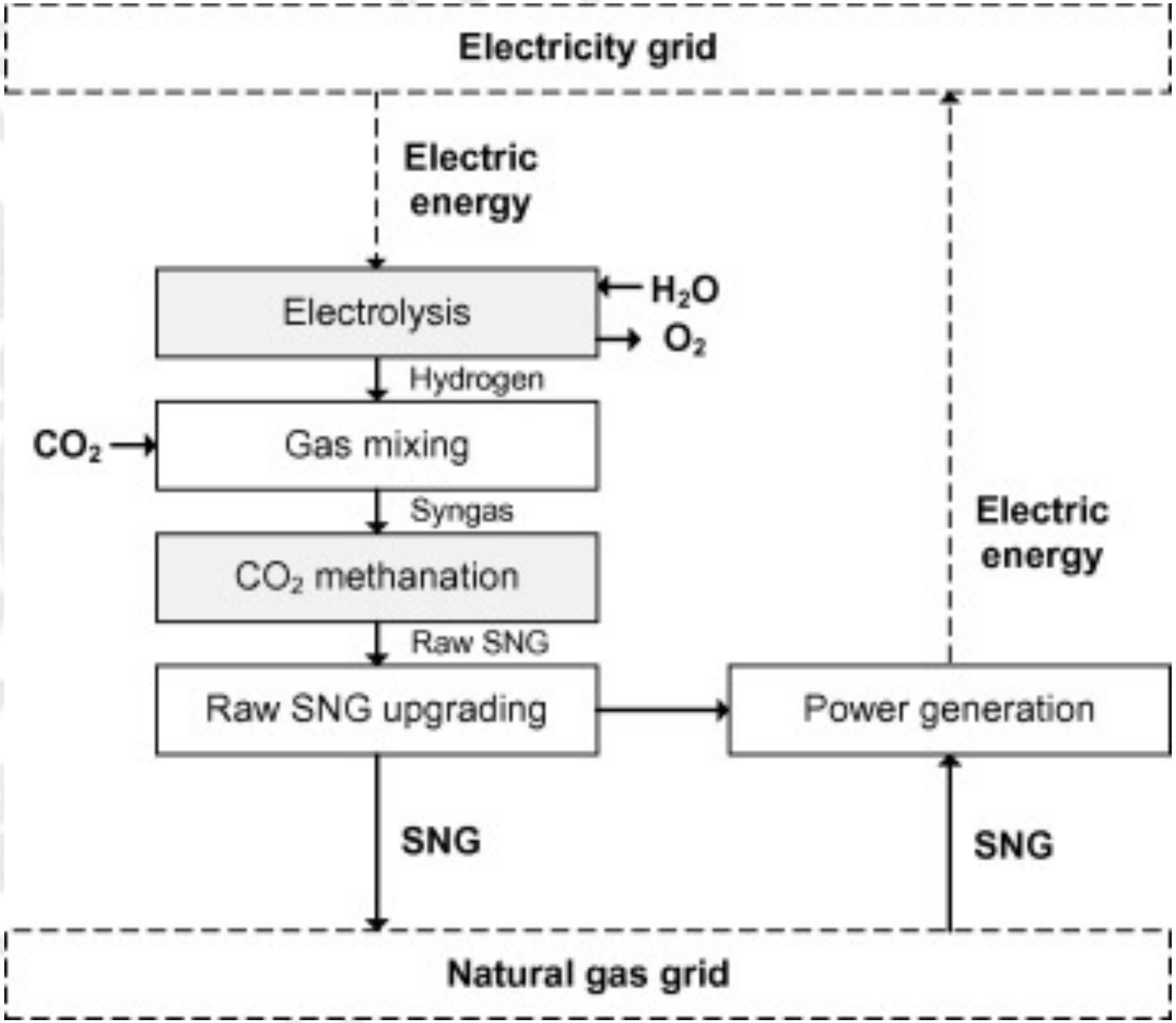
Methane – CO methanation technologies available on the market

Supplier	Concept	Technology Name
Air Liquide (formerly Lurgi)	2 adiabatic fix-bed reactors with gas recycling and intermediate cooling	Lurgi methanation
Haldor Tropsoe	3-4 adiabatic fixed-bed reactors with gas recycling and intermediate cooling	TREMP
Clariant and Foster Wheeler	3 fixed-bed reactors with steam addition and without gas recycle	Vesta
Johnson Matthey	3 adiabatic fixed-bed reactors with gas recycling and intermediate cooling	HICOM
Linde	1 isothermal fixed-bed reactor with internal contorted heat exchanger	Linde isothermal reactor

Methane – Haldor Tropsoe methanation process



Methane – CO_2 methanation



1) $4H_2 + CO_2 \Leftrightarrow CH_4 + 2H_2O$

$$\Delta H°_{298\,K} = -165\,\frac{kJ}{mol}$$

2) $3H_2 + CO \Leftrightarrow CH_4 + 2H_2O$

$$\Delta H°_{298\,K} = -49.4\,\frac{kJ}{mol}$$

3) $H_2 + CO_2 \Leftrightarrow CO + H_2O$

$$\Delta H°_{298\,K} = 41\,\frac{kJ}{mol}$$

Methane – CO_2 methanation technologies available on the market

Supplier	Concept	Technology Name
Outotec	Staged fixed-bed reactor with intermediate cooling	Outotec methanation
Etogas	Fixed-bed reactor or plate reactor with steam cooling	Etogas methanation
MAN	1 isothermal fixed-bed reactor with molten salt cooling	MAN methanation

Power-to-Methane pilot plants

- October 2012, Stuttgart (Germany) → ZSW and SolarFuel GmbH realized a demonstration project with 250 kW of electrical input (https://web.archive.org/web/20121107140857/http://www.zsw-bw.de/infoportal/presseinformationen/presse-detail/weltweit-groesste-power-to-gas-anlage-zur-methan-erzeugung-geht-in-betrieb.html)

- April 2014 →HELMETH (Integrated High-Temperature Electrolysis and METHanation for Effective Power to Gas Conversion) Project co-financed by the EU (http://www.helmeth.eu/). Integration of SOEC with CO2 methanation

- March 2016 →STORE&GO European Project, with 27 partner organizations, aimed to test 3 innovative PtG concepts in 3 different countries (https://www.storeandgo.info/)

Power-to-Methane industrial plants

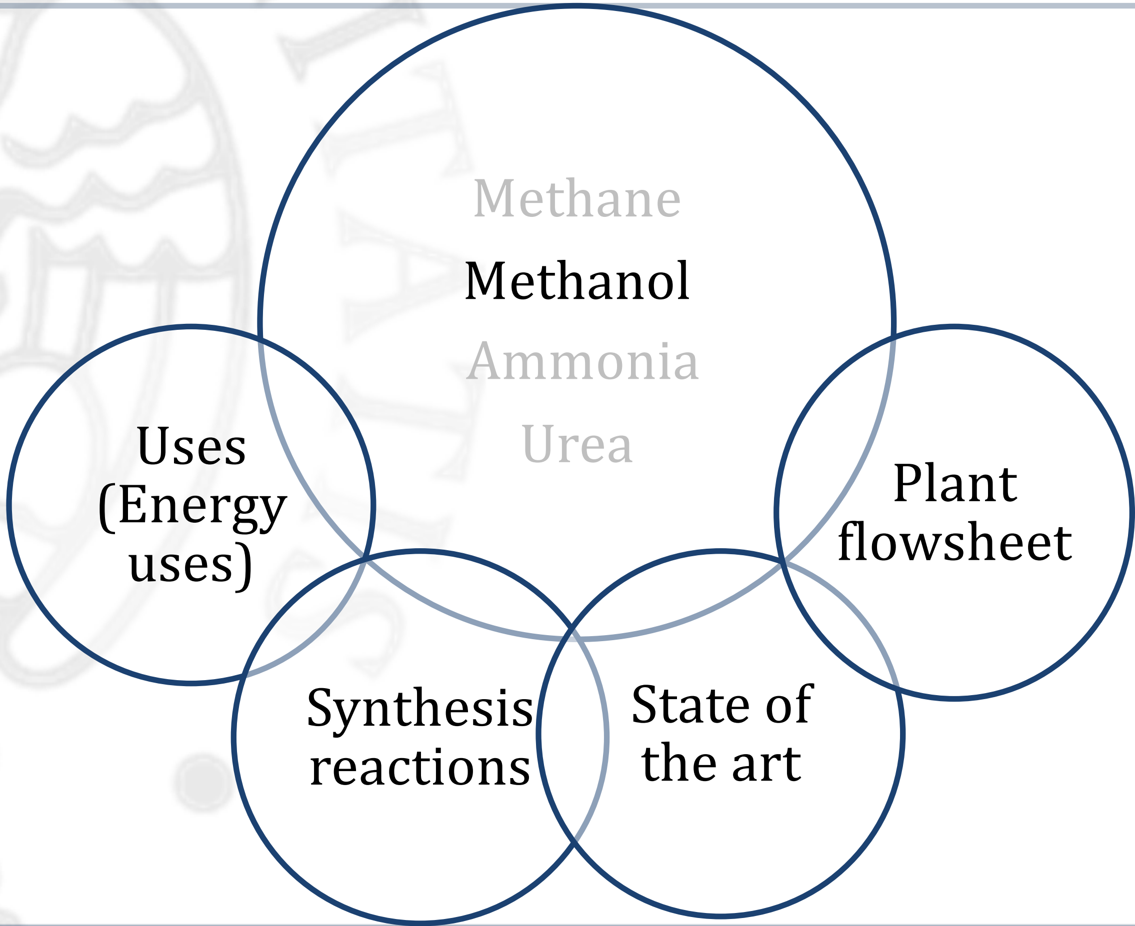
The first industrial scale Power-to-Methane plant was realized by ETOGAS for Audi in Wertle (Northern Germany) and put into operation in June 2013.

- **6 MW** electrical input power
- **2800 tons/year CO_2** from a waste-biogas plant
- **1000 tons/year SNG** ('e-gas') is directly fed into the gas grid

https://www.audi.com.au/au/web/en/models/layer/technology/g-tron/power-to-gas-plant.html

Outline

- Energy storage technologies
- Hydrogen
- Power-to-fuel technologies - overview



Methanol - Properties

Fuel	Formula	Molar Mass	Density (15°C, 1 bar)	LHV	Energy density	H_2 content (wt%)
Unit		g/mol	kg/m^3	MJ/kg	GJ/m^3	
Methanol	CH_3OH	32.04	0.796×10^3	19.9	15.58	12.5

Synthesis reaction from CO_2 and H_2:

$3H_2 + CO_2 \Leftrightarrow CH_3OH + H_2O \qquad \Delta H°_{298\,K} = -49.4 \frac{kJ}{mol}$ (exothermic)

$2H_2 + CO \Leftrightarrow CH_3OH \qquad \Delta H°_{298\,K} = -90.55 \frac{kJ}{mol}$ (exothermic)

$H_2 + CO_2 \Leftrightarrow CO + H_2O \qquad \Delta H°_{298\,K} = +41.12 \frac{kJ}{mol}$ (endothermic)

Methanol – Current production (1)

Today almost all methanol is produced from syngas obtained from reforming of fossil fuels (mainly natural gas)

1) Fossil fuels to syngas

Process	Reaction	$\Delta H°_{298\,K}$ (kJ/mol)	Operating conditions	Catalyst
Steam reforming	$CH_4 + H_2O \Leftrightarrow CO + 3H_2$	225.4	T=800~1000°C	Ni
Oxy reforming (Partial oxydation)	$CH_4 + 1/2O_2 \Leftrightarrow CO + 2H_2$	-22.6	T=800~1500°C	Ni
CO2 reforming (Dry reforming)	$CH_4 + CO_2 \Leftrightarrow 2CO + 2H_2$	260.5	T=800~1000°C	Ni

Methanol – Current production (2)

2) Syngas to methanol

Synthesis reactions:

$$3H_2 + CO_2 \Leftrightarrow CH_3OH + H_2O \qquad \Delta H°_{298\,K} = -49.4\frac{kJ}{mol}$$

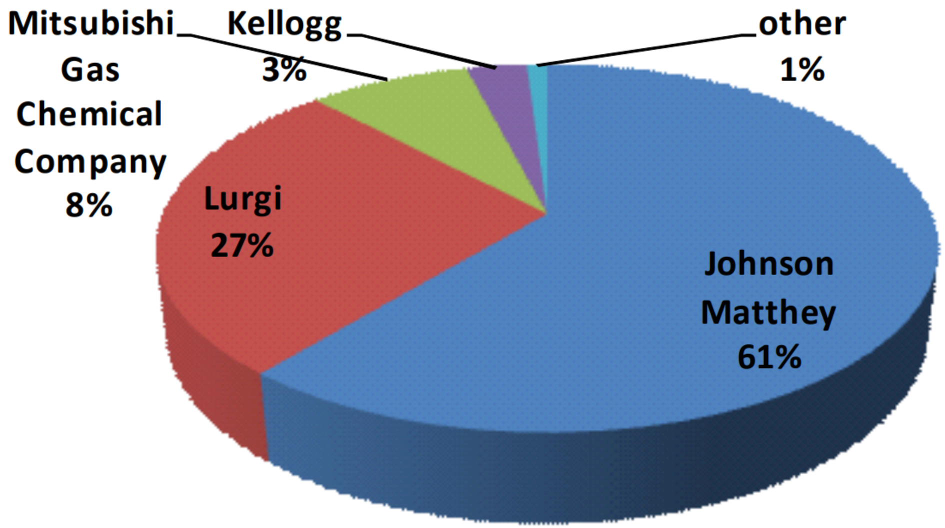
$$2H_2 + CO \Leftrightarrow CH_3OH \qquad \Delta H°_{298\,K} = -90.55\frac{kJ}{mol}$$

$$H_2 + CO_2 \Leftrightarrow CO + H_2O \qquad \Delta H°_{298\,K} = +41.12\frac{kJ}{mol}$$

Catalyst: CuO/ZnO

Operating conditions:
P=50~100 bar
T=200~300°C

Selectivity up to 99%
Energy efficiency up to 70%



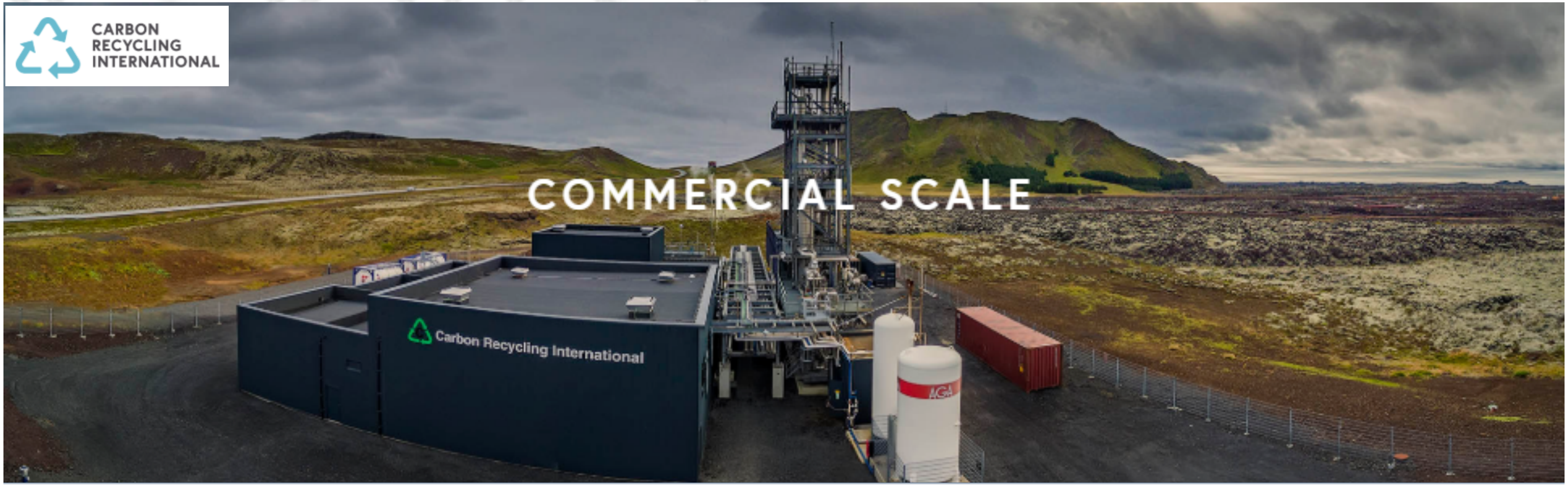
Methanol from CO_2 and H_2

$$3H_2 + CO_2 \Leftrightarrow CH_3OH + H_2O \qquad \Delta H°_{298\,K} = -49.4\frac{kJ}{mol}$$

- **Mitsui Chemicals** →pilot plant started working on May 2009 in Japan
- **Carbon Recycling International (CRI)**→in 2012 the largest CO_2 to methanol power plant was put into operation in Iceland.

  5 million L methanol/year

  5.5 thousands tons CO_2 /year captured from flue gases released from geothermal plants



Methanol - Uses

Worldwide, over 90 methanol plants have a combined production capacity of 110 million tons.
In 2015, the global methanol demand was 75 million tons, with energy applications accounting for **40%** of the total.

Chemicals	Energy	Wastewater Treatment
• Formaldehyde • Acetic Acid	• Automotive Fuel • Marine Fuel • DME • Bio Diesel • Fuel Cells • Electricity • Boiler/Cookstoves	• (denitrification process)

Methanol – Energy Uses

Energy
1. Automotive Fuel 2. Marine Fuel 3. DME 4. Bio Diesel 5. Fuel Cells (DMFC) 6. Electricity 7. Boiler/Cookstoves

1. Blended to gasoline. China is the largest user of MeOH for transportation in the world (M5, M10, M15-most used, M85, M100 gasoline methanol blends). It represents 7% of the total transportation fuel pool. In Europe, up to 3% methanol blends are allowed

2. 8 ships trading operating on methanol as fuel. ISO is working to develop the standards.

3. DME can be produced from methanol, and replace diesel fuels

4. In biodiesel synthesis, methanol is used in the transesterification step

Methanol – Energy Uses

Energy

1. Automotive Fuel
2. Marine Fuel
3. DME
4. Bio Diesel
5. Fuel Cells
6. Electricity
7. Boiler/Cookstoves

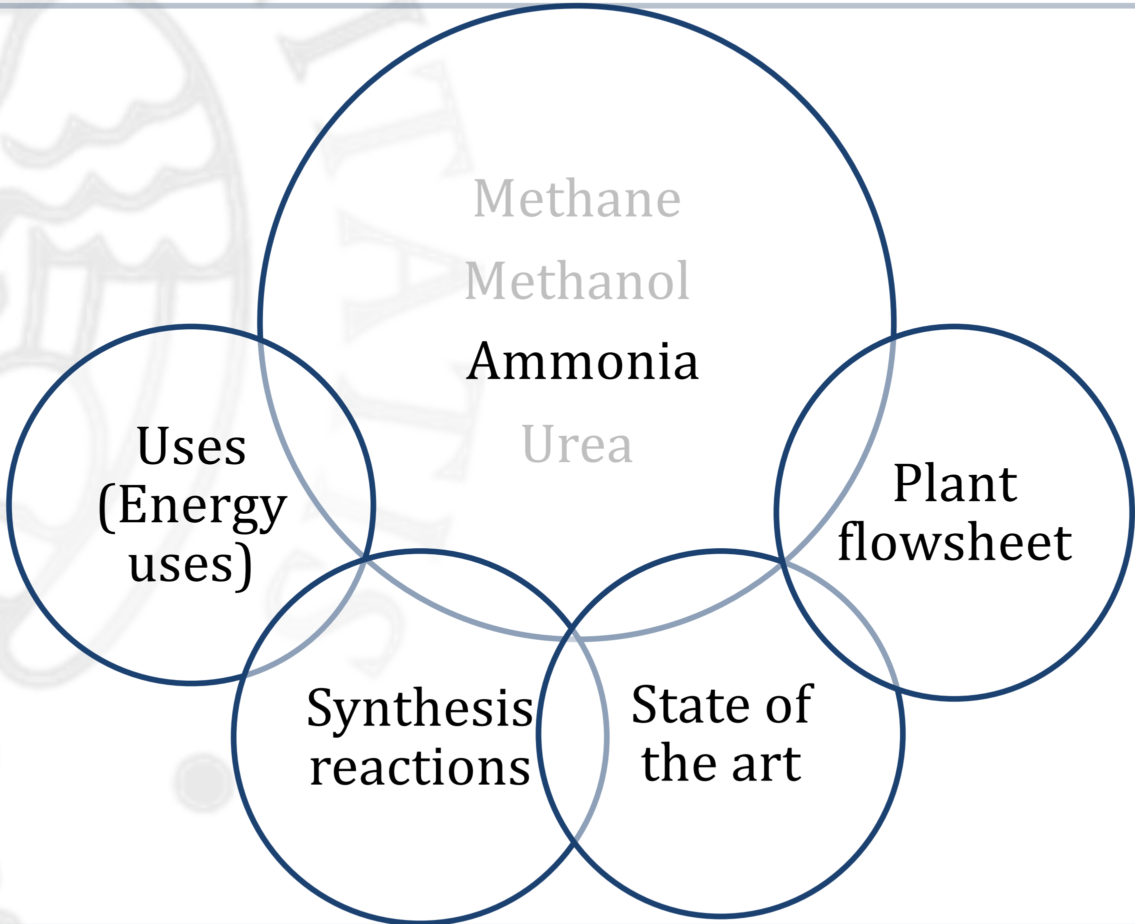
5. Direct Methanol Fuel Cells or Reformed/Indirect Methanol Fuel Cells

6. Gas turbines

7. China has banned the use of coal and diesel domestic cookstoves in favour of less polluting methanol ones.

Outline

- Energy storage technologies
- Hydrogen
- Power-to-fuel technologies - overview



Ammonia - Properties

Fuel	Formula	Molar Mass	Density (15°C, 1 bar)	LHV	Energy density	H_2 content (wt%)
Unit		g/mol	kg/m^3	MJ/kg	GJ/m^3	
Ammonia	NH_3	17.03	0.719	18.6	14.1	17.6

Synthesis reaction = Haber-Bosch process

$$3H_2 + N_2 \Leftrightarrow 2NH_3 \qquad \Delta H°_{298\ K} = -92.4\frac{kJ}{mol}\ \text{(exothermic)}$$

Operating conditions:
P=150-250 bar
T~400-500°C
Fe catalyst

Ammonia - Uses

Because of its numerous applications, ammonia is the second largest synthetic chemical product in the world (176 million tonnes). In the environmental sector ammonia is used in various processes as desulphurizing agent in fossil fuel plants.
Energy related applications include its use in **fuel cells** and **spark ignition engines**.

Fertizer production	Industrial/Manifacturing Uses	Energy
• Ammonium nitrate • Ammonium phosphate • Urea	• Refrigerant gas • Purificant of water supplies • Wastewater Treatment • Stabilizer, neutralizer in some industries • Desulphurizing agent in fossil fuel plants	• Fuel • Energy Carrier

Ammonia – Energy Uses

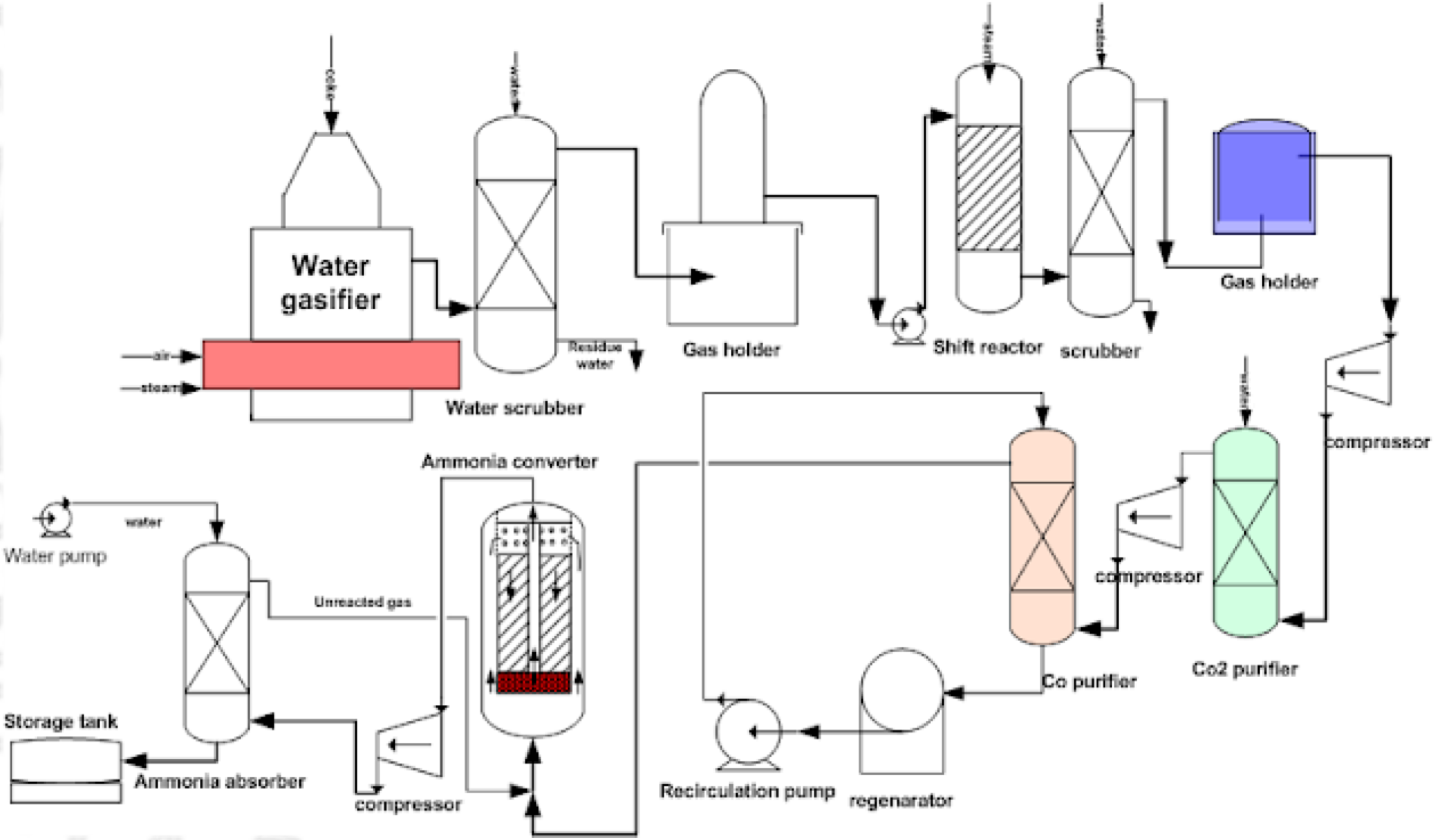
Energy

1. Fuel
2. Energy Carrier

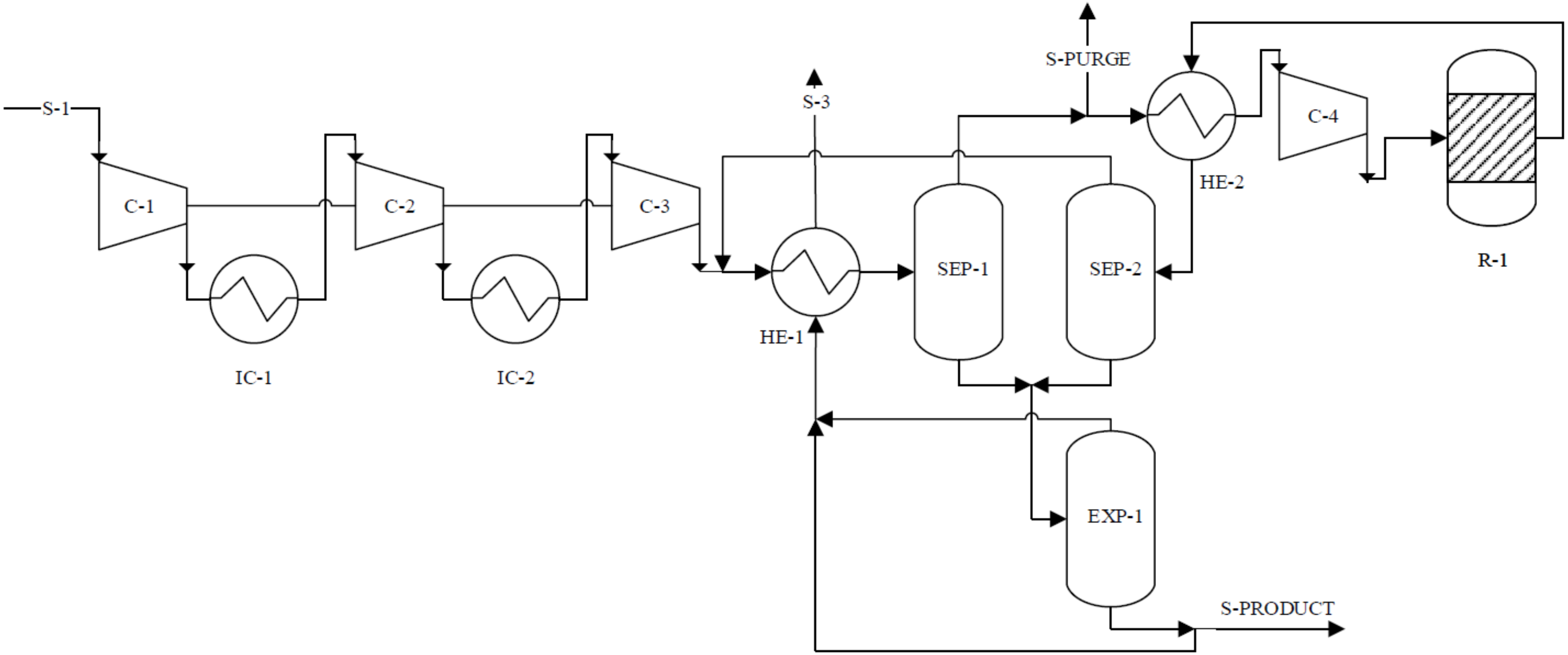
1. Gasoline and diesel ICE can be converted to run on ammonia.
   a) Spark ignition engines: high octane rating (120 vs gasoline at 86-93), so it does not need enhancer. However, it has relatively low density (half of gasoline). No CO_2 emissions when burnt.
   b) Compressione engines: ammonia compression ignites at very high pressures, so small amounts of high-cetane fule is added (i.e: 5% biodiesel, 95% ammonia)

2. Direct Ammonia Fuel Cells and Indirect Ammonia Fuel Cells

Ammonia – Haber-Bosch Process

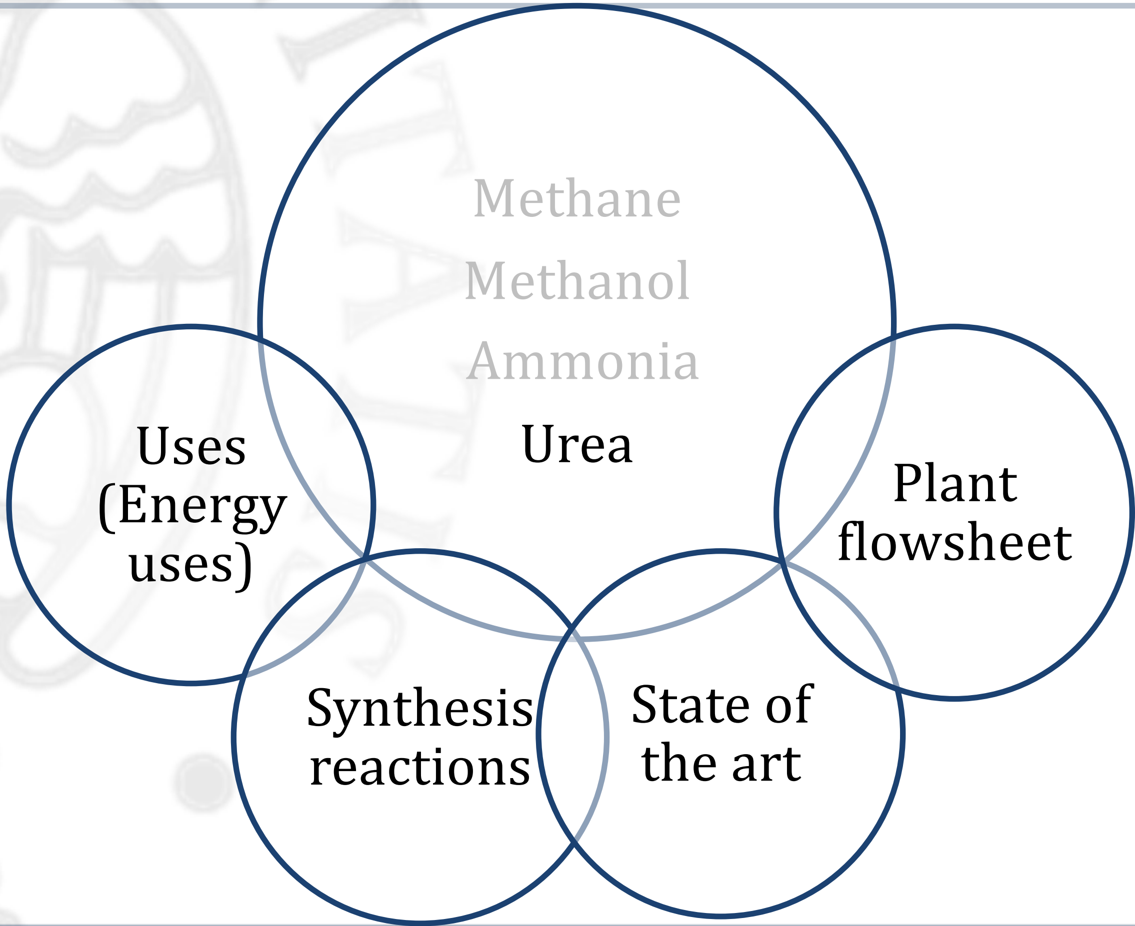


Ammonia – Haber-Bosch Process



Outline

- Energy storage technologies
- Hydrogen
- Power-to-fuel technologies - overview



Urea - Properties

Fuel	Formula	Molar Mass	Density (15°C, 1 bar)	LHV	Energy density	H_2 content (wt%)
Unit		g/mol	kg/m^3	MJ/kg	GJ/m^3	
Urea	CH_4N_2O	60.05	1.32×10^3	10.5	13.89	6.7

Synthesis reaction = Bosch-Meiser reaction

$$2NH_3 + CO_2 \Leftrightarrow H_2N - COONH_4 \qquad \Delta H°_{298\,K} = -117\frac{kJ}{mol} \text{ (exothermic)}$$

$$H_2N - COONH_4 \Leftrightarrow (NH_2)_2CO + H_2O \qquad \Delta H°_{298\,K} = +15.5\frac{kJ}{mol} \text{ (endothermic)}$$

Operating conditions:
P=140-250 bar
T~180-210°C

Urea - Uses

Urea is a non-toxic low-cost solid powder, mainly used as fertilizer. The world's urea production was estimated around 69.2 million tonnes in 2016.

Agricolture

- Nitrogen-release fertilizer

Chemical industry

- Plastics (Urea-formaldehyde resins)
- Adhesives (urea-formaldehyde, urea-melamine-formaldehyde)
- Urea nitrate (explosive)
- NO_x reduction in power plants (SNCR and SCR)

Energy

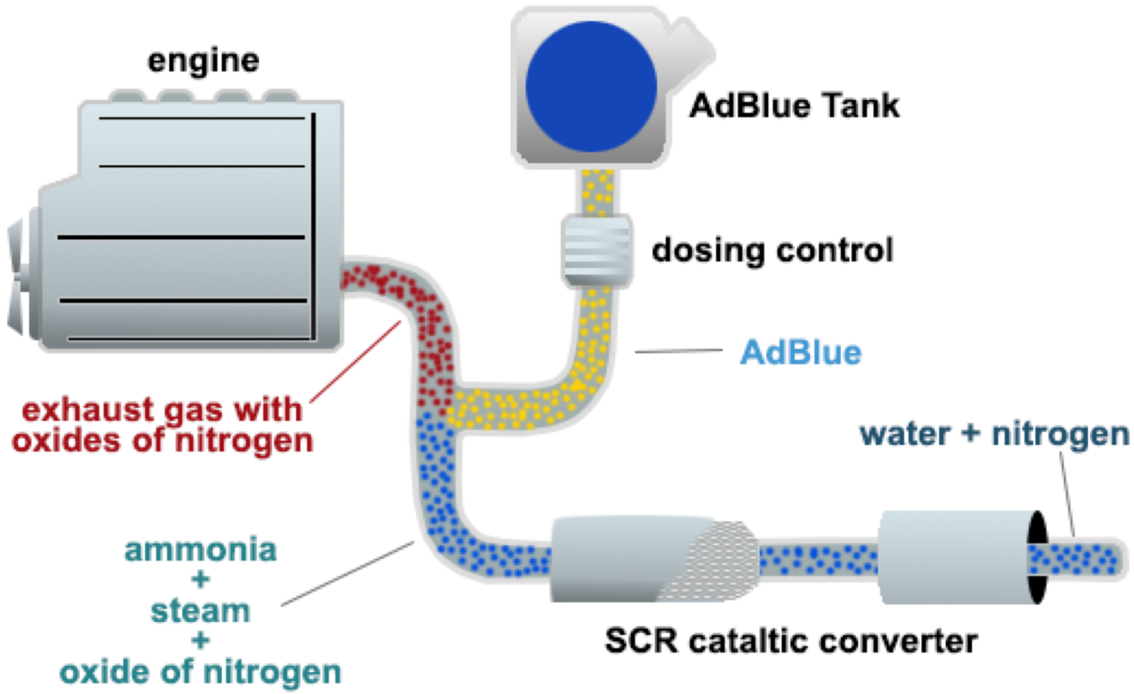
- NO_x reduction (SNCR and SCR, diesel engines-AdBlue)
- Energy Carrier

Urea – Energy Uses

Energy

1. NO_x reduction (SNCR and SCR, diesel engines- AdBlue)
2. Energy Carrier

1. AdBlue is a 32.5% urea solution that performes urea-selective catalytic reduction (SCR) to remove NO_x generated by diesel power vehicles.



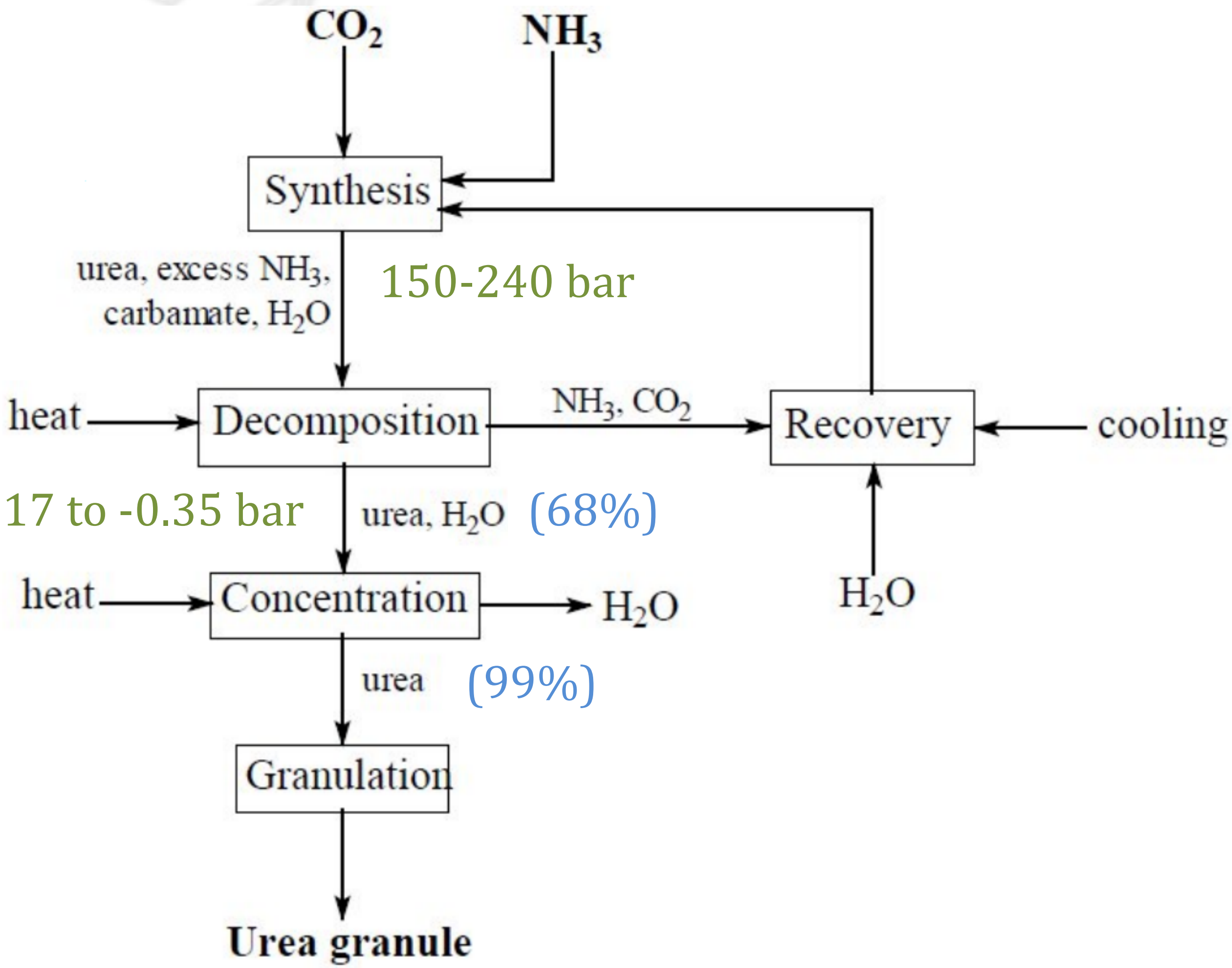
2. Direct Urea Fuel Cells

Urea – Production processes

- Once-through
- Partial recycle
- Total recycle →
  - Stamicarbon
  - Snamprogetti (Snam)
  - Mitsui-Toatsu
  - Advanced Cost and Energy Saving by TEC

- Carbamate decomposition
  - Hot-gas mixture recycle
  - Separated gas recycle
  - Slurry recycle
  - Carbamate – solution recycle
- Stripping

Urea – Block diagram for modern production processes



Urea – Stamicarbon CO_2 stripping process