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EFCE AIDIC ESBES European Society of Biochemical Engineering Sciences

Perspectives for CO_2 Utilization

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Anthropogenic CO_2 emissions: about 33 Gt/y[1]

CO_2 as feedstock, *today*
Where and how much?

[1] **Le Quéré et al.**, *Earth System Science Data Discussions*, **2012, 2015, 2018**.

Urea plant

Main use: fertilizer

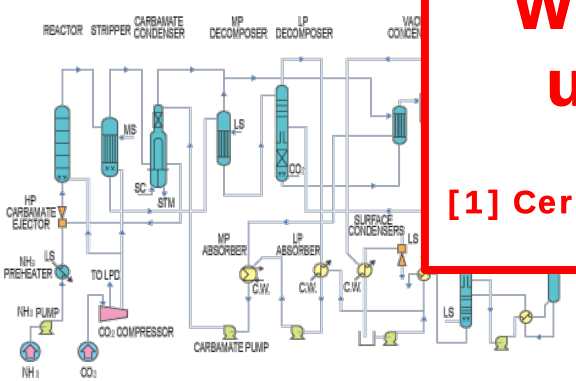
Plant: large size, downstream the ammonia plant

Toyo, Casale, Uhde, Stamicarbon, Eni…

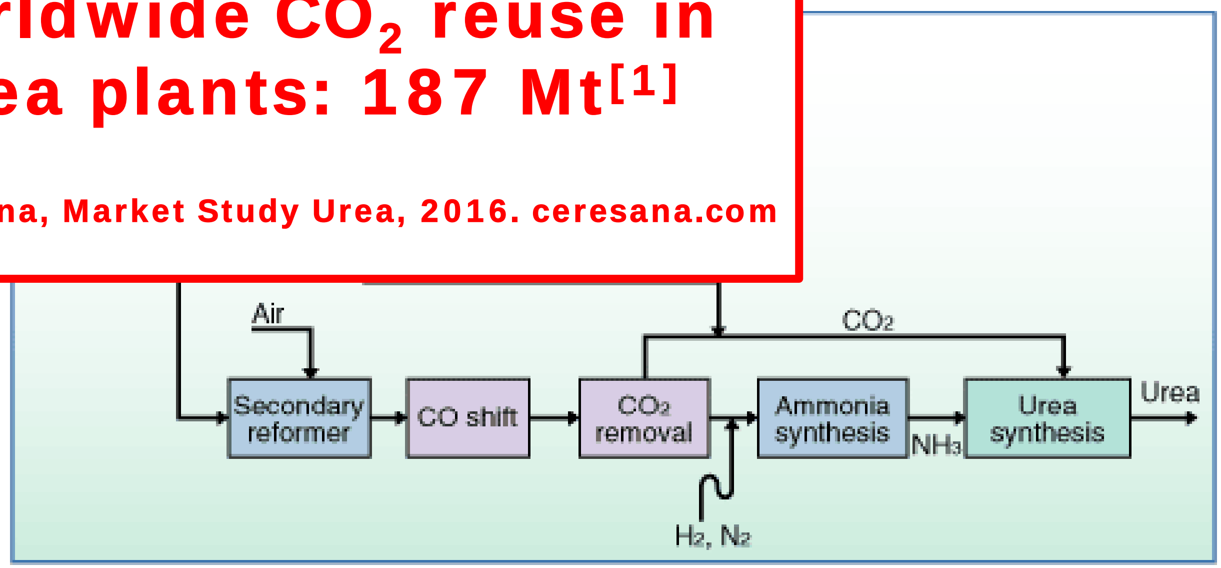
Synthesis: 2

Worldwide CO_2 reuse in urea plants: 187 Mt[1]

[1] Ceresana, Market Study Urea, 2016. ceresana.com



Ref.: http://www.unido.or.jp/en/technology_db/428/



Ref.: https://www.mhi-global.com/products/expand/km-cdr_application_03.html

Methanol plant

Main uses: energy carrier, fuel, base chemical

Perspectives: methanol economy[1]

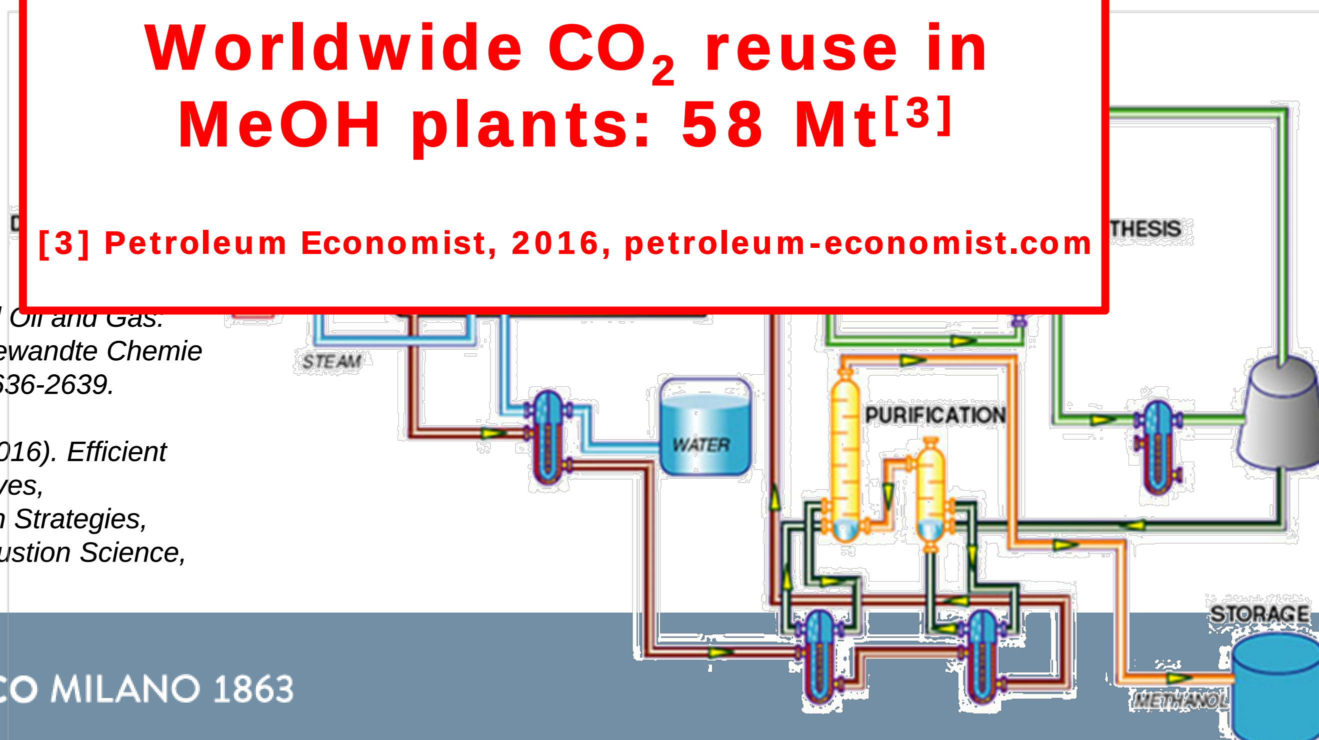
Plant: large size, downstream the syngas production

Lurgi, Davy, Toyo, Casale, Air Products, Topsoe…[2]

Synthesis + H_2O; WGS

Worldwide CO_2 reuse in MeOH plants: 58 Mt[3]

[3] Petroleum Economist, 2016, petroleum-economist.com



[1] ***Olah, G. A.*** *(2005). "Beyond Oil and Gas: The Methanol Economy." Angewandte Chemie International Edition 44(18): 2636-2639.*

[2] ***Bozzano, G., Manenti F.*** *(2016). Efficient Methanol synthesis: Perspectives, Technologies and Optimization Strategies, Progress in Energy and Combustion Science, 56, 71–105*

Other technologies

Dry reforming
- Pilot-scale
- Synthesis [1]
  - $CH_4 + CO_2 \rightarrow 2\ CO + 2\ H_2$

Sabatier process
- Pilot-sc
- Peak-tc
- Synthe
  - CO

GTL
- Demo-scale, few large-scale
- Synthesis [3]
  - $CO + 2\ H_2 \rightarrow -[CH_2]- + H_2O$
  - Water Gas Shift (WGS)

Current worldwide CO_2 reuse is negligible

[1] *Pakhare, D., Spivey, J. (2014), A review of dry (CO2) reforming of methane over noble metal catalysts, Chemical Society Reviews, 43(22), 7813-7837*

e in chemistry 1912 to emistry or catalysis? 19, 162-171, 2013

[3] *Pirola, C. et al., Fischer–Tropsch synthesis: EXAFS study of Ru and Pt bimetallic Co based catalysts, Fuel, 132 (2018) 62–70*

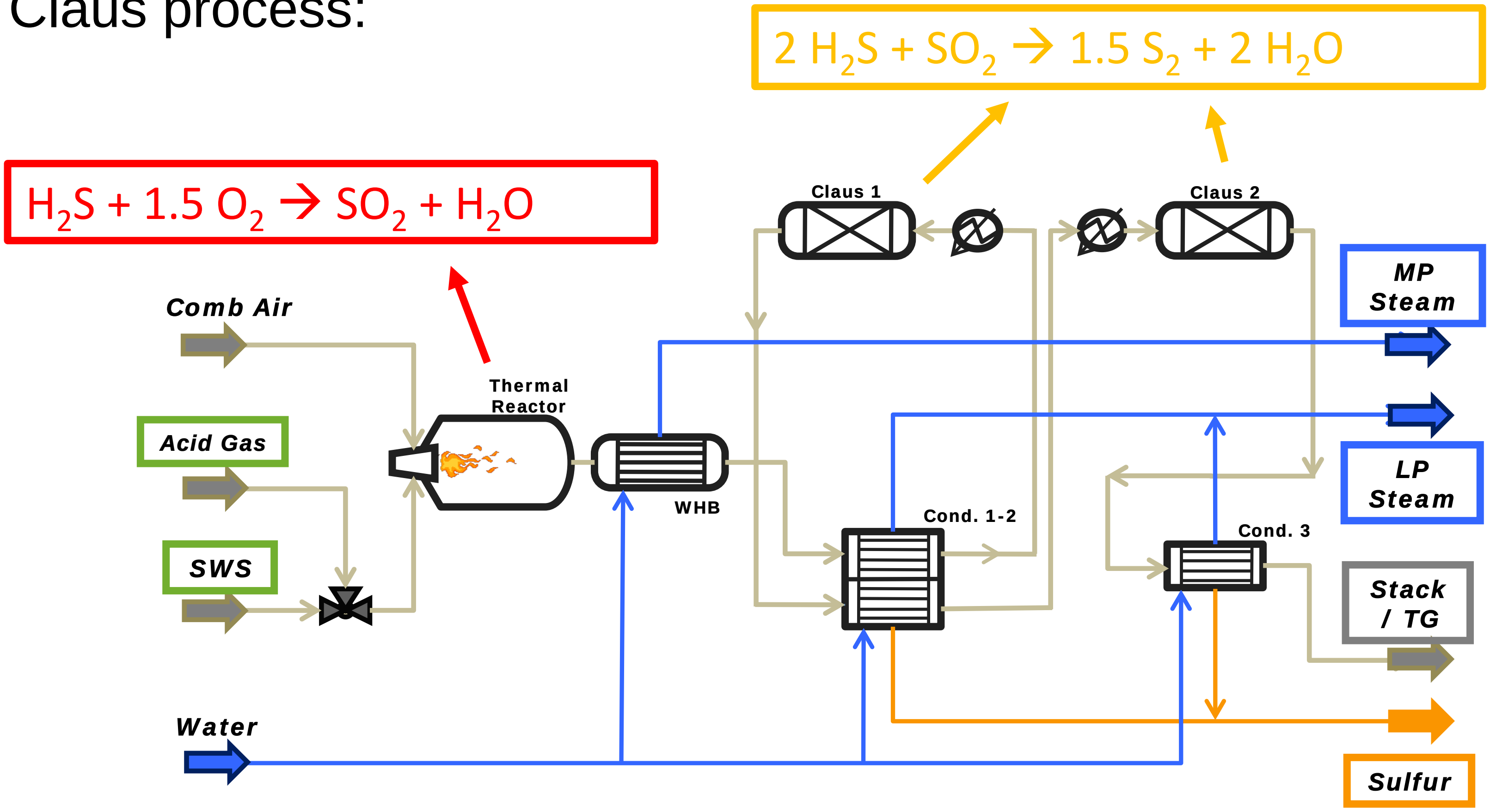
H_2, CH_4, CH_3OH, NH_3, H_2O...

... and H_2S?

A natural and synthetic compound

H_2S processing *today*

Claus process:



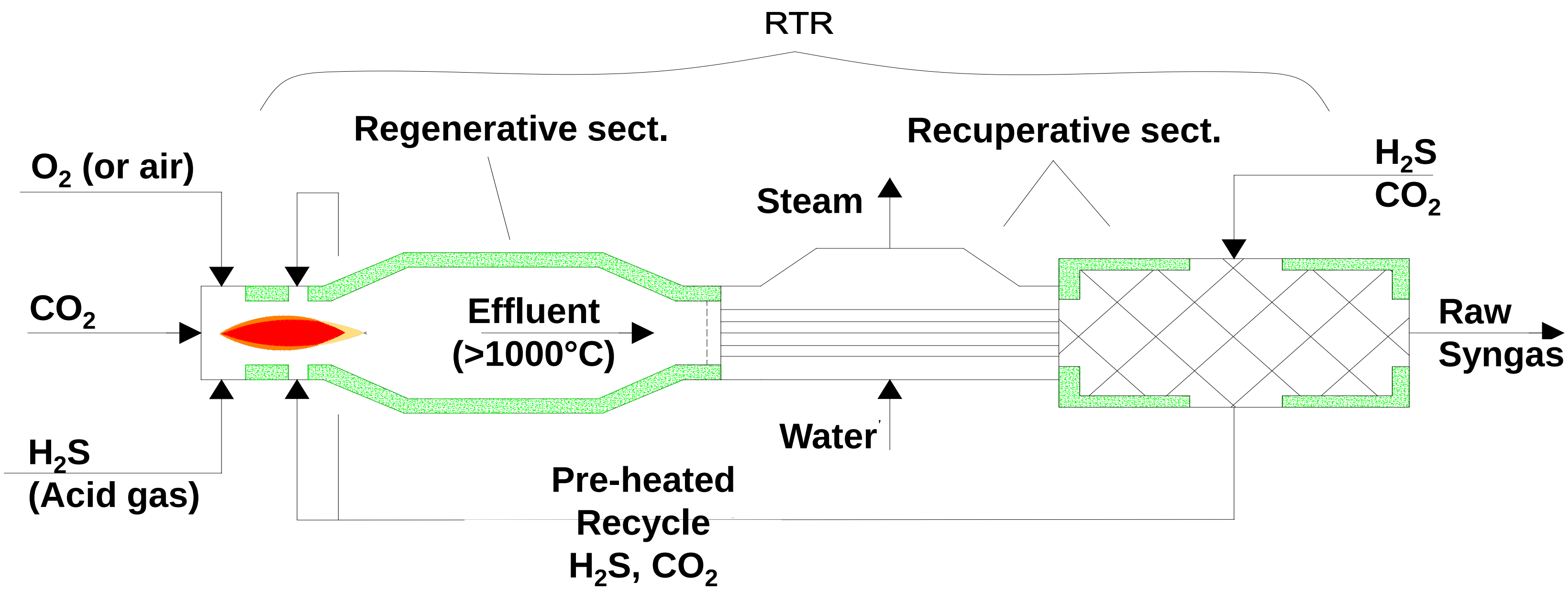
New: Acid gas to Syngas technology

Manenti, Pierucci, Molinari, WO 2015/015457 A1

New technology (Regenerative Thermal Reactor)

- Overall reaction: **$2\ H_2S + CO_2 \rightarrow CO + H_2 + S_2 + H_2O$**
- 3 moles of emissions into 2 moles of syngas
- Energy self-sustainability (minor O_2 injection)

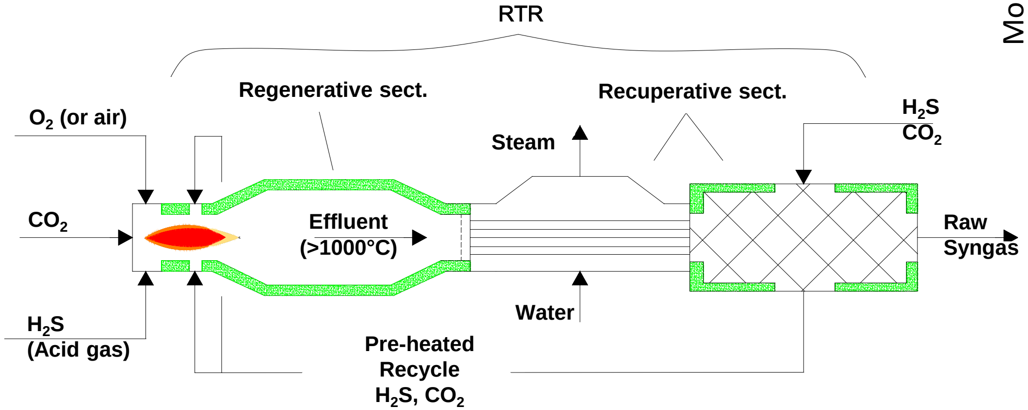
AG2S™

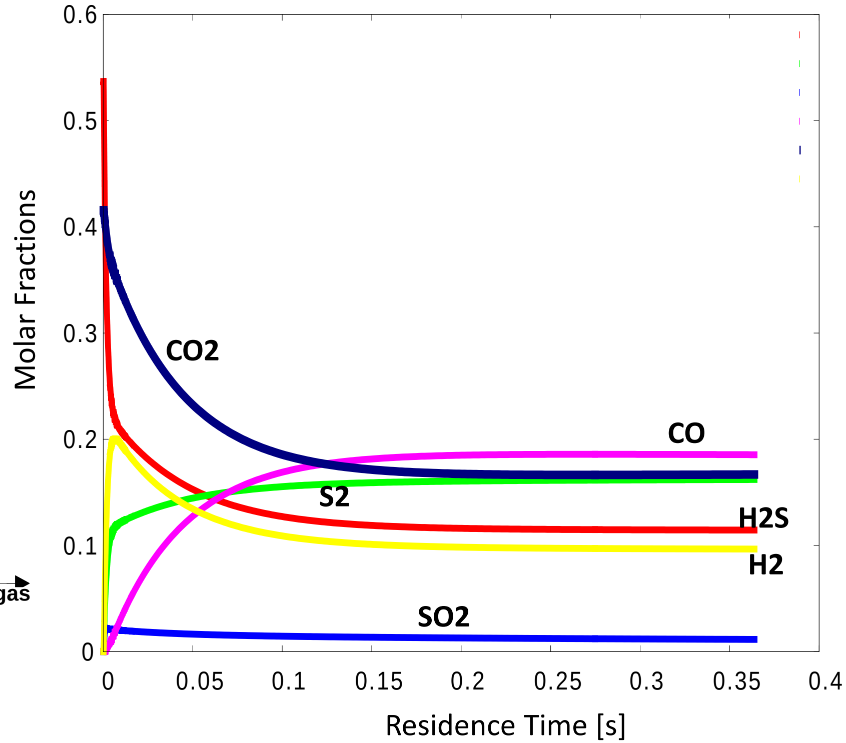


Regenerative Thermal Reactor (RTR)

Main effects using RTR[1]

- Good CO_2 and H_2S conversion at relatively mild conditions
- Handling impurities
- Inhibition of side-reactions



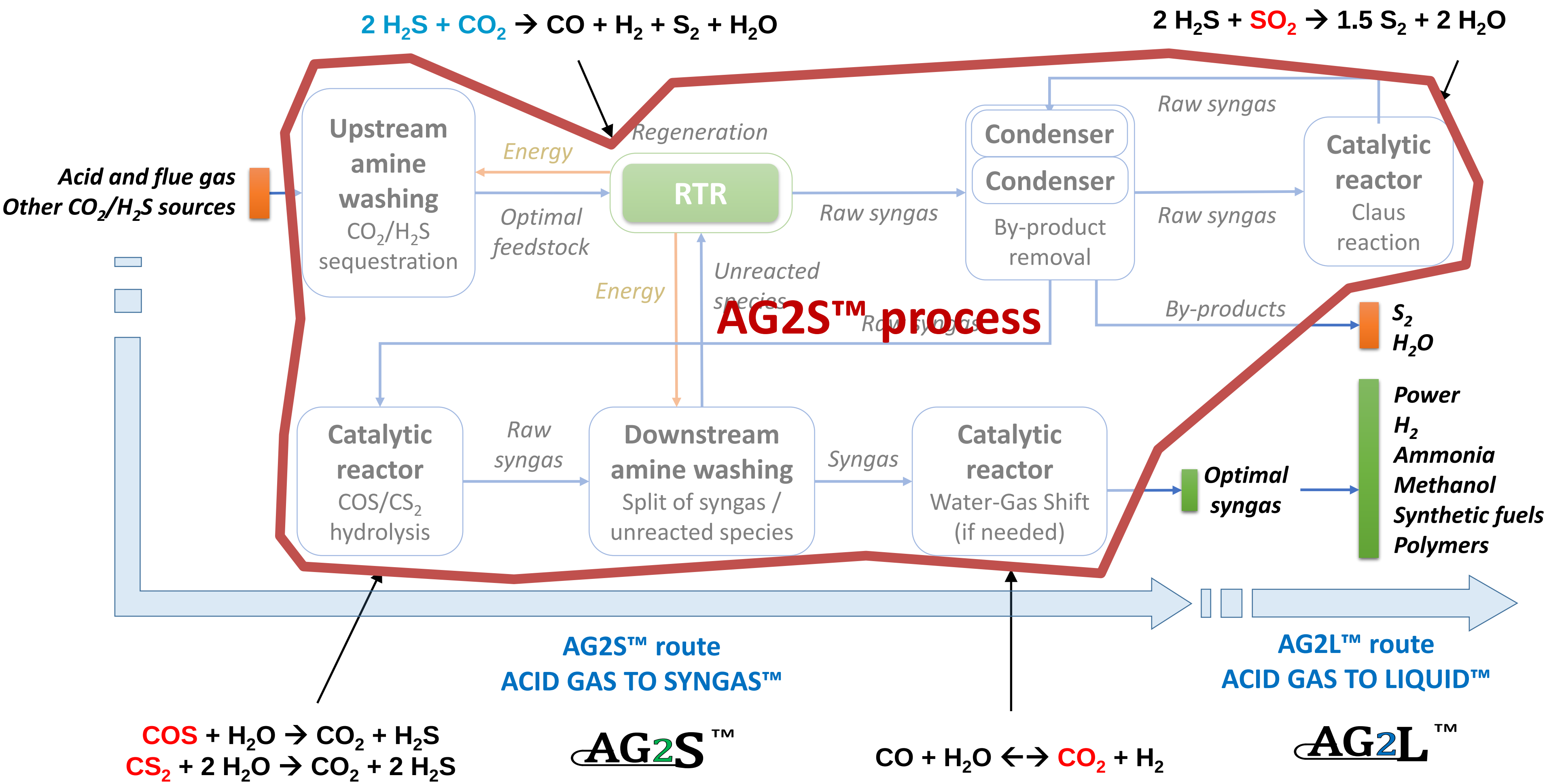


[1] **Manenti et al.**, *Syngas from H_2S and CO_2: an Alternative, Pioneering Synthesis Route?, Hydrocarbon Processing, 38-41, June 2016*

Process scale

Technology layout

AG2S™ complete layout



Main benefits and potential

Complete conversion of H_2S (as per Claus process)

Cut of CO_2 emissions

Reduced use of air or O_2

Product

Exploita

Based on worldwide sulfur

Pr

Perspective: debottlenecking sulfur-rich sources, AG2S™ potential is estimated in 8.8 % of total CO_2 emissions

Re

CO_2-free synthesis of base chemicals

– Methanol, (synthetic) fuels, olefins, polymers…

Pilot-scale plant
AG2S™ validation

Pilot-scale plant at team/network facilities

SOTACARBO

A case study
Coal gasification

Coal gasification[1]

Use: syngas production

Plant

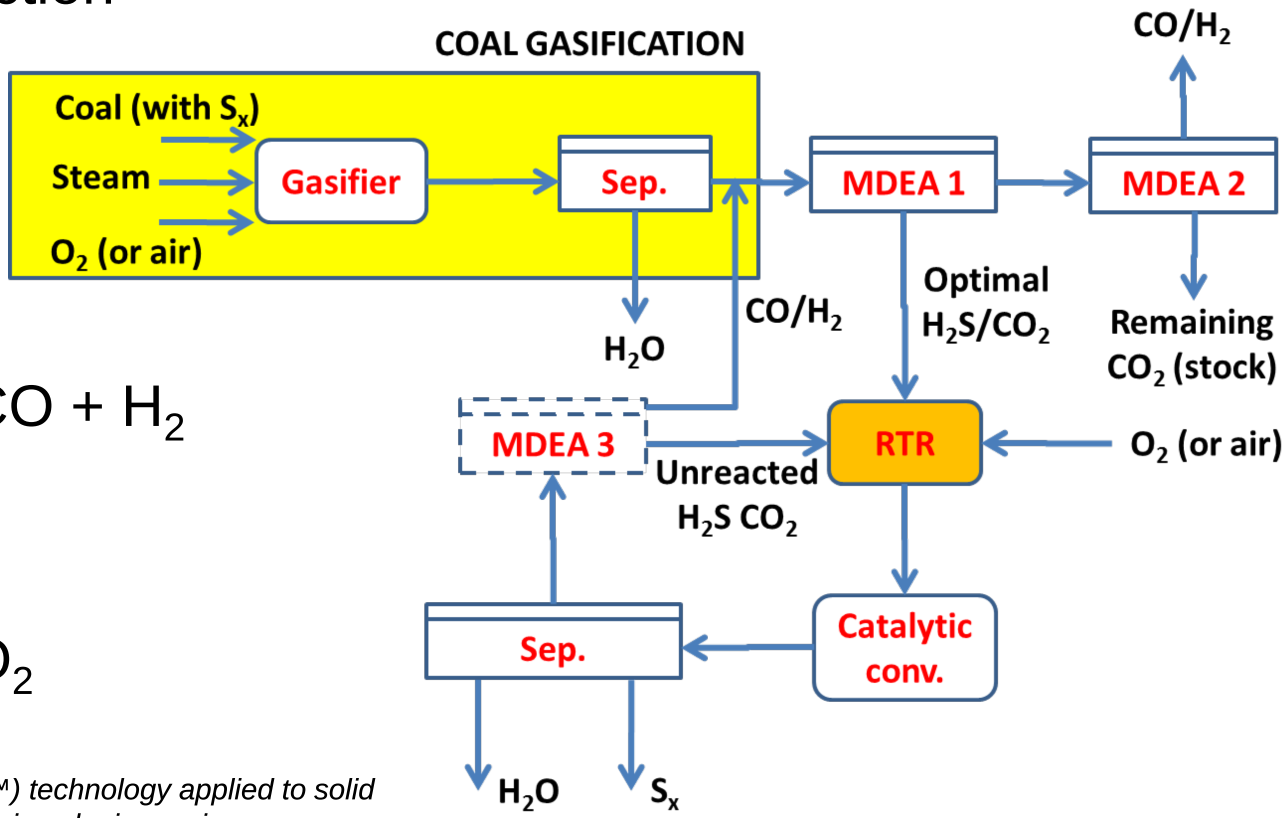
- large size
- CTX plants

Synthesis

- $C + H_2O \rightarrow CO + H_2$

Energy supply

- In situ
- $C + O_2 \rightarrow CO_2$

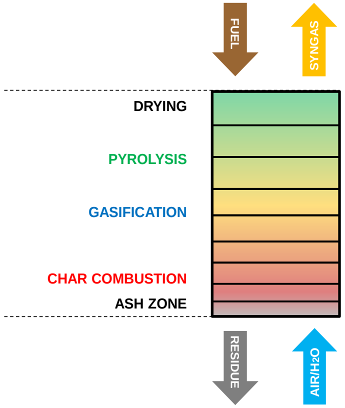


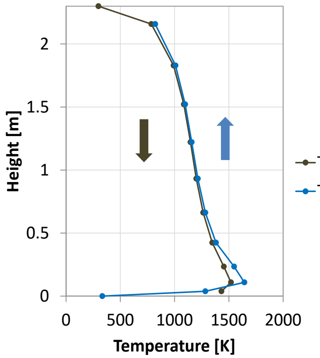
[1] **Bassani, A.**, *Acid Gas to Syngas (AG2S™) technology applied to solid fuel gasification: Cutting H2S and CO2 emissions by improving syngas production, Applied Energy, 2016,* doi:10.1016/j.apenergy.2016.06.040

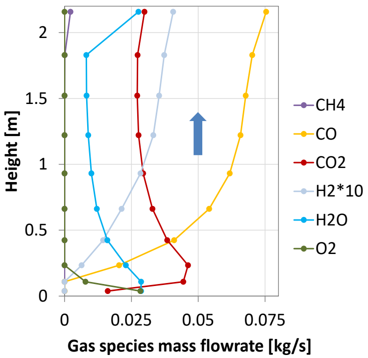
Tools & pilots

Pilots at Sotacarbo facilities
GasDS suite[1] & AspenHysys-PRO/II
GasDS suite

- Chemical kinetics
  - Torrefaction, pyrolysis, gasification, combustion
- Reactor configurations
  - Updraft, Downdraft, Traveling grate, Fluidized, …
- Design & operational purposes
  - Support, Optimization, Validation, Dynamics
  - Monitoring, Prediction, Control, Start-up assistant







[1] *Ranzi, E., Faravelli, T., Manenti, F., Pyrolysis, Gasification, and Combustion of Solid Fuels, Advances in Chemical Engineering, Elsevier, ISSN 0065-2377, 1-94, 2016.*

Techno-economic study

Manenti, G., Molinari, L., Manenti, F., Syngas from H_2S and CO_2: an Alternative, Pioneering Synthesis Route?, *Hydrocarbon Processing*, 6, **2016**

Input:

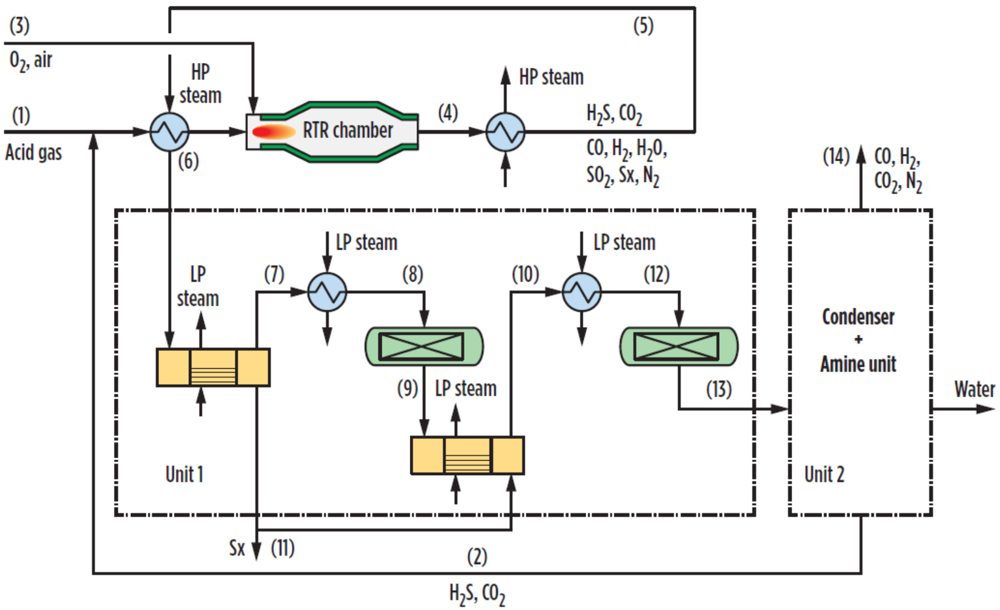
- Coal with 5%w sulfur
- Coal gasifier: 77 t/h

Revamp

- Gas/gas heat exchanger
  - 49700 kg, **727 k$**
- Burner
  - **165 k$**
- Amine washing
  - New unit (in spare)
  - 30 m3/h, **6.16 M$**

Payback: 1.63y

- Accounting for syngas only
  - Not considered: CO_2 certificates, sulfur, sulfur-rich resources



Technology potential
Application areas

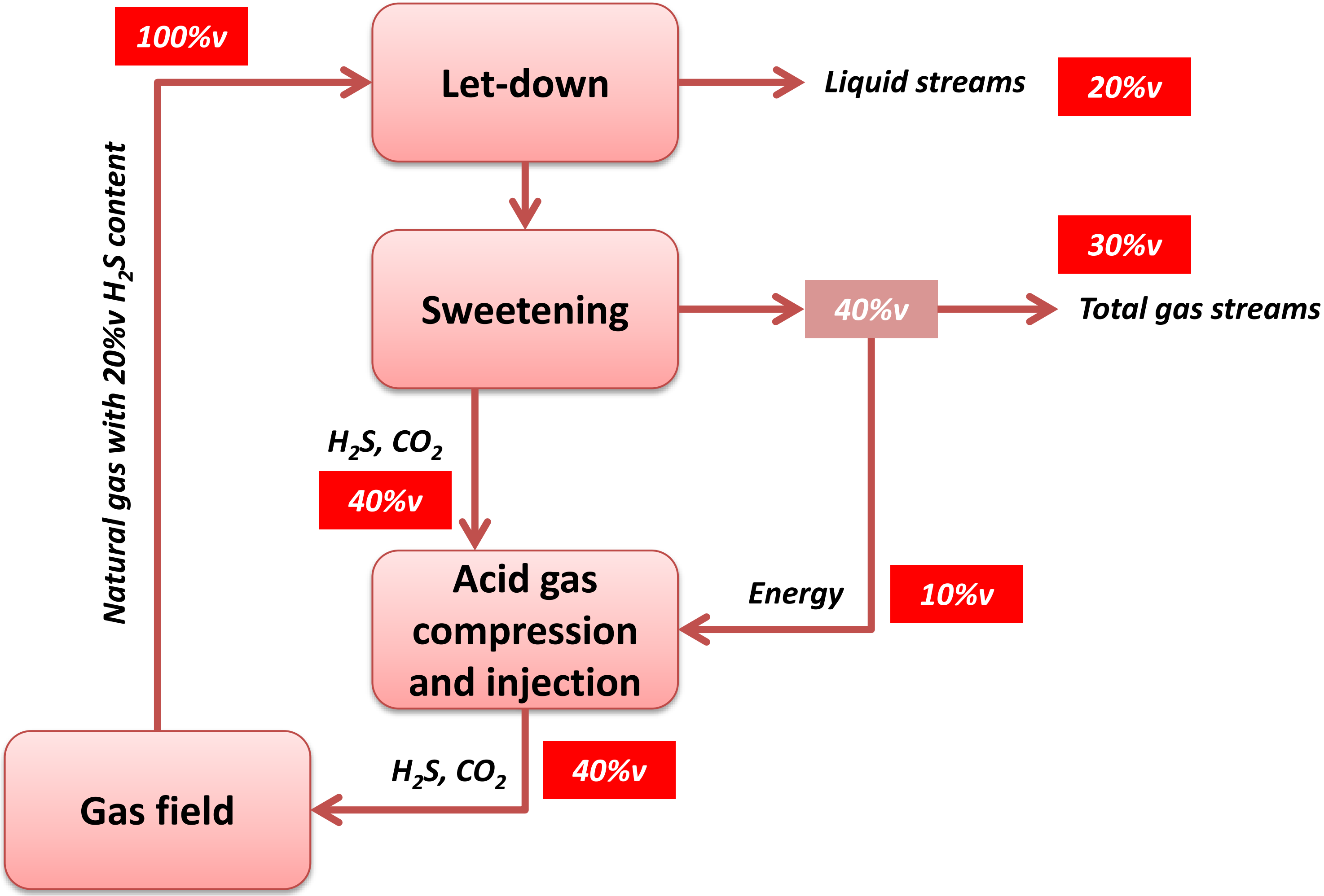
Potential application areas

- Coal
  - **Coal gasification**
  - Coke oven gas
- Shale
  - **Shale oil**
  - Shale gas
- Oil&gas
  - **Natural gas**
  - Crude oil
  - Heavy oil
- Renewables
  - Biomass/biogas
  - **Geothermal**

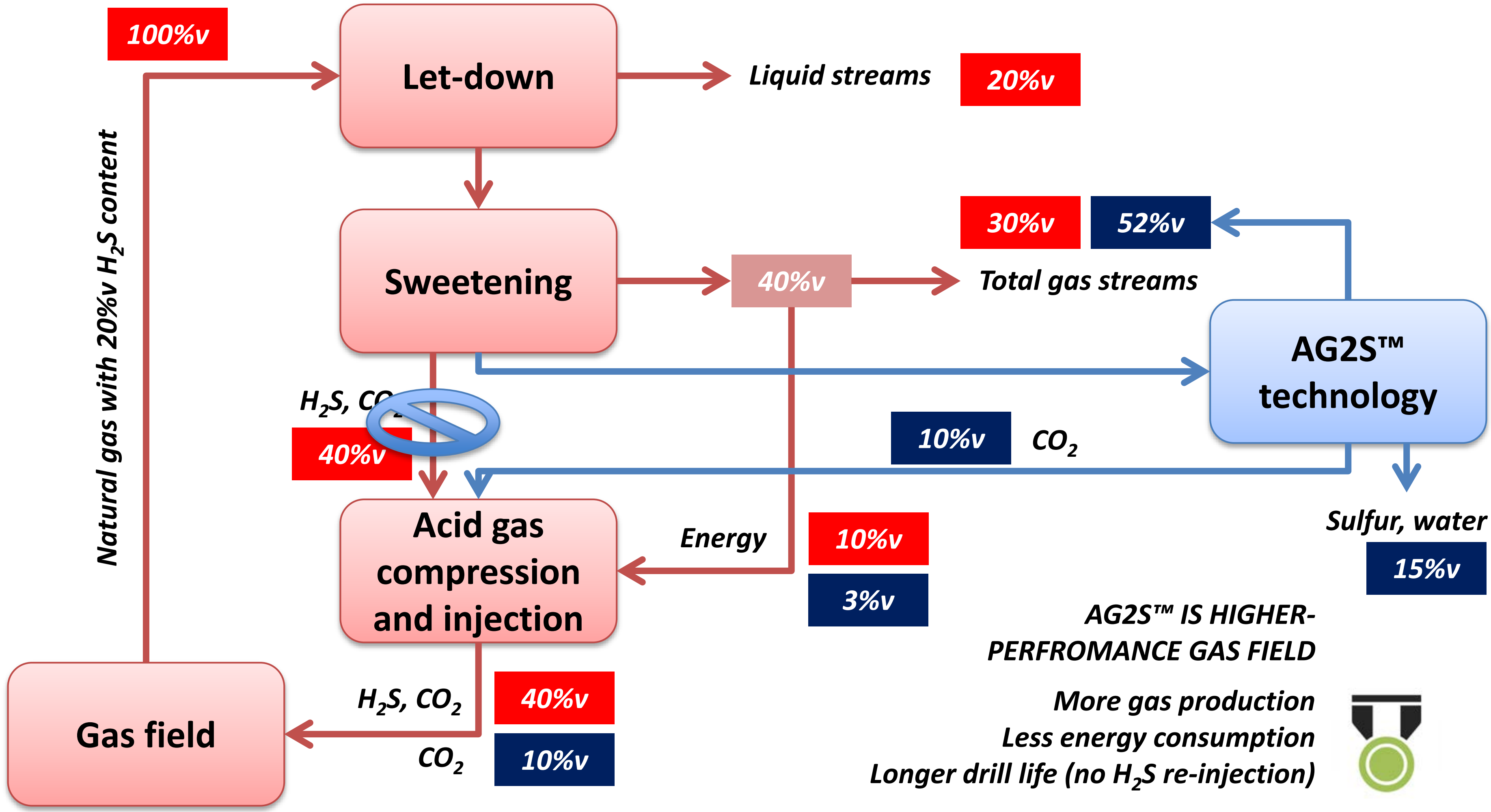
- Hydrogen
  - Power generation
  - Hydrotreating
  - Gasification
  - **Reforming**
  - Fuel
  - …
- Syngas
  - Ammonia
  - Synthetic fuels (GTL)
  - Methanol/DME
  - Acetic acid
  - Superior alcohols/ethers/acids

- CO
  - Formylation
  - Carbonylation
  - Metals
  - Metal carbonyls
  - Acetic acid
  - Superconductors
- Sulfur
  - Sulfuric acid
  - Claus
  - **Hydrodesulfurization**

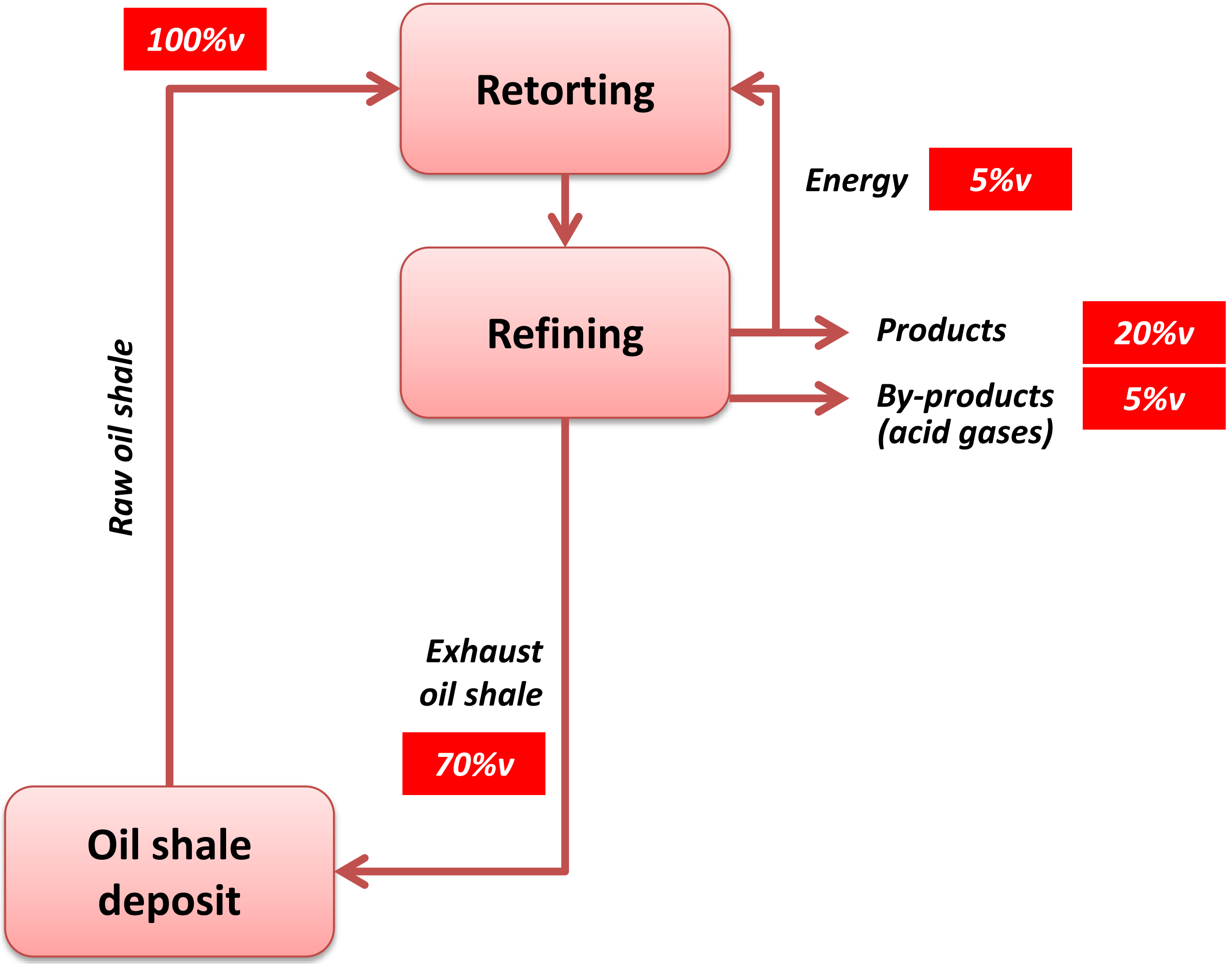
Natural gas field



Natural gas field

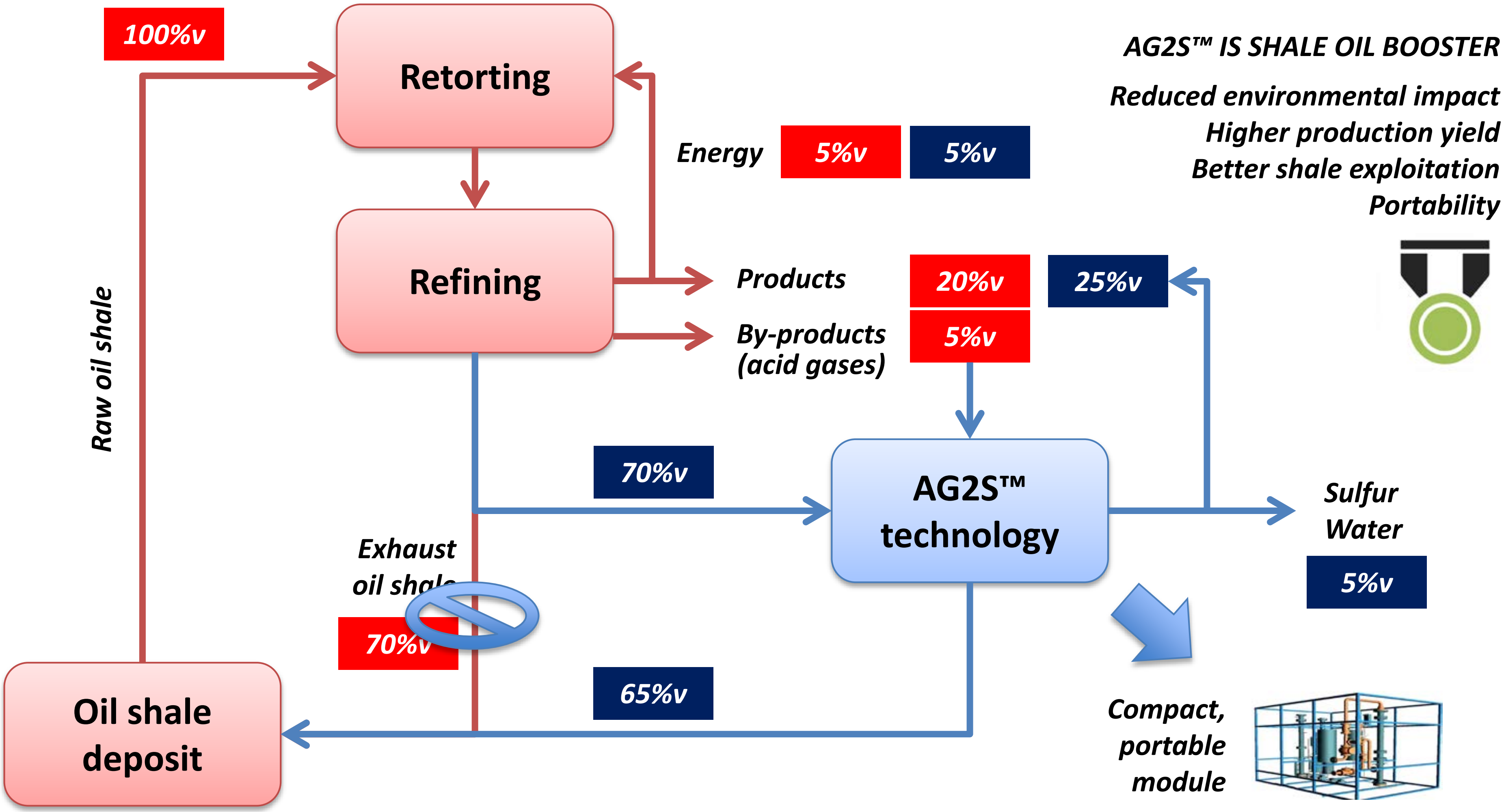


Oil shale



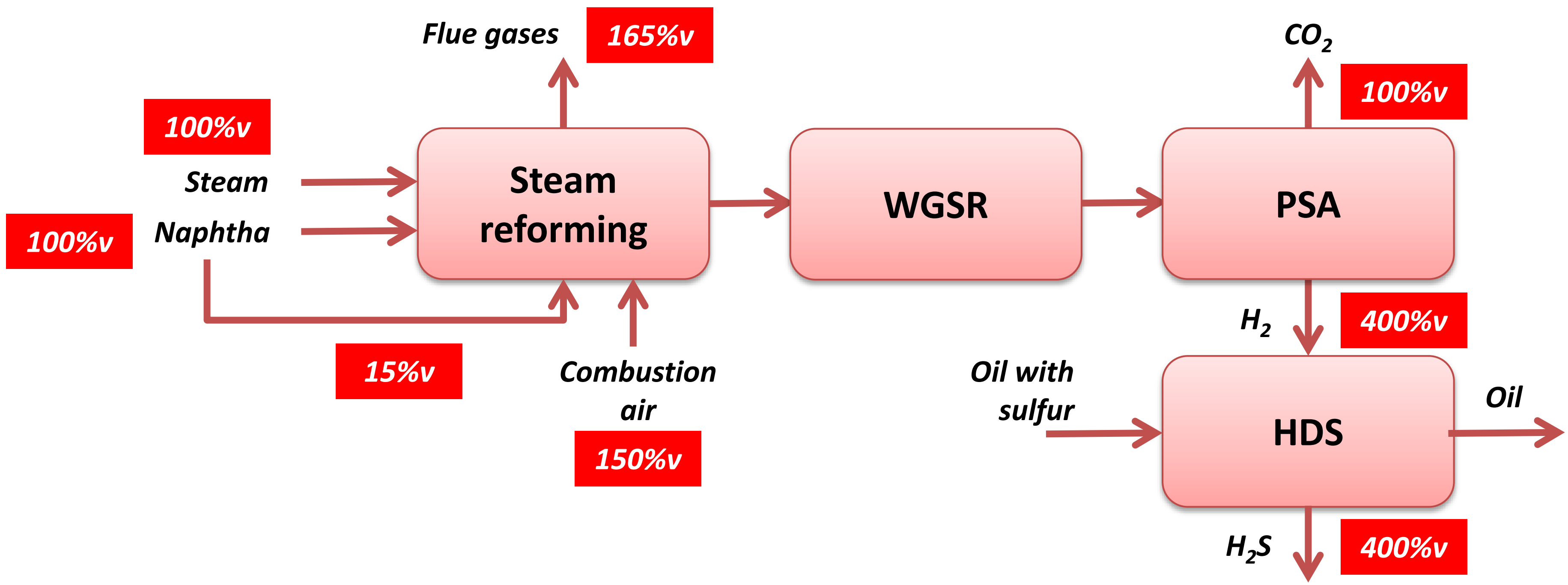
100%v
Retorting
Energy
5%v
Refining
Products
20%v
By-products
(acid gases)
5%v
Raw oil shale
Exhaust
oil shale
70%v
Oil shale
deposit

Oil shale

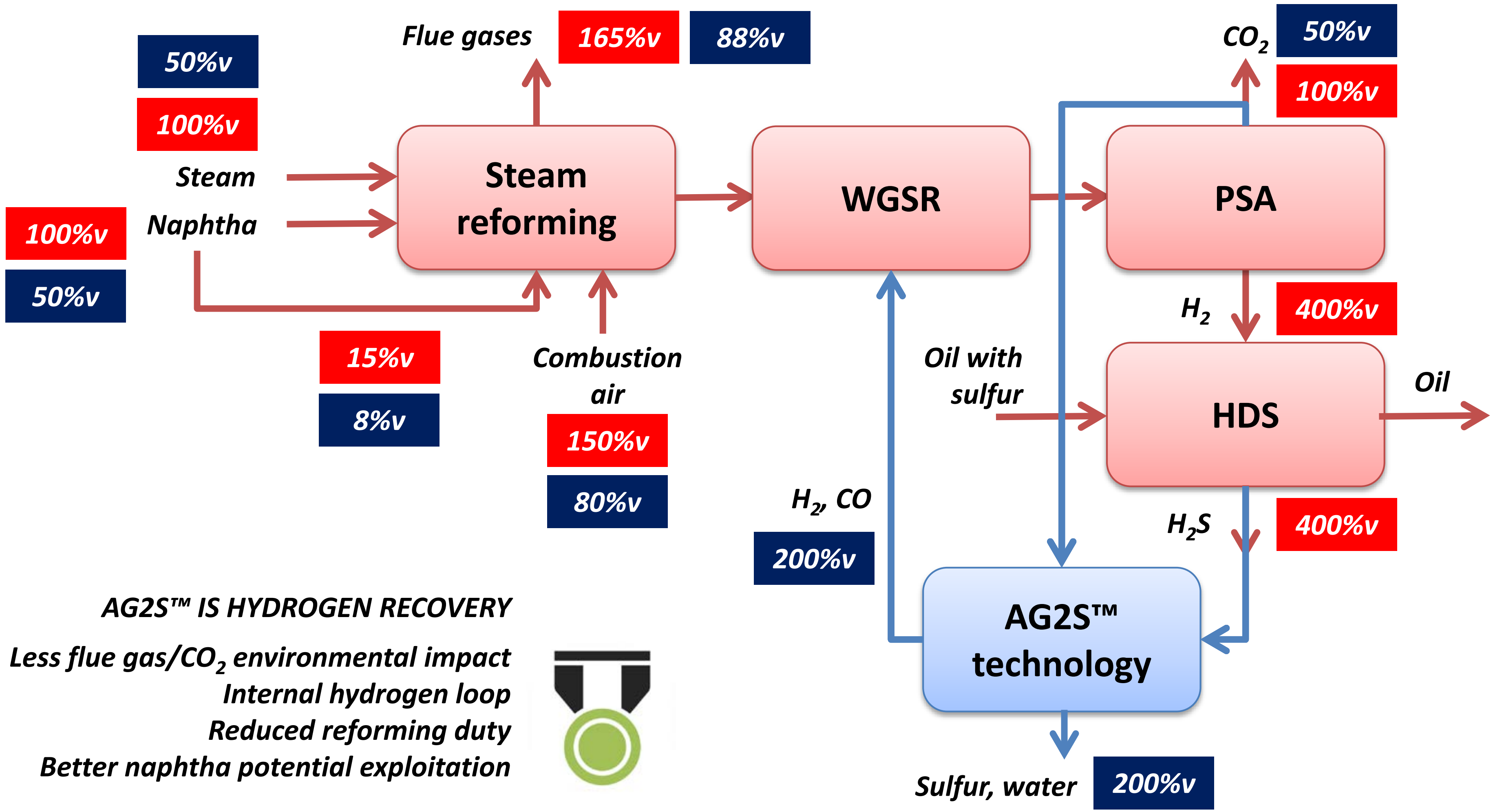


100%v
Retorting
Raw oil shale
Energy
5%v
5%v
Refining
Products
20%v
25%v
By-products
(acid gases)
5%v
AG2S™ IS SHALE OIL BOOSTER
Reduced environmental impact
Higher production yield
Better shale exploitation
Portability
70%v
AG2S™
technology
Sulfur
Water
5%v
Exhaust
oil shale
70%v
65%v
Oil shale
deposit
Compact,
portable
module

Oil refining – HDS/Reforming



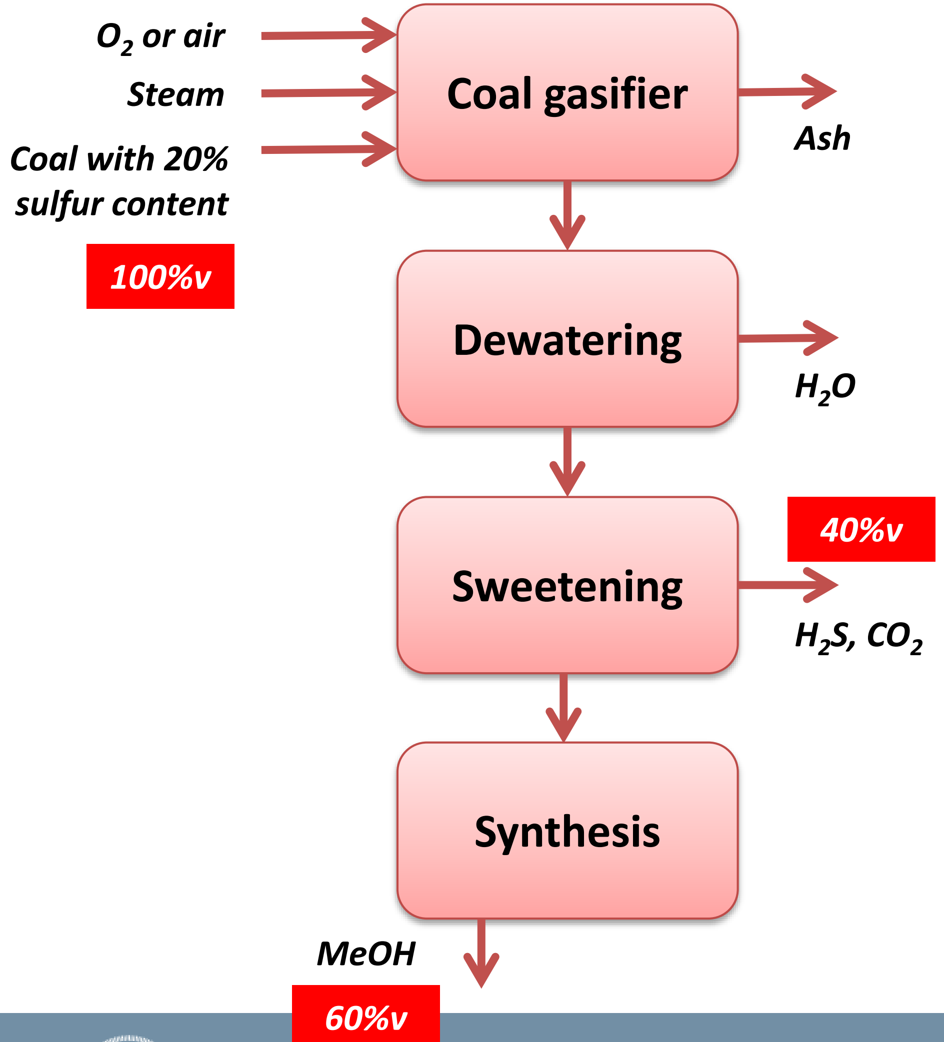
Oil refining – HDS/Reforming



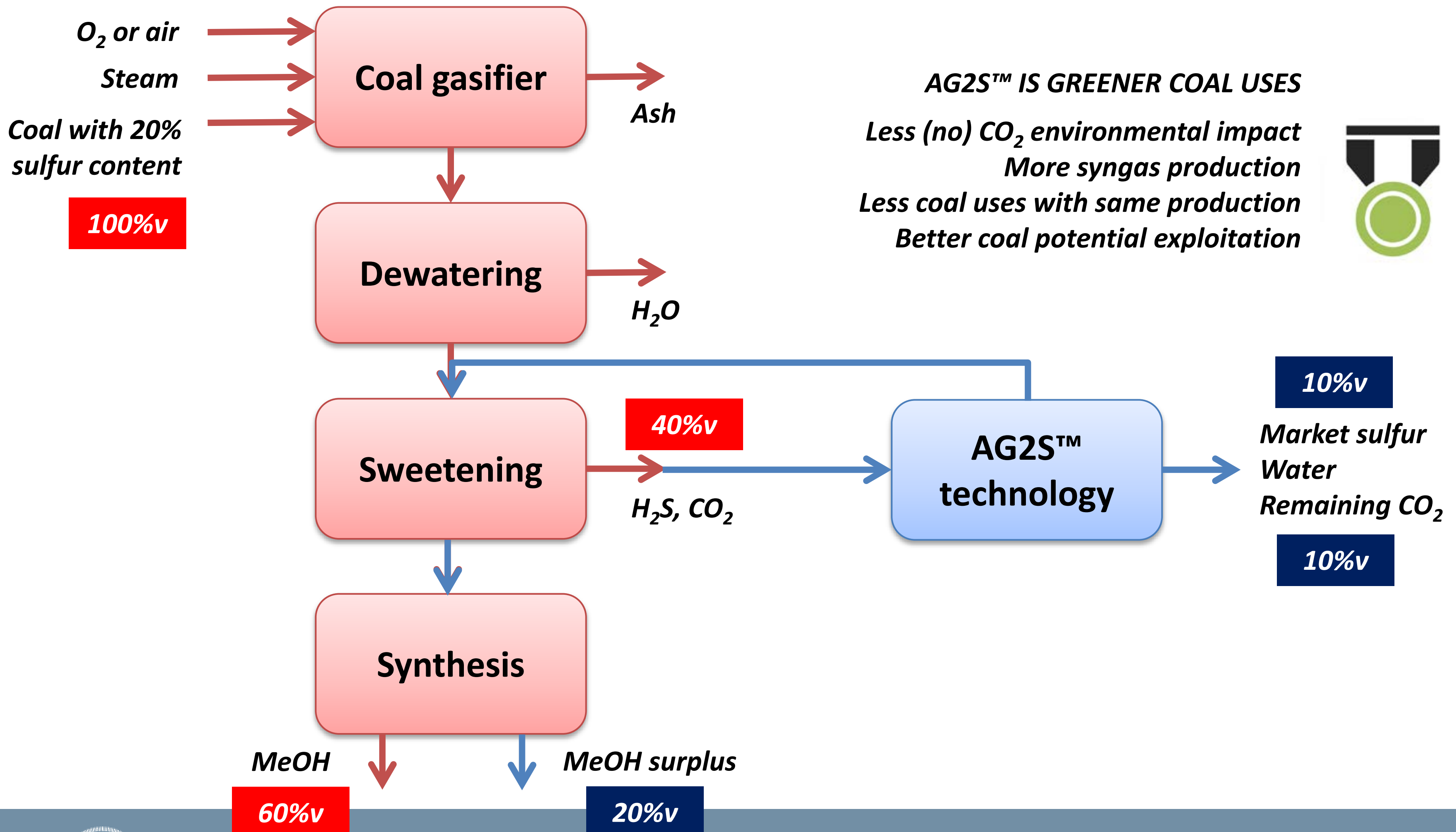
AG2S™ IS HYDROGEN RECOVERY

Less flue gas/CO_2 environmental impact
Internal hydrogen loop
Reduced reforming duty
Better naphtha potential exploitation

CO_2-free coal-to-methanol process



CO_2-free coal-to-methanol process



Geothermal power generation

Greener and greener…

Geothermal power generation

Geothermal power is considered to be a sustainable, renewable source of energy

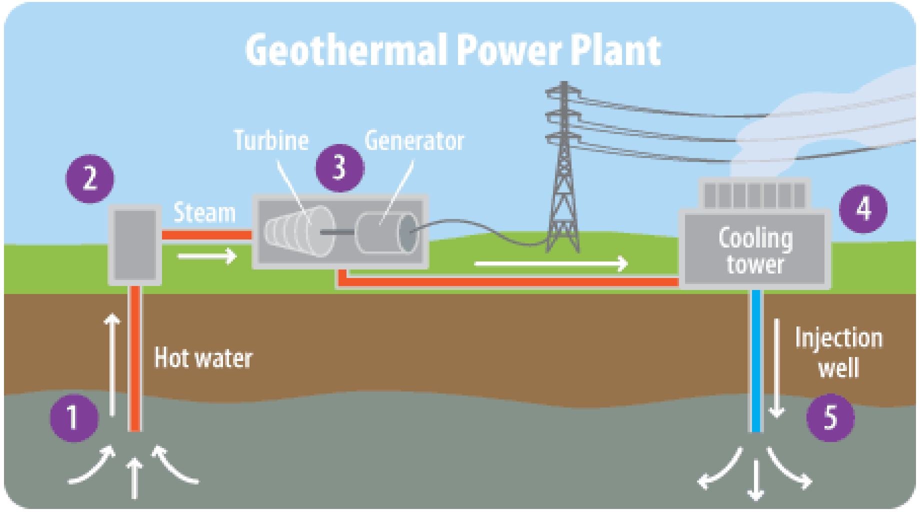
Tomasini-Montenegro C. et al., 2017, Life cycle assessment of geothermal power generation technologies: An updated review, Applied Thermal Engineering, 114, 1119-1136.

The greenhouse gas emissions → 45 gCO2/kWh

Geothermal electricity → use in more than 24 countries

Geothermal heating → use in more than 70 countries

Holm A., Blodgett L., Jennejohn D., Gawell K., 2010, Geothermal energy: international market update, Geothermal energy association, 7.

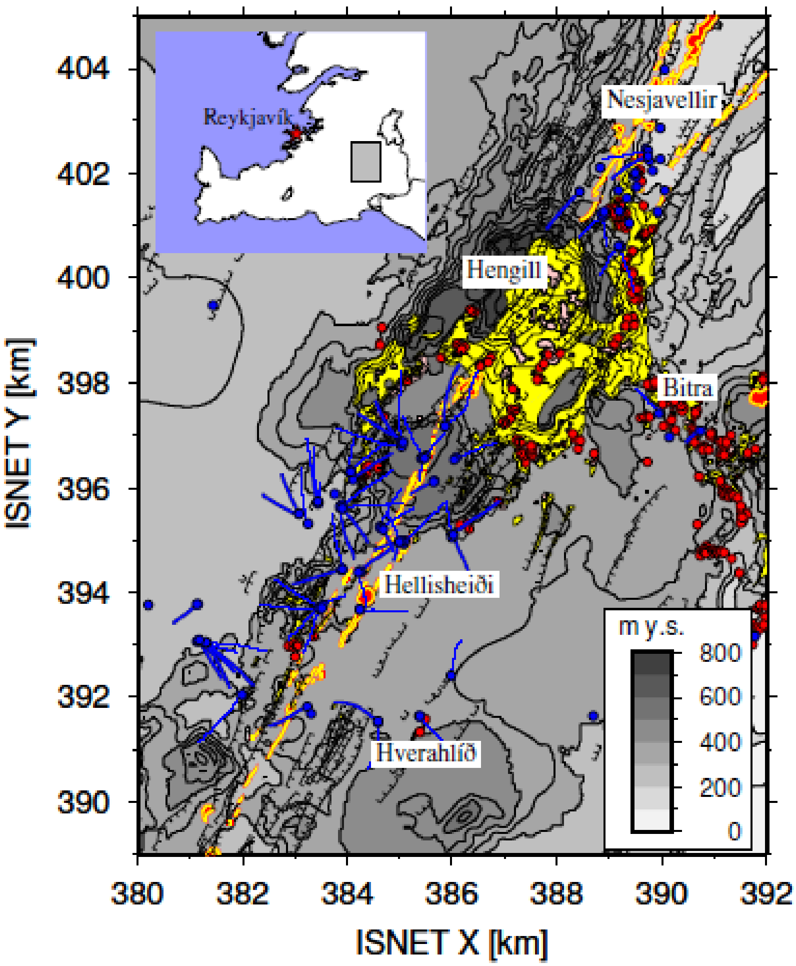


In 2015, the worldwide geothermal power capacity amounts to 12.8GW

Global geothermal power capacity is expected to reach 14.5–17.6GW by 2020

Ruggero B. (Ed.), 2017, Perspectives for Geothermal Energy in Europe, World Scientific.

Case studies (Iceland)



Case I: Nesjavellir power station

- Produce 290 MWth and 120 MWe
- Annual emission of H_2S was around 11300 tons
- Annual emission of CO_2 in was around 18600 tons

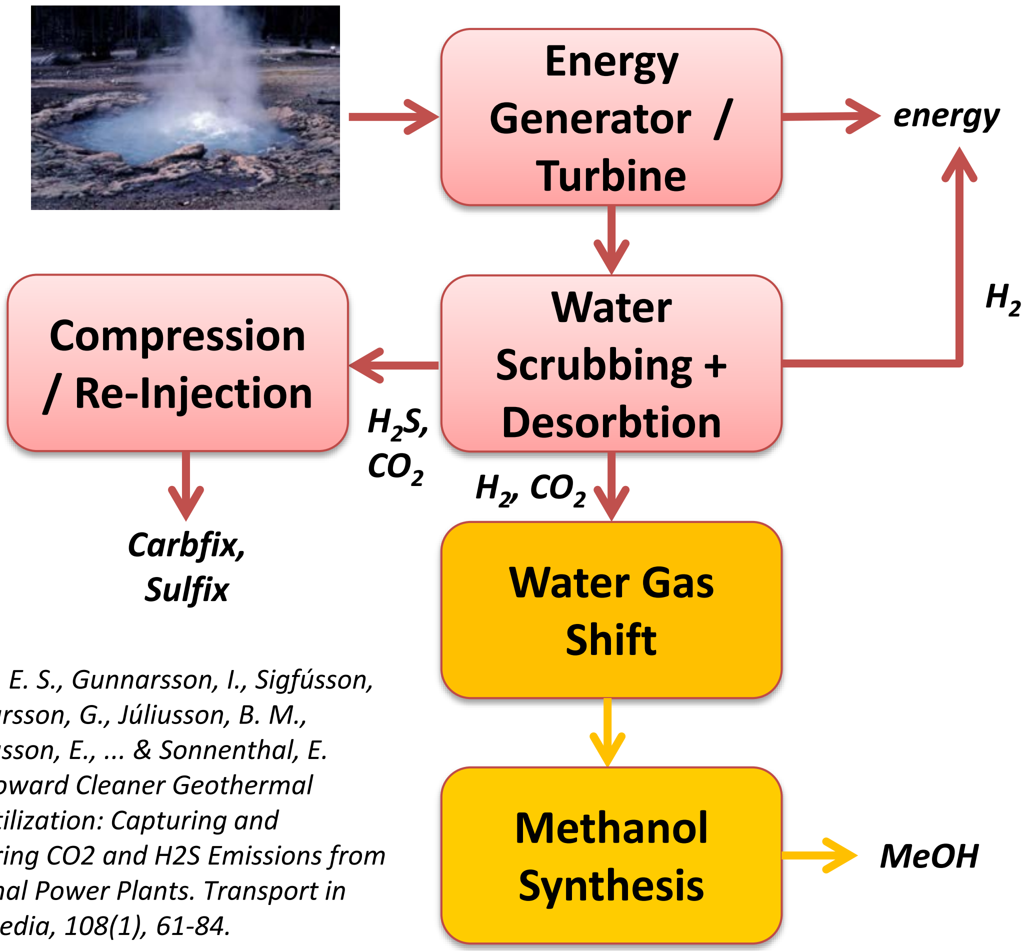
Case II: Hellisheiði power station

- Produce 303 MWth and 133 MWe
- Annual emission of H_2S was around 16900 tons
- Annual emission of CO_2 in was around 43200 tons

Composition of geothermal gas emitted from the two power station

	CO_2	H_2S	H_2	CH_4
Nesjavellir	43.0%	33.9%	23.0%	0.2%
Hellisheiði	58.1%	29.4%	12.3%	0.2%

Existing (Traditional) Geothermal Power Plant



Aradóttir, E. S., Gunnarsson, I., Sigfússon, B., Gunnarsson, G., Júliusson, B. M., Gunnlaugsson, E., ... & Sonnenthal, E. (2015). Toward Cleaner Geothermal Energy Utilization: Capturing and Sequestering CO2 and H2S Emissions from Geothermal Power Plants. Transport in Porous Media, 108(1), 61-84.

Sequestration Technologies

CarbFix

- dissolve the gases into formation fluids and well water during injection (i.e.) solubility trapping
- promotes carbonation of the host rock→facilitates sequestration of CO_2 and H_2S in the subsurface

SulFix

- In situ H_2S mineral sequestration in basaltic rocks
- similar to CarbFix. The main difference between
- Dissolved gases are injected back into the high-temperature geothermal reservoir (below 800-m depth)

Existing (Traditional) Geothermal Power Plant: Case I

Energy Generator / Turbine → *energy*

Water Scrubbing + Desorbtion

→ *H_2S, CO_2* → **Compression / Injection** → *Carbfix, Sulfix*

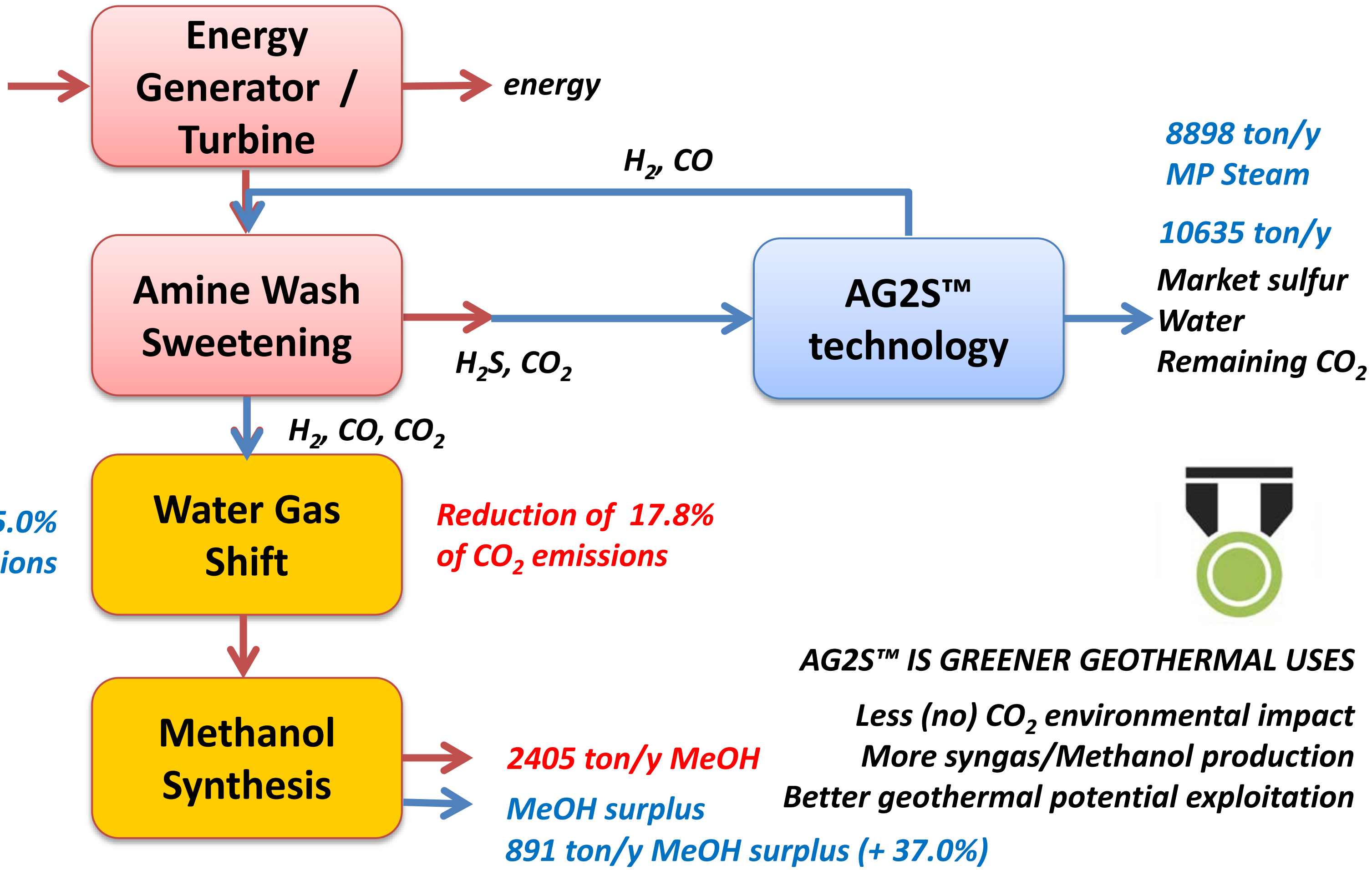
→ *H_2, CO_2* → **Water Gas Shift** → **Methanol Synthesis** → *2405 ton/y MeOH*

Compression cost of the outlet acid gases emissions up to 40 bar

Reduction of 17.80 % of CO_2 emissions

	I	
	n/n	*m/m*
H2	23.00%	1.50%
CH4	0.10%	0.10%
CO2	43.00%	61.21%
H2S	33.90%	37.19%
MW [g/mol]	30.94	
m [kt/y]	30.38	

AG2S™ Geothermal Power Plant: Case I



AG2S™ IS GREENER GEOTHERMAL USES

Less (no) CO_2 environmental impact
More syngas/Methanol production
Better geothermal potential exploitation

AG2S™ Geothermal Power Plant: Case II

	I	
	n/n	*m/m*
H2	12.30%	0.71%
CH4	0.20%	0.09%
CO2	58.10%	71.32%
H2S	29.40%	27.90%
MW [g/mol]	35.84	
m [kt/y]	30.57	

Energy Generator / Turbine → *energy*

H_2, CO

Amine Wash Sweetening → *H_2S, CO_2* → **AG2S™ technology**

5632 ton/y O_2

15906 ton/y

Market sulfur
Water
Remaining CO_2

13376 ton/y
MP Steam

H_2, CO, CO_2

Water Gas Shift

Reduction of 11.8 % of CO_2 emission (5082 ton/y)

Methanol Synthesis

2218 ton/y MeOH

1563 ton/y MeOH surplus (+ 70.5%)

	Hellsheidi
Inlet H_2S/CO_2 Ratio	4.0
H_2 Produced [kg/h]	17.5
CO Produced [kg/h]	267.7
CO_2 Reuse [%]	7.5
H_2S Converted [%]	100.00

Conclusions

We are **preventing CO_2 formation**

Thanks to renewables

We are **capturing CO_2**

by pre-/post-combustion CCS technologies

We definitely are **not yet reusing CO_2** as in our possibilities

Just less than 1% is currently reused

Demonstration of **AG2S™** technology potential and its application areas

Better exploitation of (fossil and renewable) sources

Thanks for the kind attention

Flavio Manenti

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Charity Trustee at the European Federation of Chemical Engineering (**EFCE**)
President-elect of the Computer Aided Process Engineering (***CAPE***), EFCE's Working Party
UEFA-licensed & Federal Soccer Coach (***U13, SGS Italia***)
Executive Board Member of EFCE, AIDIC, AIAC, CAPE-WP

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