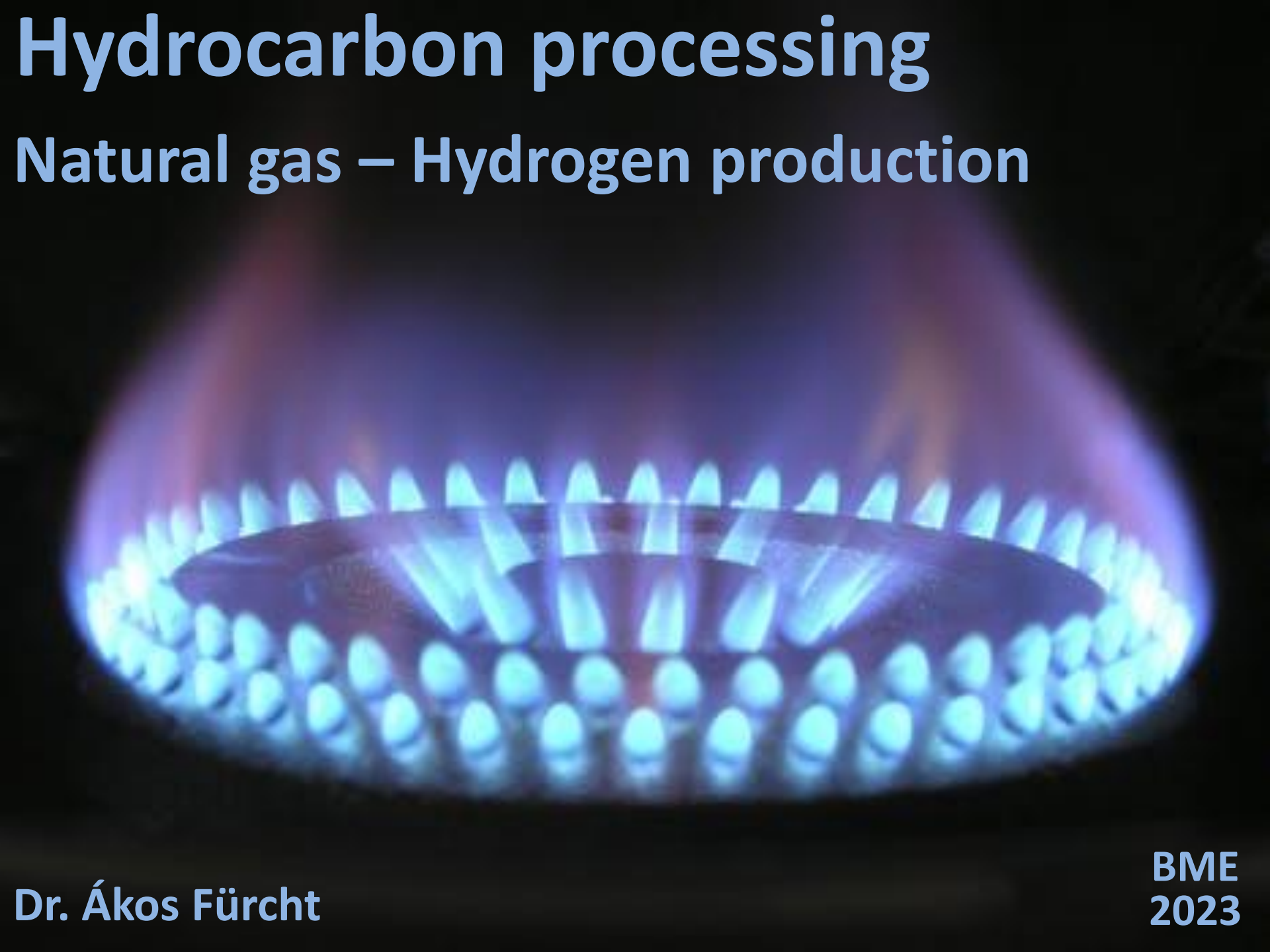
Hydrocarbon processing

Natural gas – Hydrogen production



Dr. Ákos Fürcht

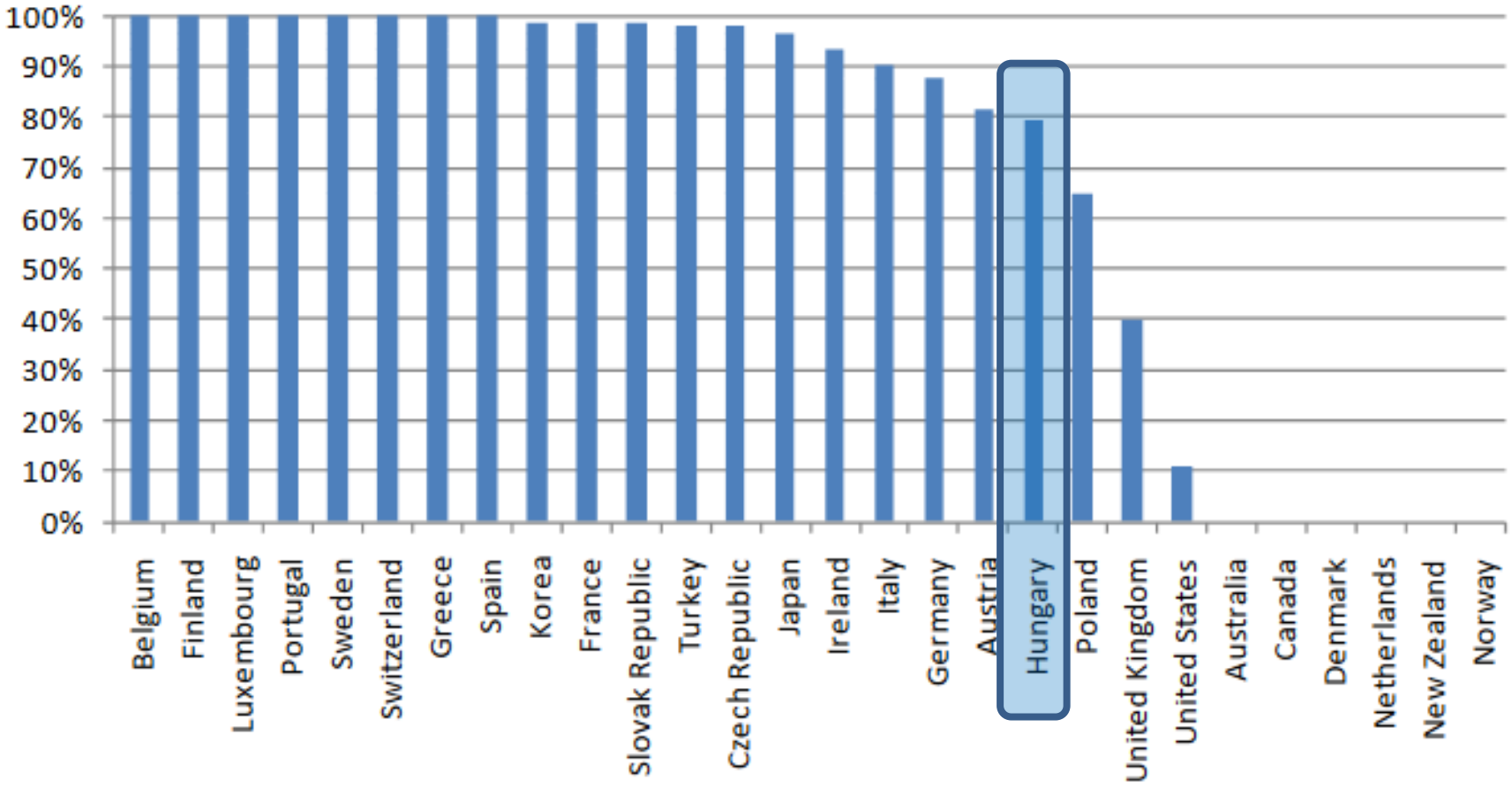
BME
2023

1.
Natural gas supply security in the IEA member countries

International Energy Agency

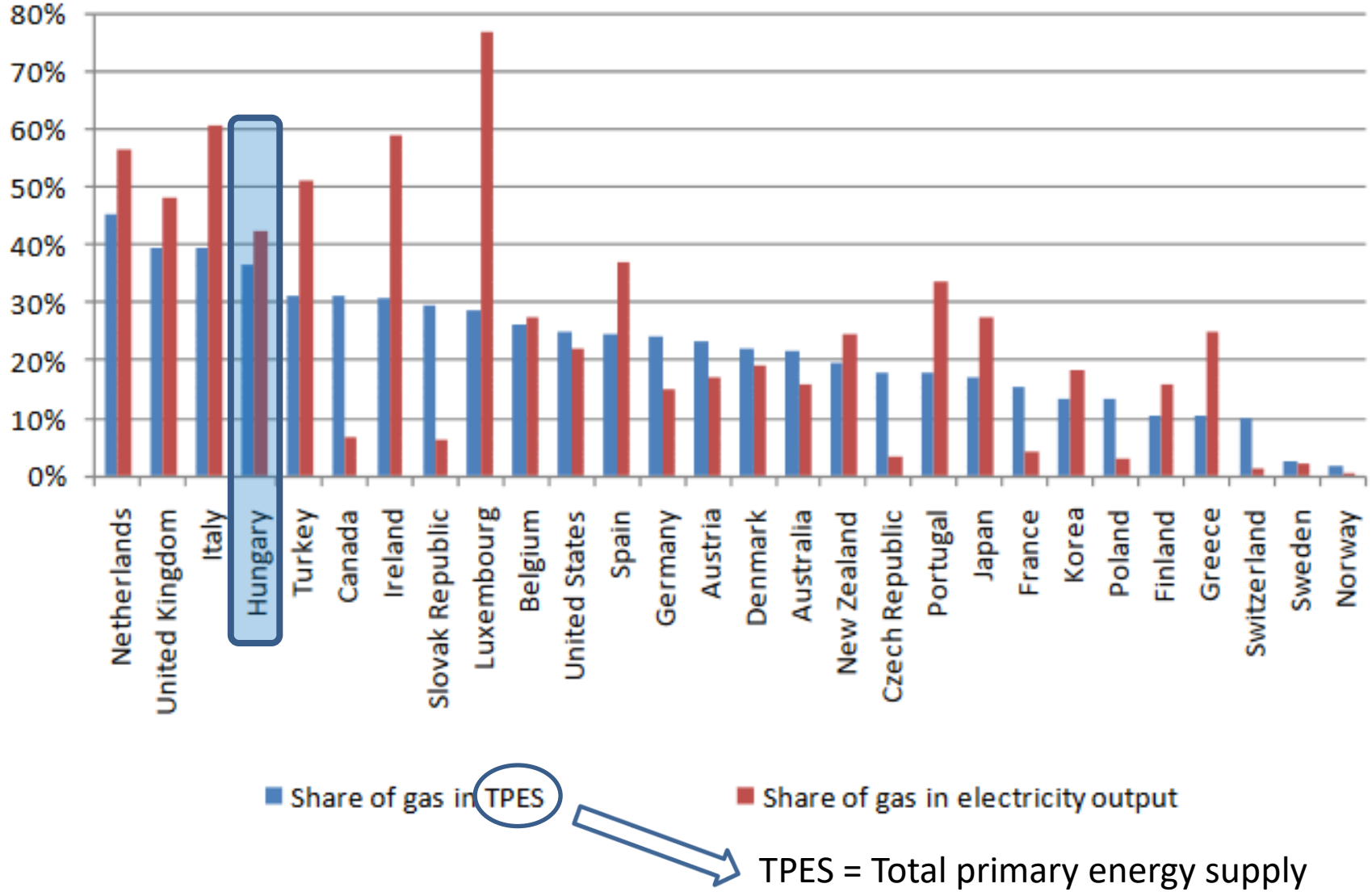
- IEA: International Energy Agency[1]
- **Independent organisation**, founded in 1974
- Membership conditions:
  - to be **net crude oil importer**
  - **reserves of** crude oil and/or product equivalent to **90 days** of the prior year's average net oil imports to be available
  - the government (even if it does not own those stocks directly) must have immediate access to the **strategic reserves**
  - legislation and measures in place to ensure that all oil companies operating under the country's jurisdiction **report information** as is necessary
- Made up of 29 member countries (see later)
- **Operating focus areas**:
  - Energy Security: Promoting diversity, efficiency, flexibility and reliability
  - Economic Development: Supporting free markets
  - Environmental Awareness: Analysing policy options to offset the impact of energy production and use on the environment
  - Engagement Worldwide: Working closely with partner countries

Natural gas **import dependence**



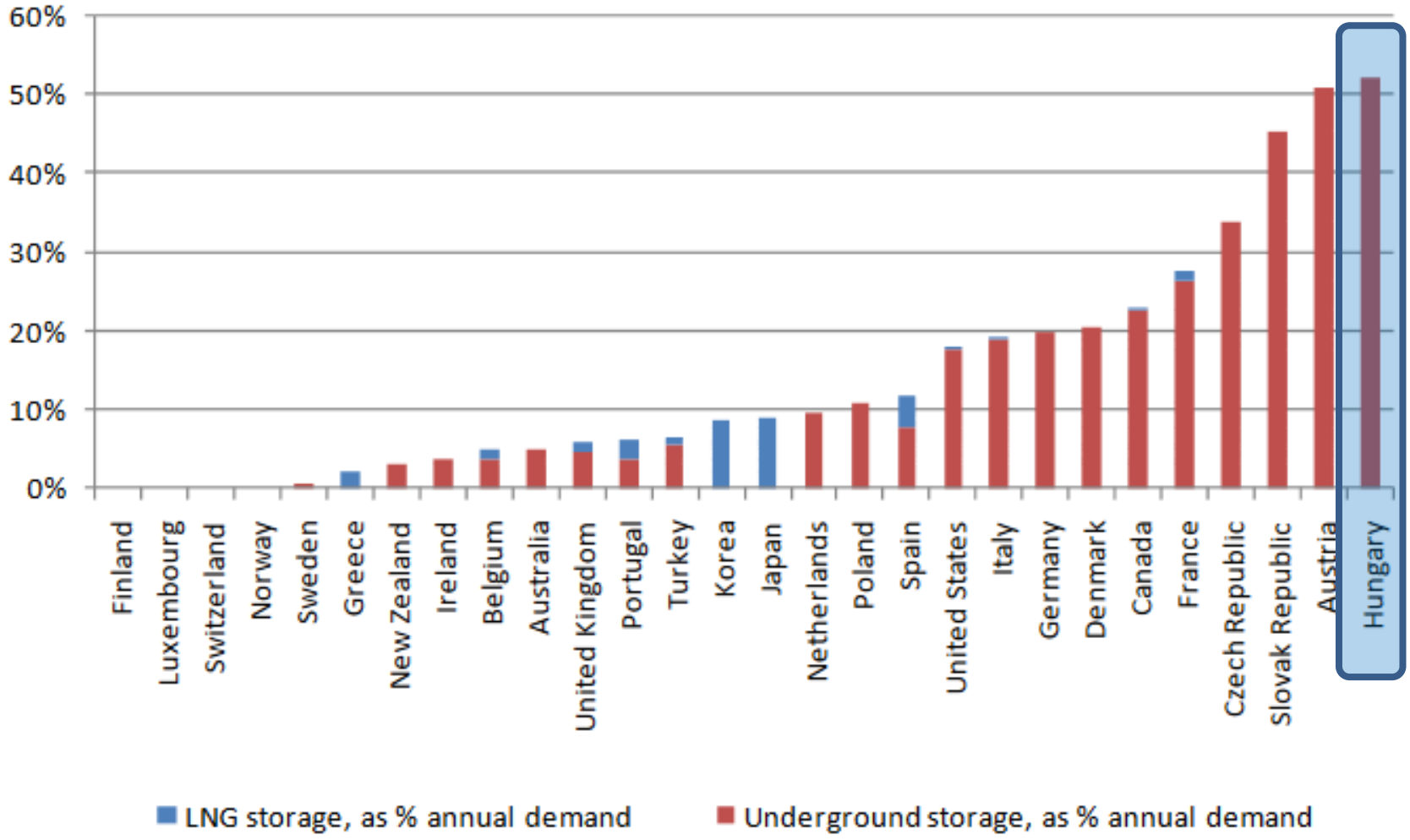
Source: IEA Gas Emergency Policy 2011[2]

Importance of natural gas in the energy mix



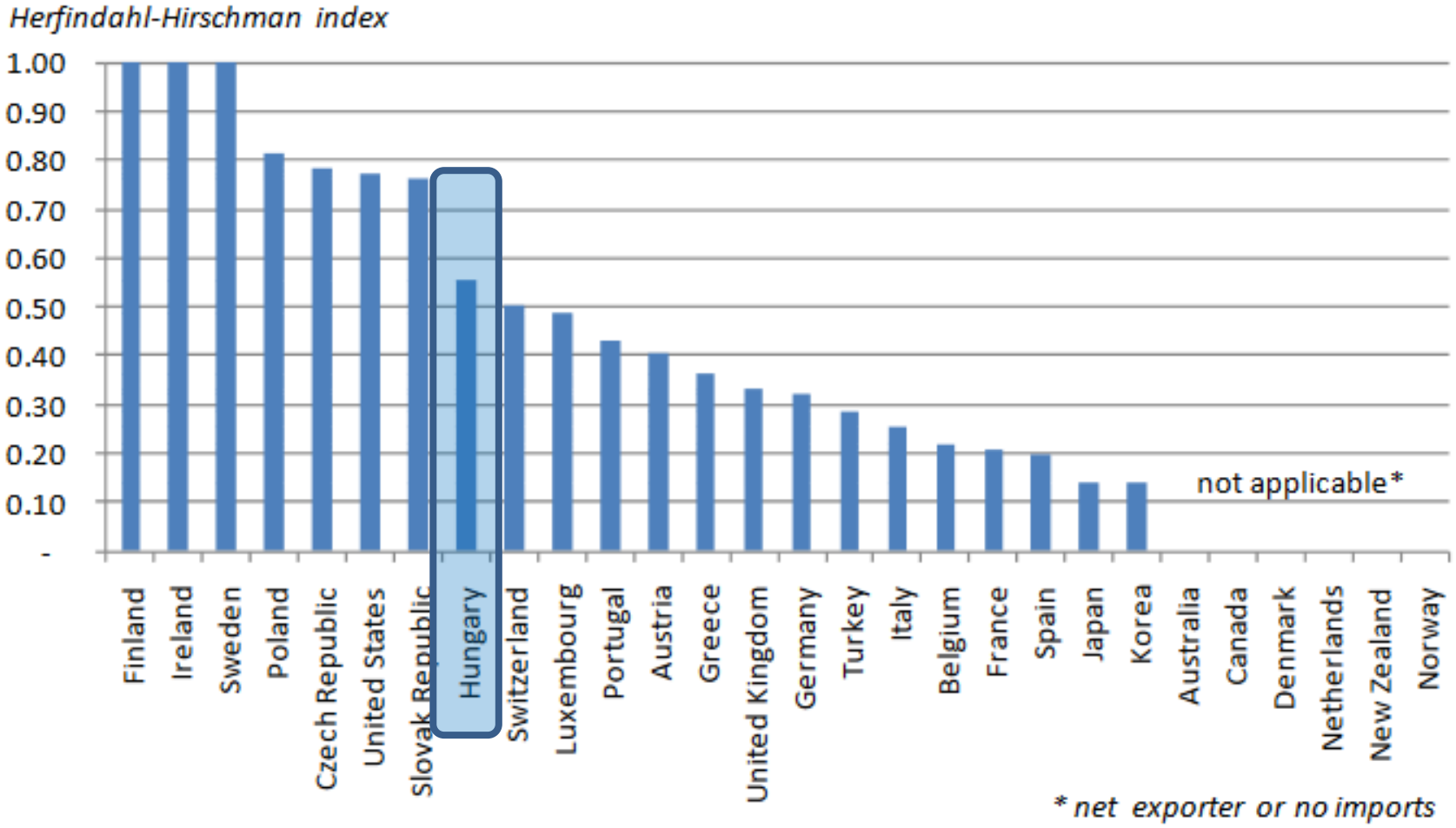
Source: IEA Gas Emergency Policy 2011

Natural gas **storage capacities**



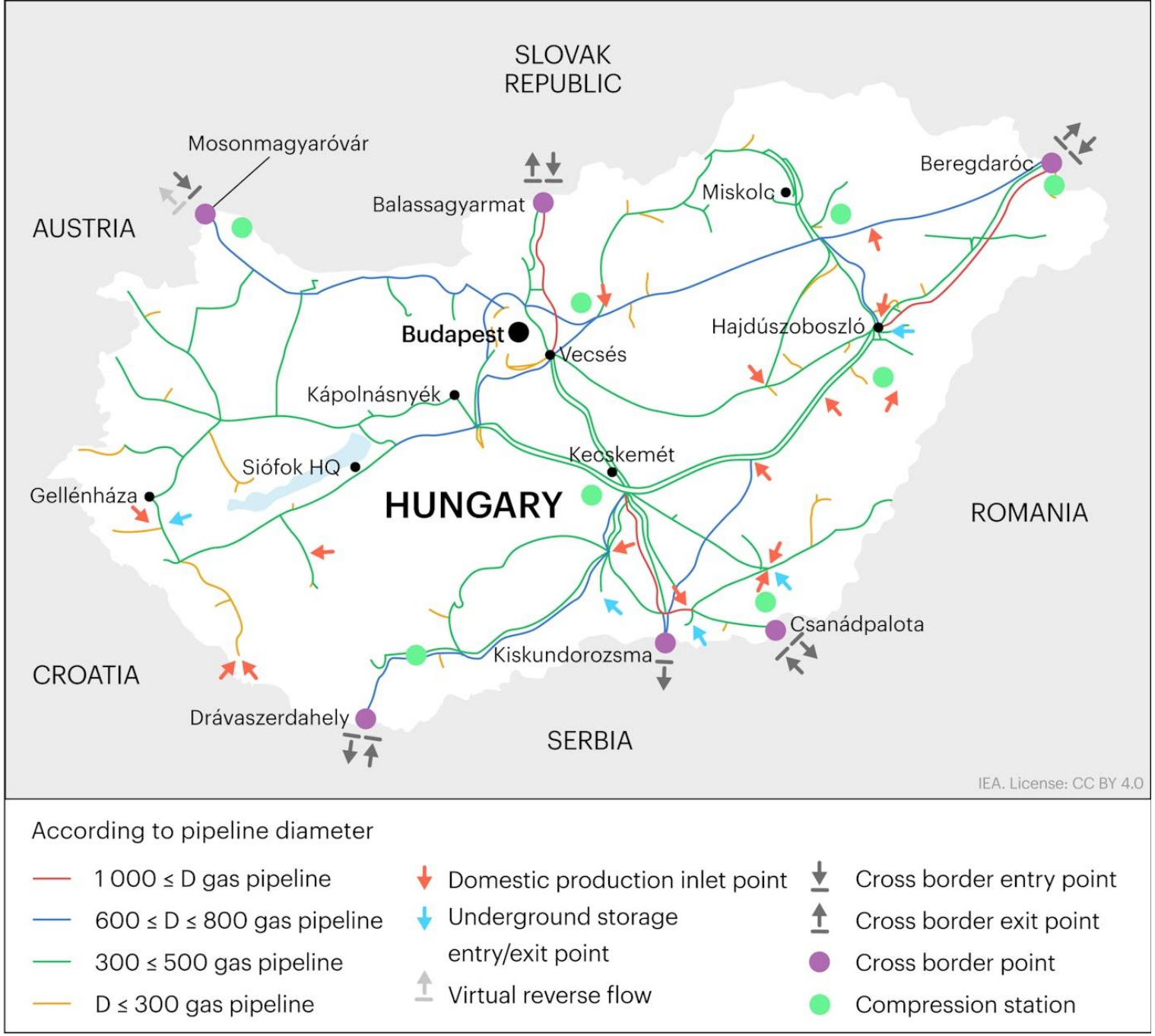
Source: IEA Gas Emergency Policy 2011

Import diversity of NG supplies



Note: The Herfindahl-Hirschman Index, an economic concept widely applied in anti-trust and competition law, is defined in this context as the sum of the squares of the market shares of the countries of imports for any given country. The index ranges from 0 (high diversified supplies) to 1.0 (one monopolistic supplier).

Source: IEA Gas Emergency Policy 2011



Source: IEA, Hungary's natural gas infrastructure, 2022

Southern Gas Corridor: Combination of three pipelines

- South Caucasus Pipeline (SCP): Azerbaijan and Georgia,
- Trans Anatolian Pipeline (Tanap): Turkey,
- Trans Adriatic Pipeline (Tap): Greece, Albania, Italy

Source: Caucasus Business Week[8]

Southern Gas Corridor is being constructed in Turkey

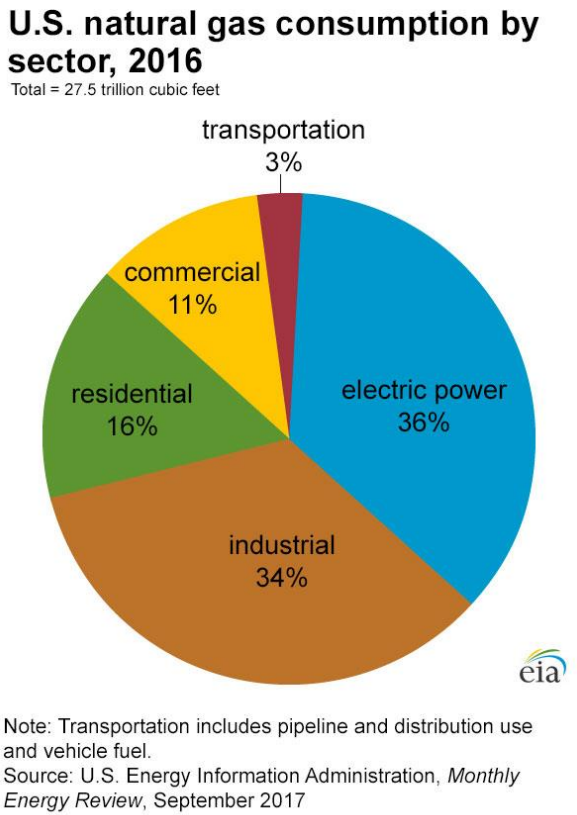
- The pipeline is supposed to reduce the EU's dependence on Russian gas.
- Transports NG from Azerbaijan to the EU (Italy) via Turkey (3500 km)
- A total estimated cost of **45 bn$** project (for reference: the 10 mt/y STAR refinery project[4] cost in Turkey is estimated as **6,5-8,5 bn$**)

Source: Climate Home News[3]

2.
Natural gas

Attributes of natural gas[5,6]

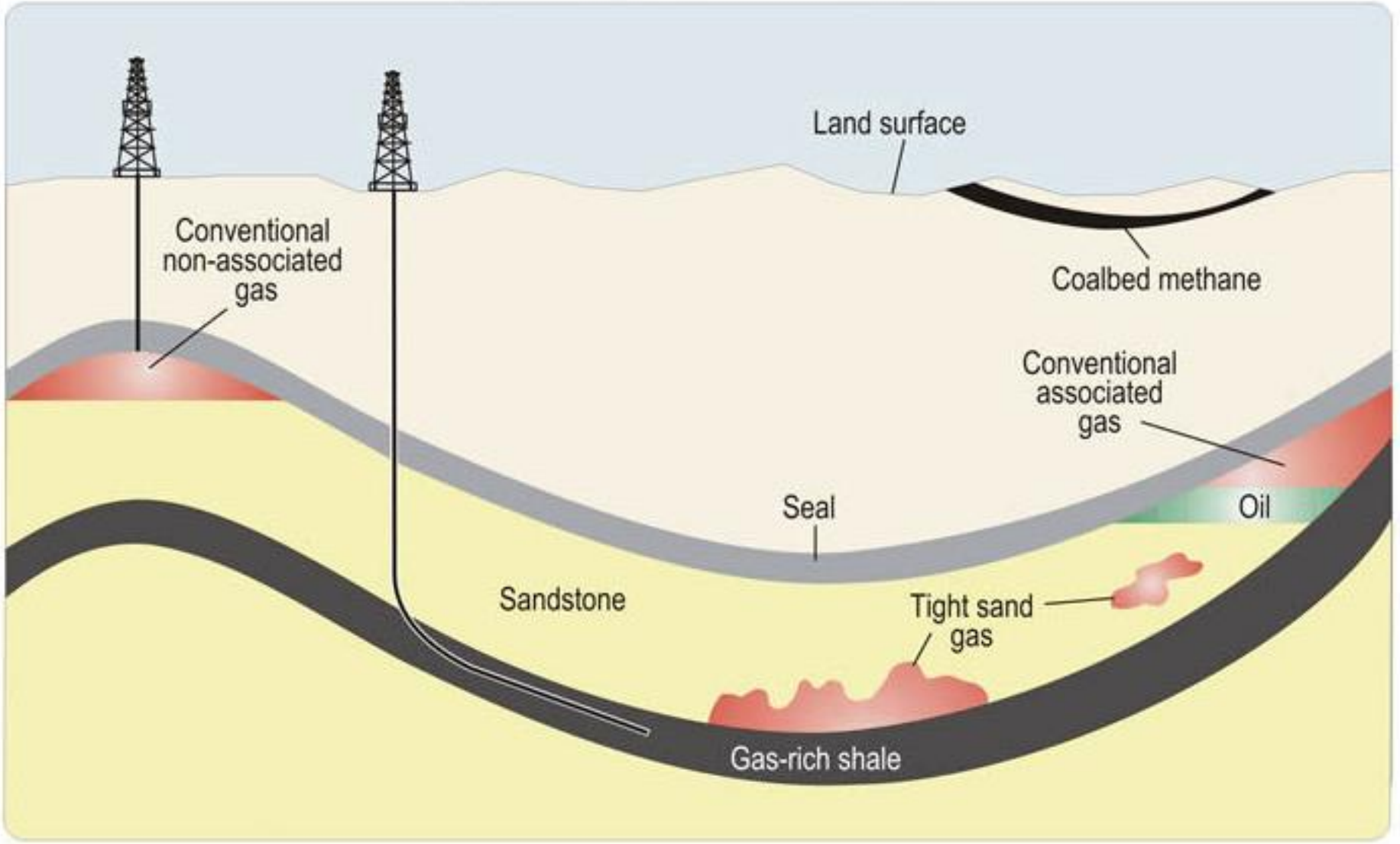
- Pure form: colourless, odourless
- The „cleanest” fossil fuel – lowest specific CO_2 emission (half of the coal’s emission)
- In liquid state the volume is 1/600 compared to gas phase
- **LNG** = Liquefied Natural Gas
- **Usage:**
  - Energy production (heat/electricity)
  - **Feedstock to hydrogen production** (in crude oil refining)
  - **Petrochemical feedstock** (via synthesis gas)
  - **Fertilizer feedstock** (via ammonia synthesis)



Formation and **accumulation**

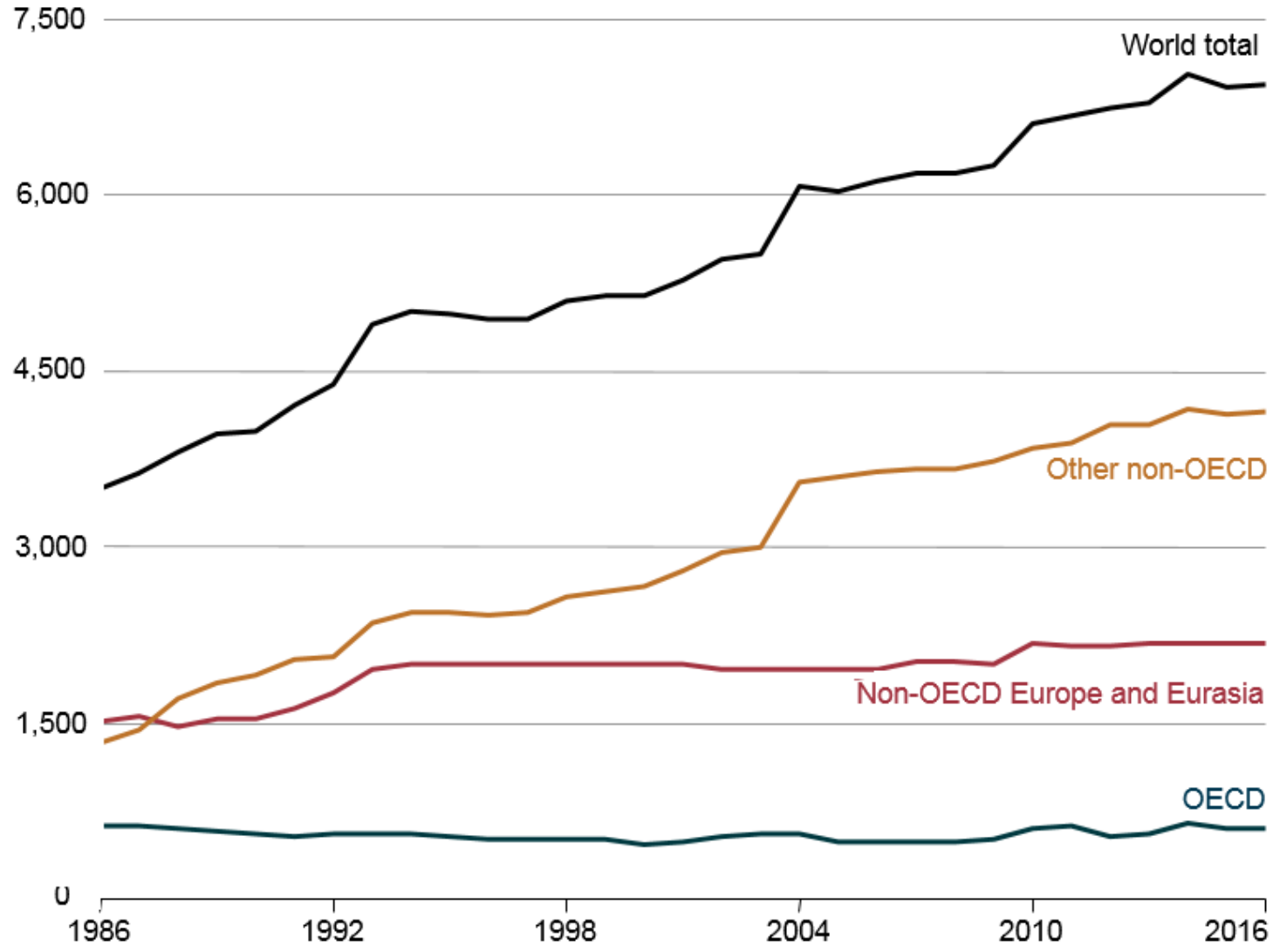
- The natural gas is the **decomposition product** of plants, animals, microorganisms lived millions of years ago
  - **Termogen process**: down in the earth under high pressure and temperature conditions the organic material was transformed during the times
    - During the times inorganic material sedimented over the organic layer, which pushed it deeper and deeper (higher pressure and temperature) and destroyed its original chemical structure
    - More oil is formed in shallower areas (bigger molecules)
    - More gas in deeper areas (more severe conditions)
    - As a consequence, oil occurs predominantly mixed with gas
  - **Biogen process**: methane forming microorganisms do destroy the organic material (surface-close formation)
- The formed gas (oil) is moving towards the surface (**migration**), until a sealing geological formation hinders the movement (**capturing**); the collected material forms a **reservoir**

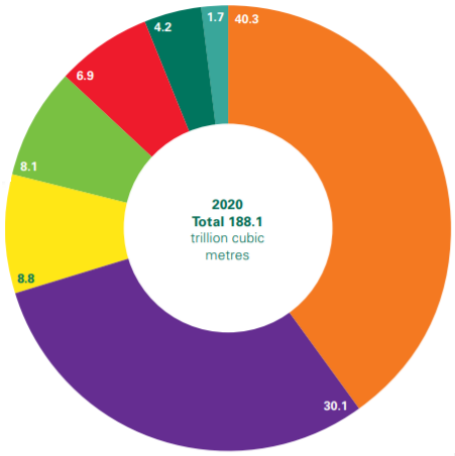
Hydrocarbon occurence types

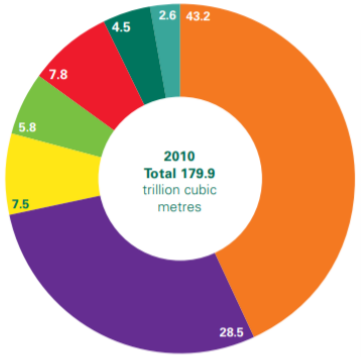


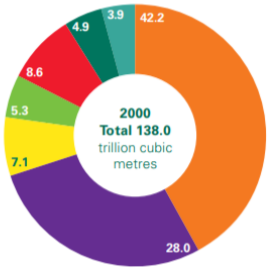
Source: EIA

Proved NG reserves









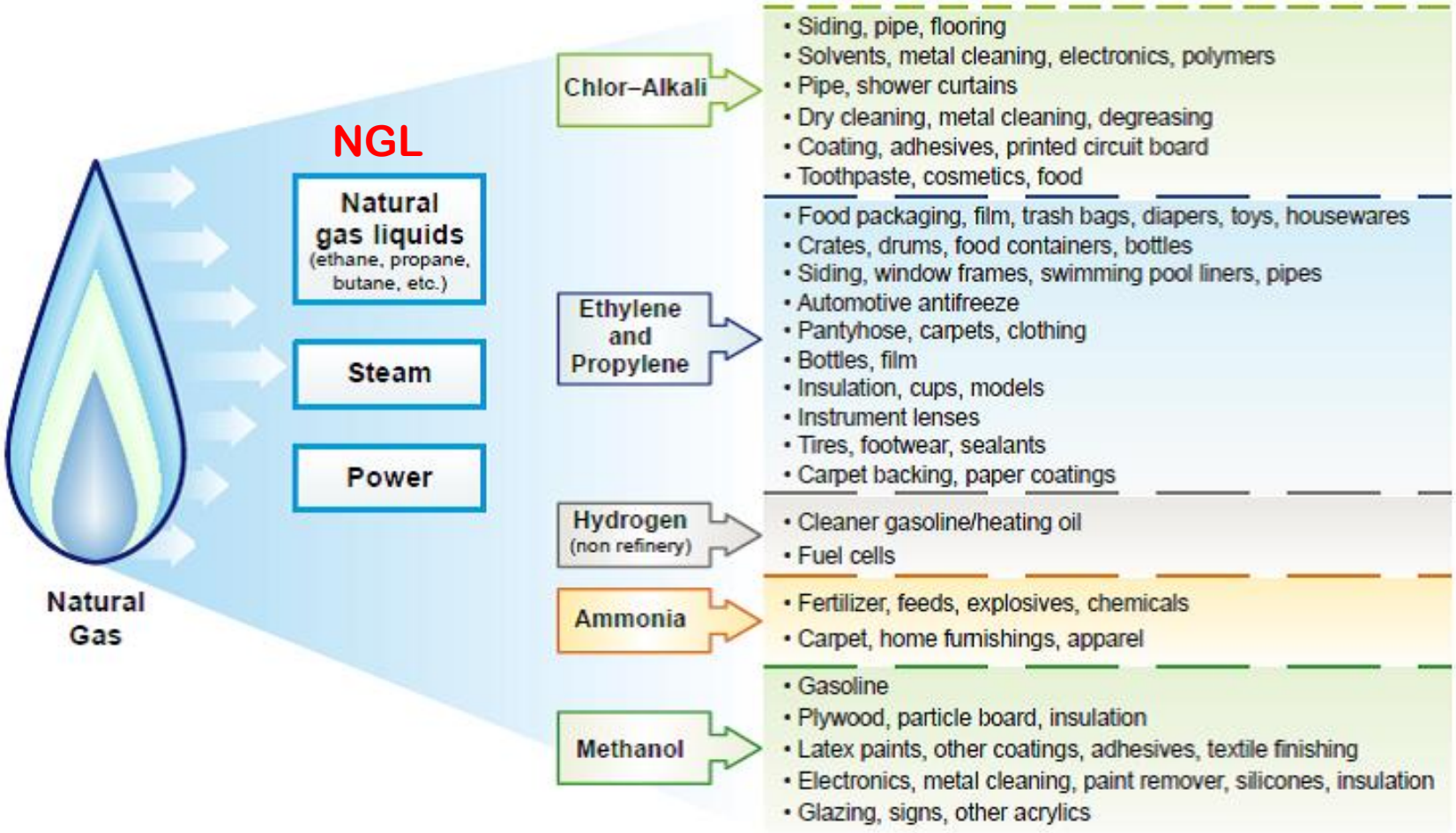
Middle East
CIS
Asia Pacific
North America
Africa
S. & Cent. America
Europe

Source: EIA International Energy Outlook 2016[7] and BP Statistical Review of World Energy 2021[10]

Value chain pieces

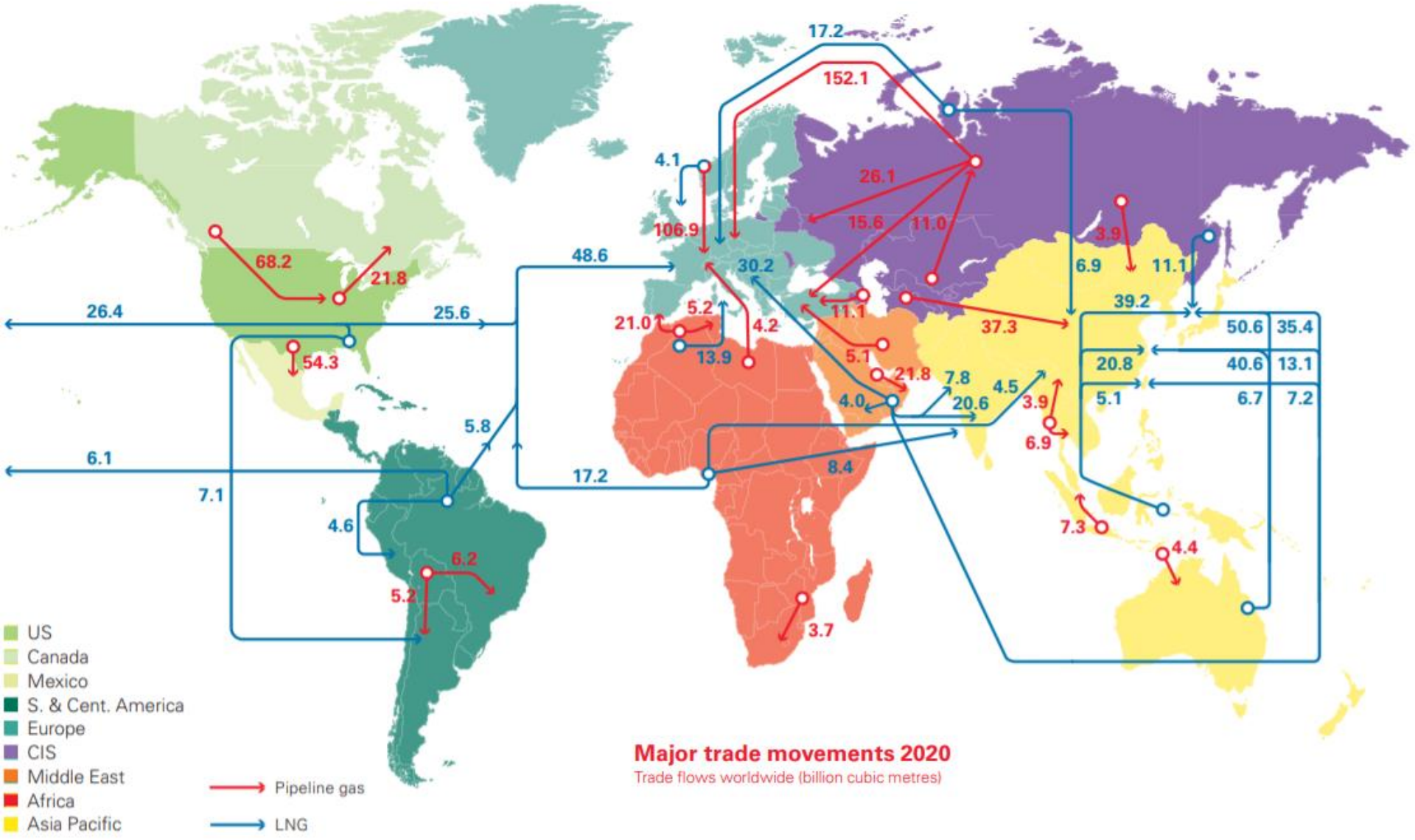
- Exploration – production
- **Processing – separation**
- Logistics
  - Pipeline transport
  - LNG transport
- Storage facilities
  - Underground
  - LNG containers
- Trading
  - LNG regasification
- Local distribution networks
- Usage
  - residential
  - industrial

NG **industrial usage**



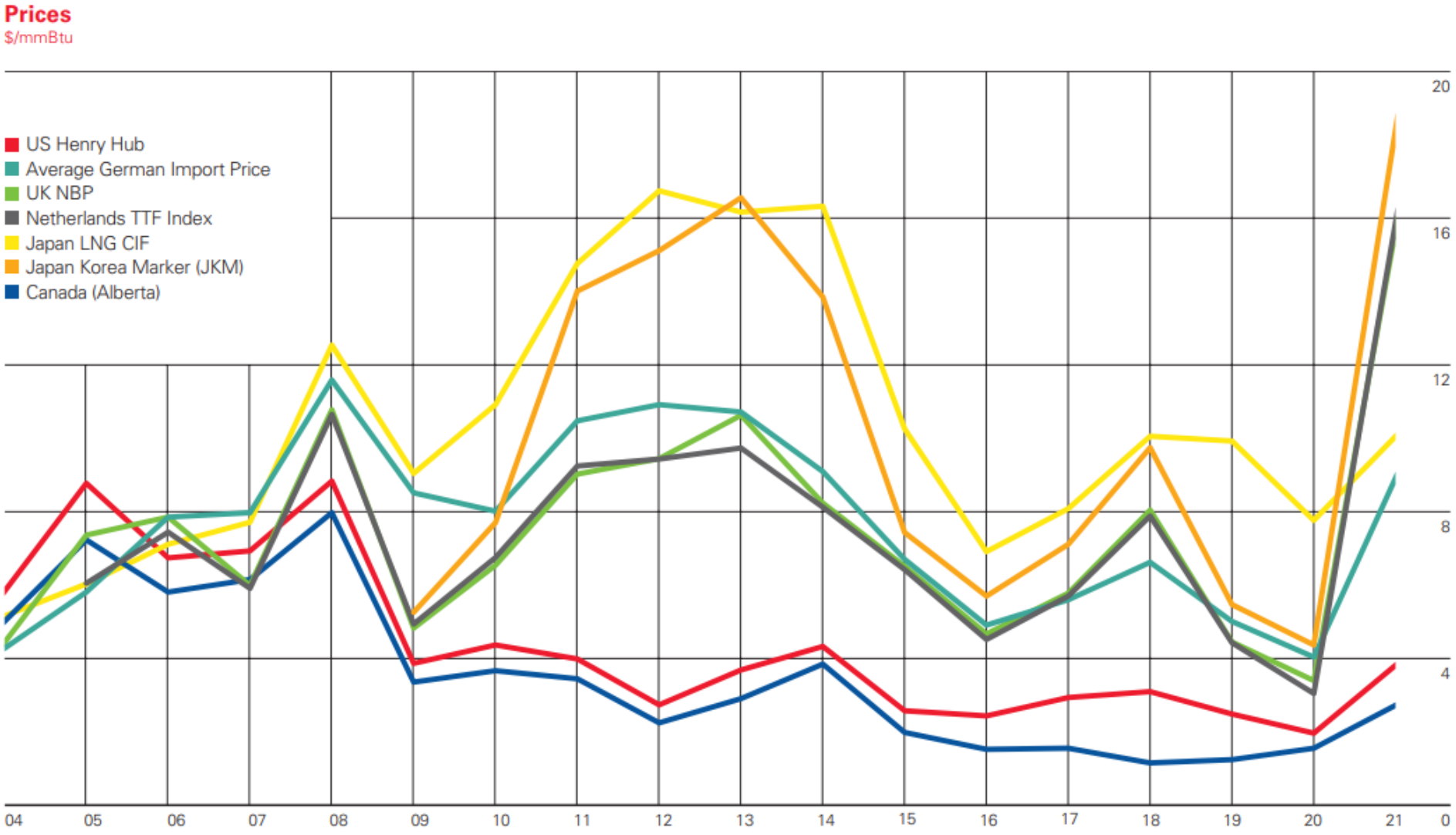
Source: IHS Chemical

Major trade movements 2020



Source: BP Statistical Review of World Energy 2021

Natural gas prices

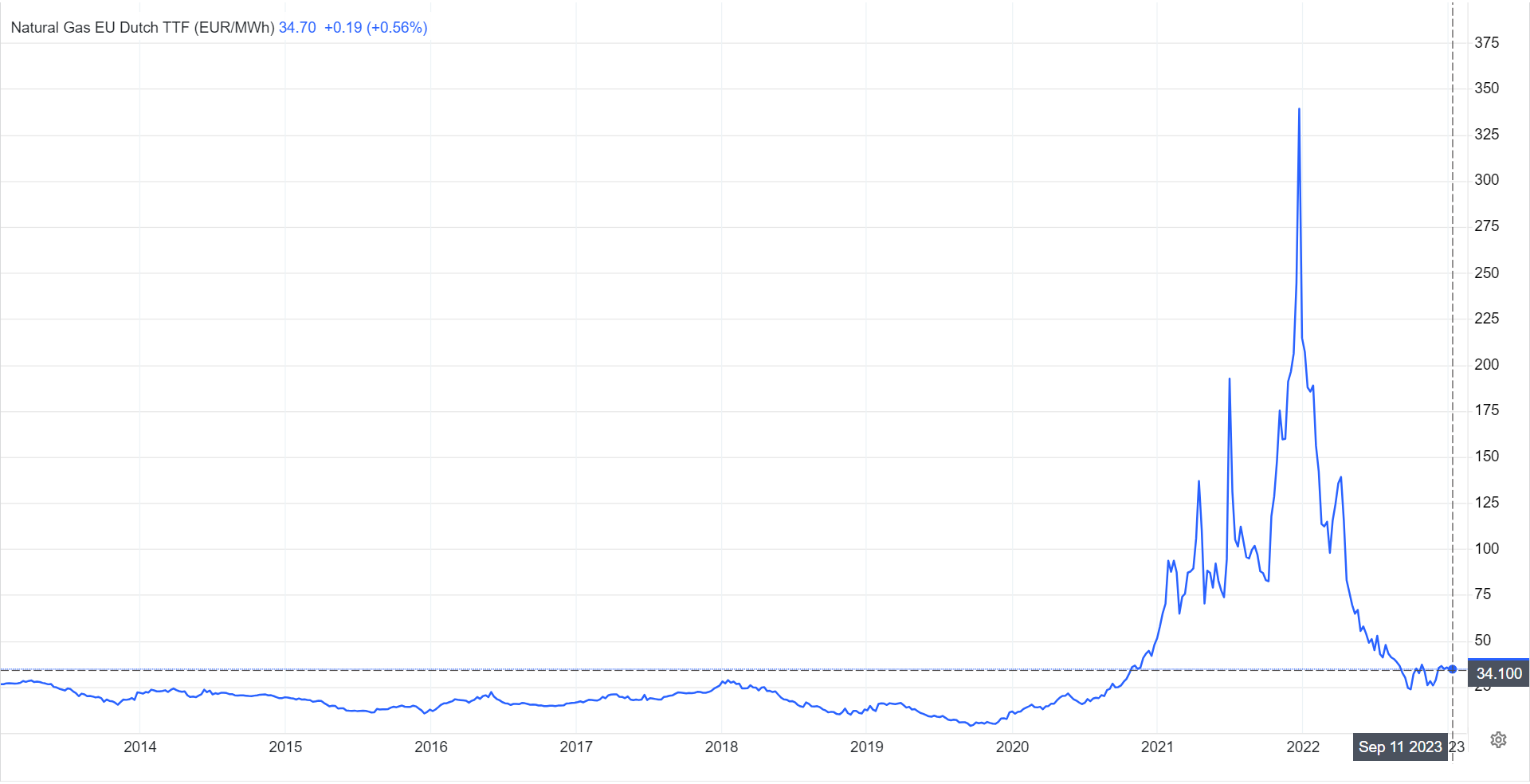


Source: BP Statistical Review of World Energy 2022

USD/MMBtu, Henry Hub, 1 year (2022.09.06.)

source: tradingeconomics.com

EUR/MWh, Dutch TTF
10 year (2023.09.11.)



NG **composition**

- **Hydrocarbons** (typically the main component)
  - **Methane** (mp: -182,5°C, bp: -161,5°C)
  - Ethane (mp: -182,8°C, bp: -89°C)
  - Propane (mp: -187,6°C, bp: -42°C)
  - i/n-Butane (mp: -160/-138°C, bp: -12/0°C)
  - Heavier hydrocarbons

NGL

- Non condensing gases:
  - He (bp: -269°C)
  - N_2 (bp: -196°C)
- Water vapour (**mp: 0°C**, bp: 100°C)
- **CO_2** (sublimation point: **-78,5°C**, at 1 bar) – could be the main component, eg. Répcelak
- Sulphur compounds
  - **H_2S** (**mp: -82°C**, bp: -60°C)
  - COS (mp: -139°C, bp: -50°C)
  - **CH_3SH** (mp: -123°C, bp: 6°C)
- Mercury compounds

Processing of raw natural gas

- Main pretreatment steps:
  - Mercury removal (typically in the desulphurisation unit in separate adsorber or as the upper catalyst layer)
  - Desulphurisation
  - Carbon-dioxid removal (must be below 50 ppm, to avoid formation of dry-ice)
  - Drying

Mercury removal

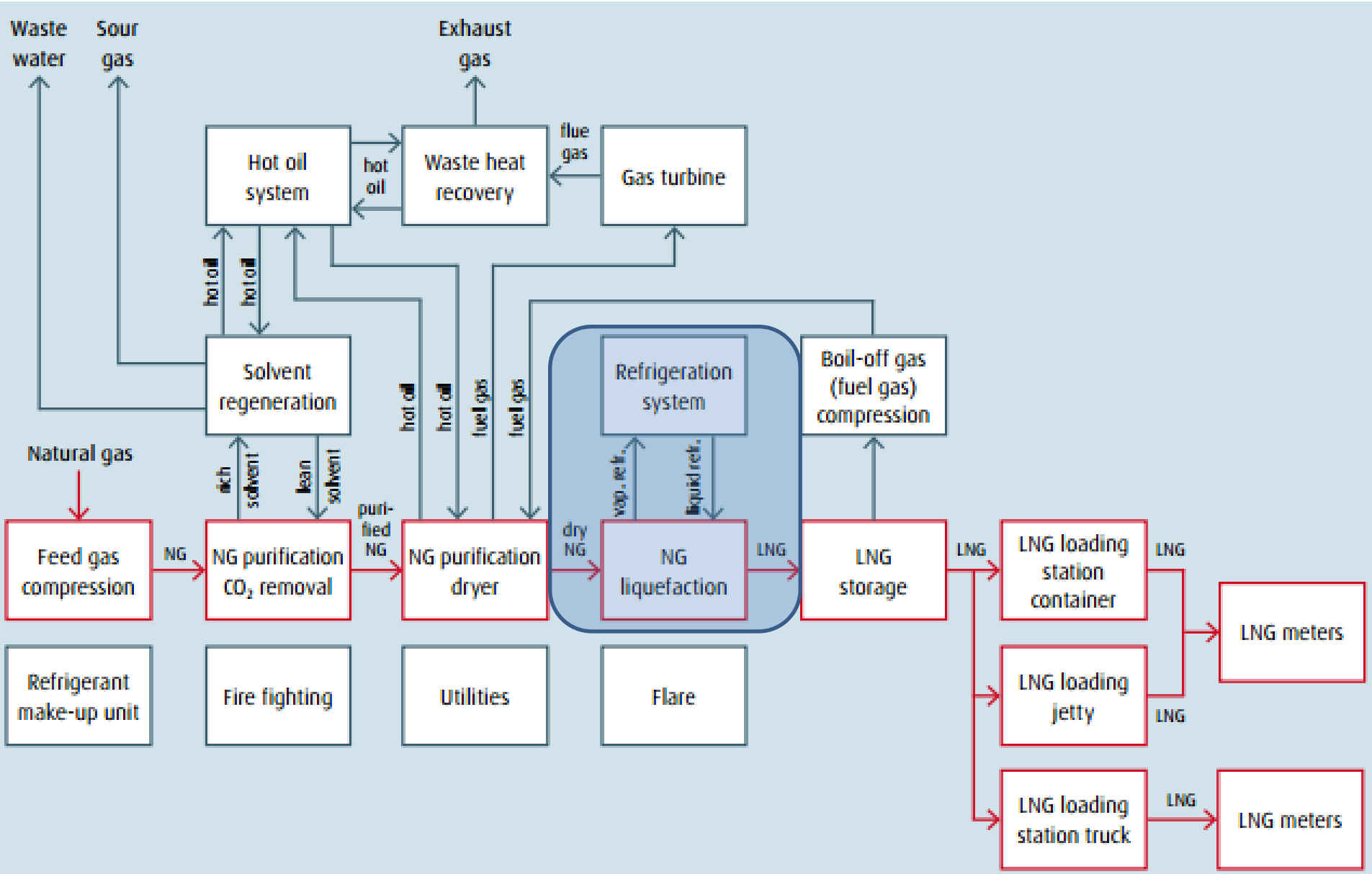
- It is present in the NG most of the time in very low concentrations
- **Problem**: the mercury corrode the aluminium heat exchangers (which are typically used during liquefaction)
- Adsorbent: special active carbon, impregnated with sulphur
- Usual specification for the treated gas: 10 ng/Nm^3
- Urban air: ~ 7ng/Nm^3 (traceability limit: 2 ng/Nm3)
- Natural gas: 0-120 µg/Nm^3 Hg
- Adsorber operating conditions:
  - temperature: 30°C,
  - residence time: ~10-20 s
  - Phase: gas phase

More info on mercury[12]

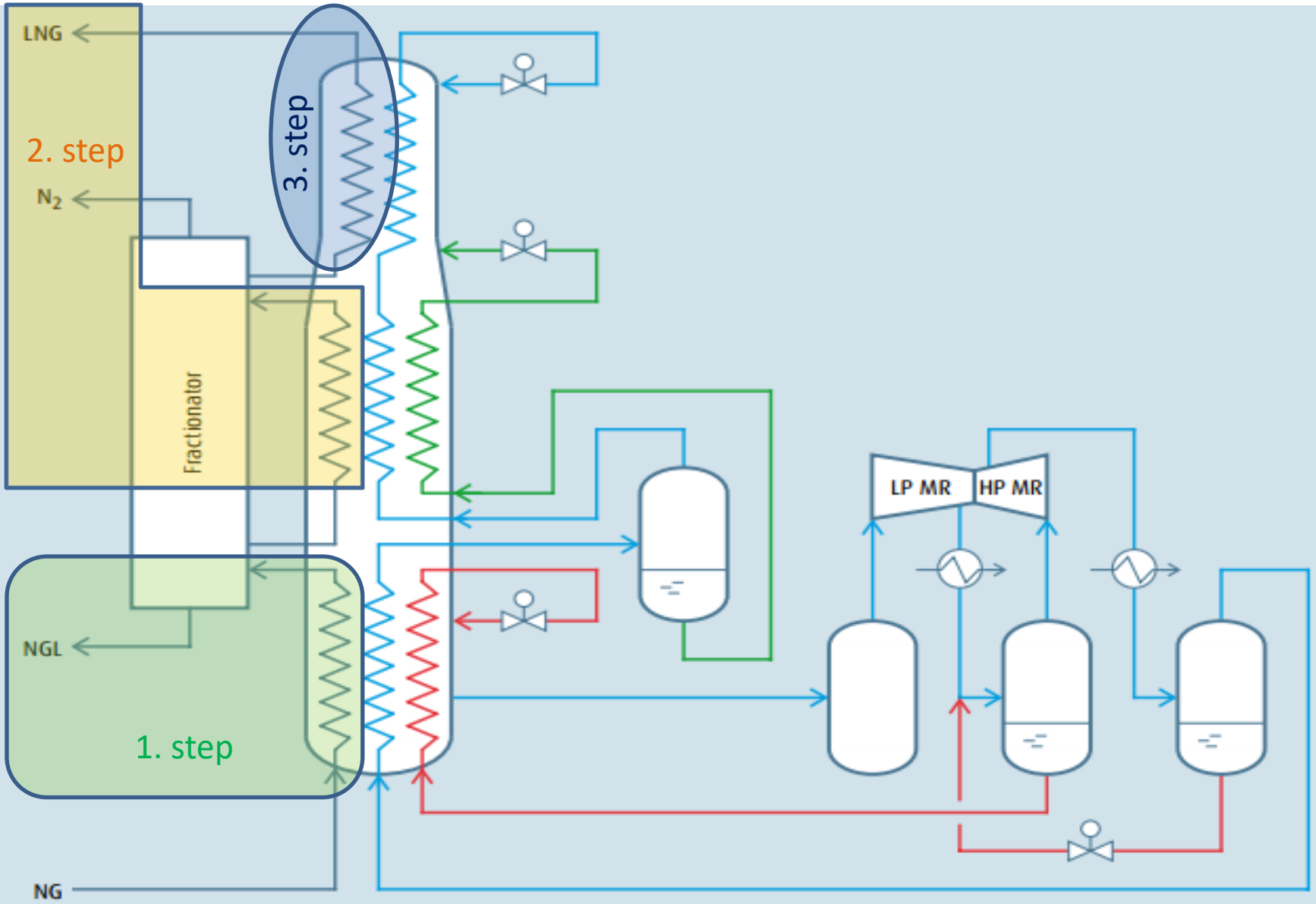
Separation of raw NG

- Objective:
  - Production/separation **of valuable heavier components**
  - To meet NG quality specification
- **Refrigeration/cryogenic** process
  - Most economic, operates with multicomponent cooling media
  - Depending on size and design, the **specific energy consumption** may be <250 kWh/t
- Main separated „products”
  - „Pure natural gas” (high purity methane)
  - Condensate (NGL – Natural Gas Liquids)
  - CO_2
  - He

LNG facility **flowsheet**



LNG facility **heat exchanger system**



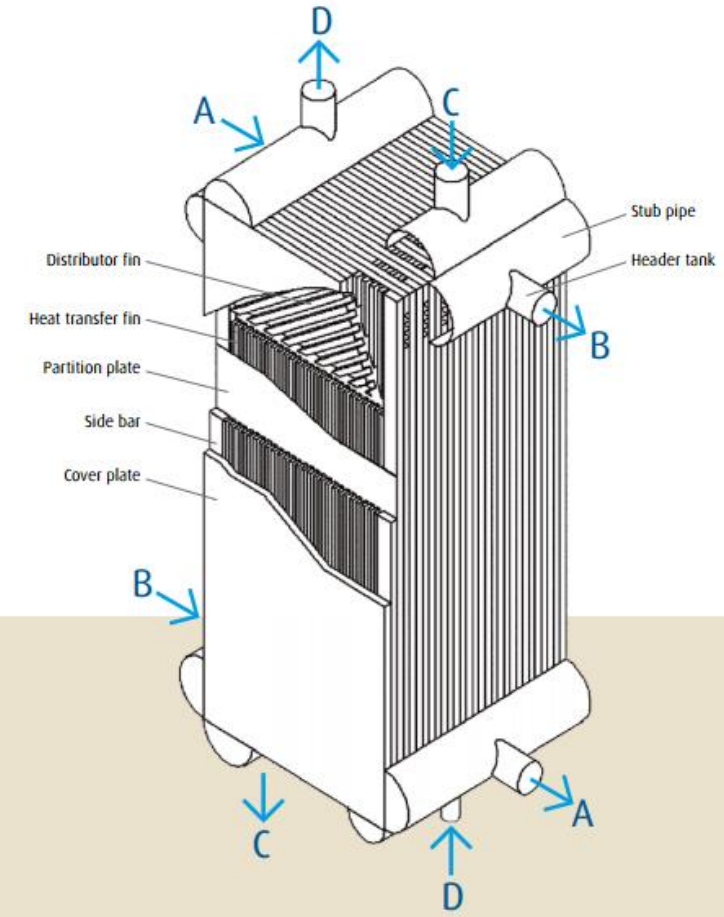
Steps of refrigeration

- 1. step: precooling
  - The heavier components are condensing
  - Separated in the fractionator
- 2. step: NG liquefaction
  - The methane is condensing
  - Separated in the fractionator from the non-condensing gases (N_2, He)
- 3. step: LNG supercooling
  - To set the final storage, transport temperature by further cooling (below boiling point)

Heat exchanger solutions

- Plate-fin heat exchanger (<0,5 mtpa)

Source: Linde[11]

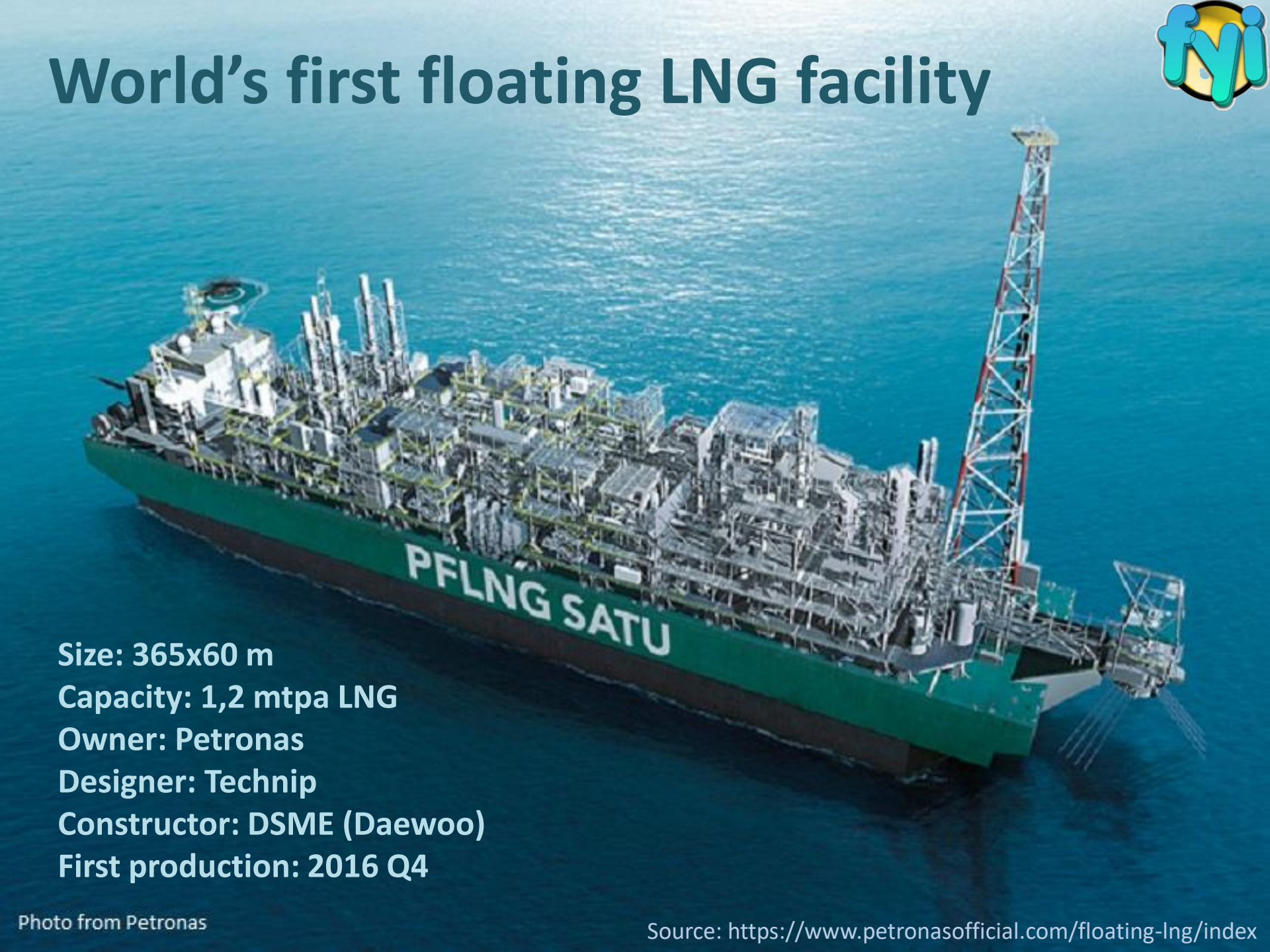


Heat exchanger solutions

- Coil-wound heat exchanger (0,2-1,0 mtpa)

Source: Linde[11]

World’s first floating LNG facility



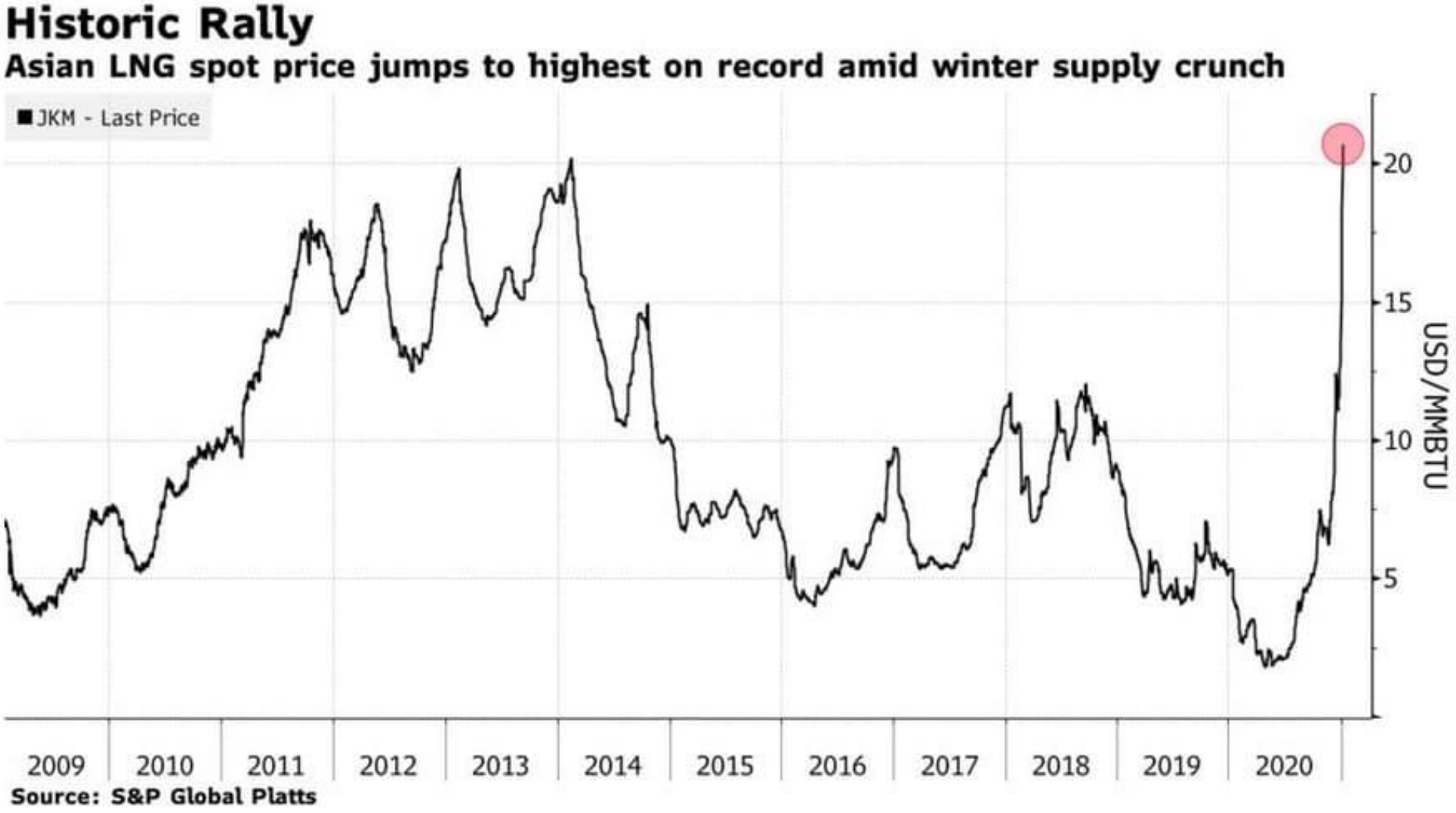
Size: 365x60 m
Capacity: 1,2 mtpa LNG
Owner: Petronas
Designer: Technip
Constructor: DSME (Daewoo)
First production: 2016 Q4

Photo from Petronas

Source: https://www.petronasofficial.com/floating-lng/index

LNG price

Order: 2012 (LNG price: ~15 $/MMBtu)
Actual LNG price: ~6 $/MMBtu (2021/09)
Many similar projects were halted



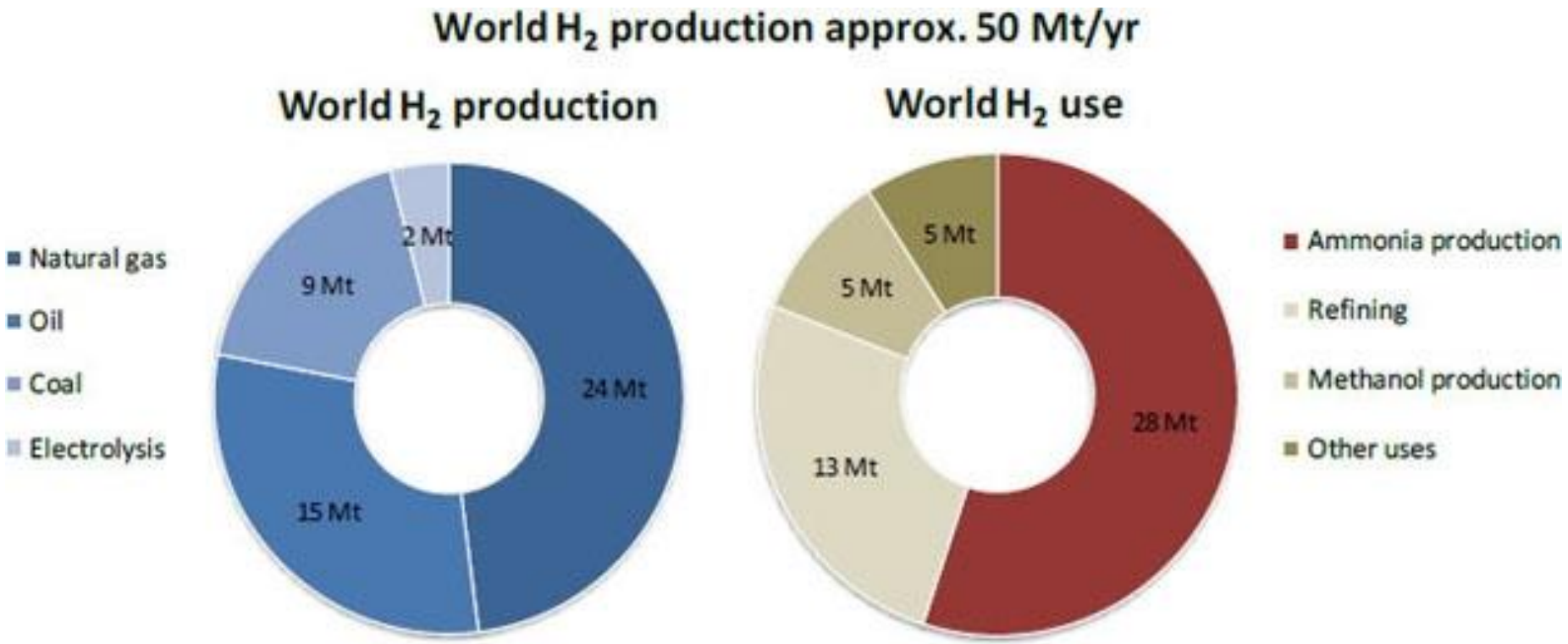
World’s biggest floating LNG facility

Shell’s Prelude

Size: 488x74 m
Capacity: 3,6 mtpa LNG
First cargo: 2019 Q2

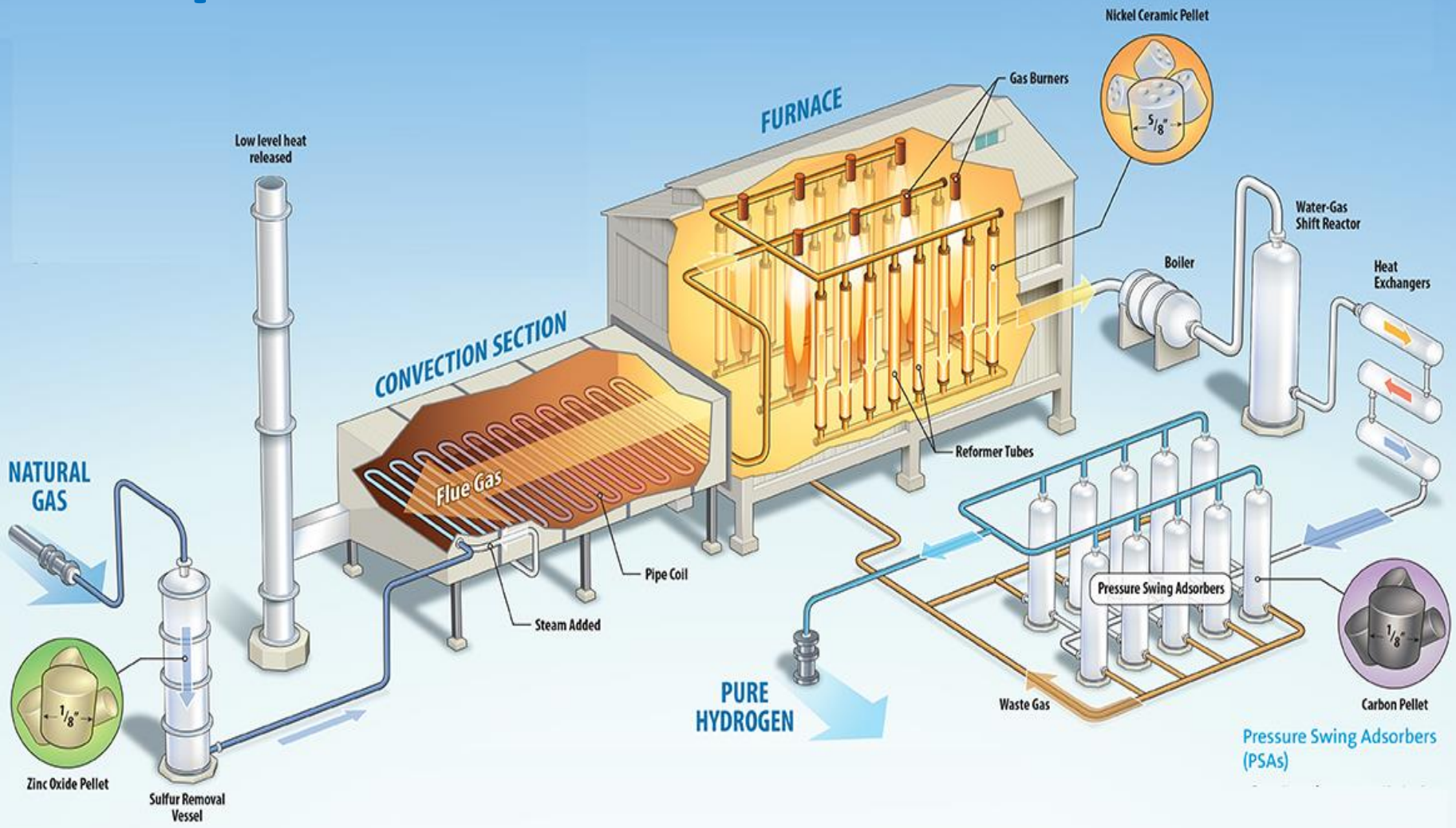
https://www.shell.com/about-us/major-projects/prelude-flng/prelude-flng-video-gallery.html

3.
Hydrogen production



Source: Global CCS Institute[14]

SMR plant overview



Picture from Air Products[9]

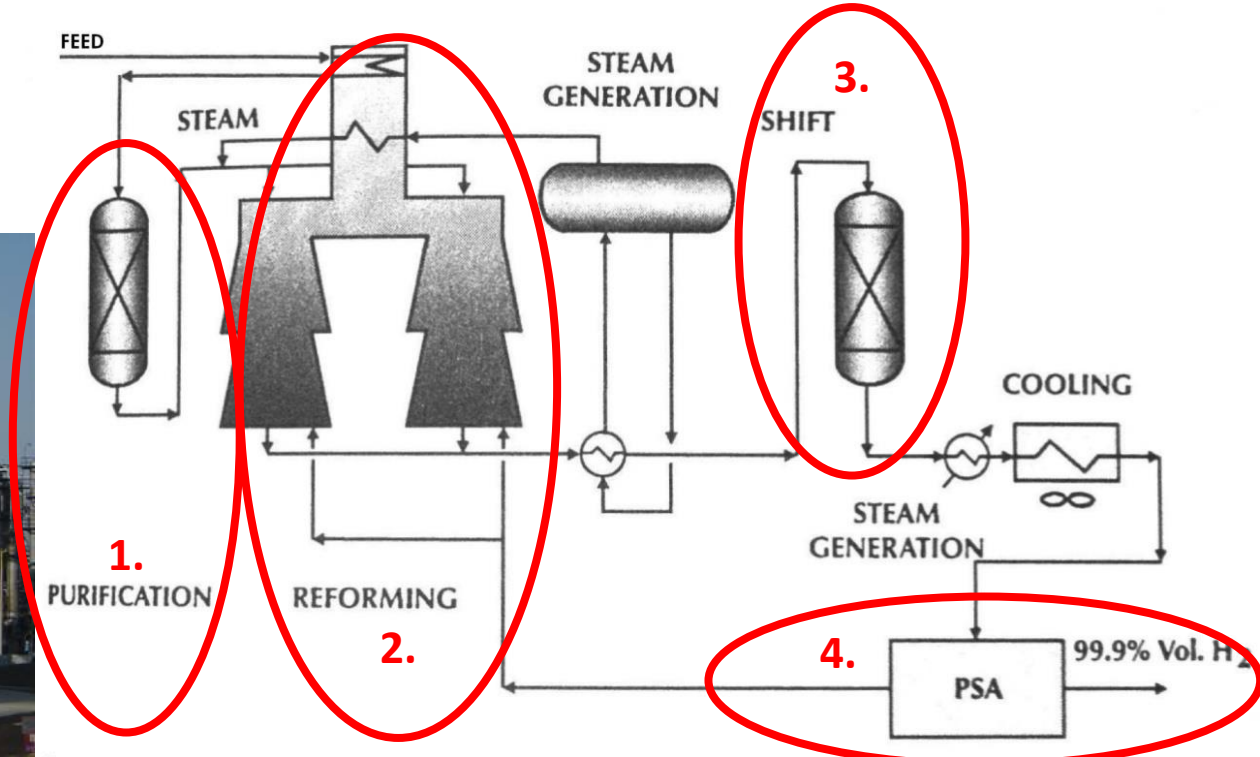
Steam Methane Reforming (SMR)

Task: Hydrogen production for hydrotreaters

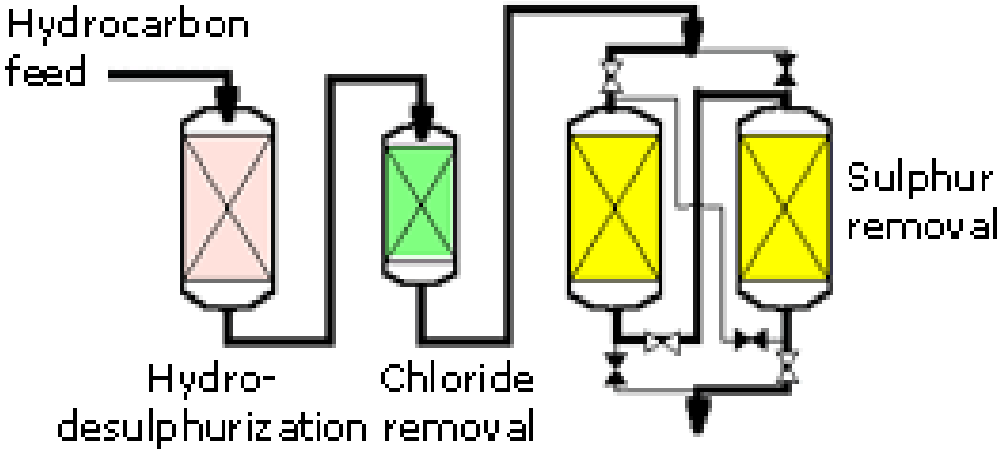
Feedstock: **natural gas** + water (any hydrocarbon fraction)

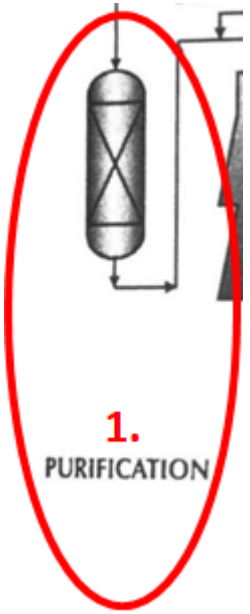
Product: hydrogen (**99,9% purity** downstream PSA)

Challenges: coking at low steam/carbon, high conversion requires high temperatures



First step: **Purification** of the feedstock





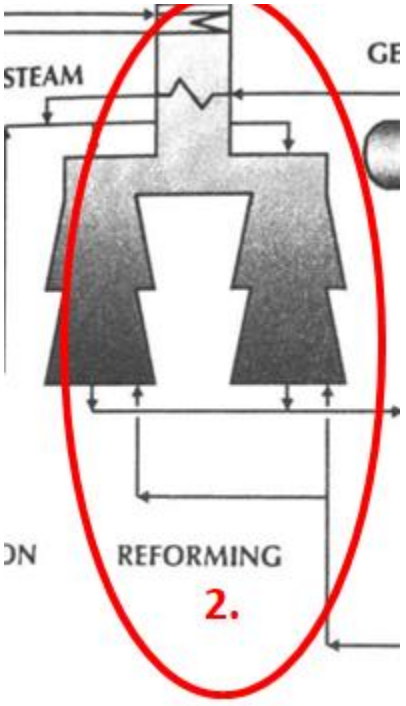
Task: removal of sulphur and chloride content of feed natural gas, in order to **avoid deactivation and poisoning of the reforming catalyst**.

Method: Transformation of all sulphur and chloride compounds to hydrogen-sulphide (H_2S) and hydrochloric acid (HCl)

Catalysts: Hydrodesulphurisation: Co/Mo

H_2S and chloride removal: **ZnO**/CaO

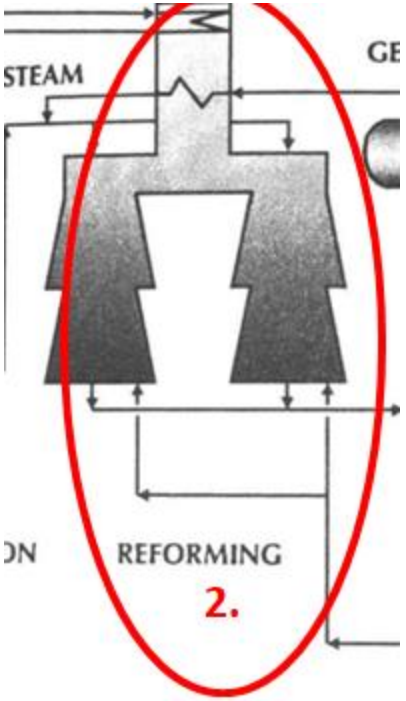
Second step: **Reforming** with steam



A. Prereforming

- Main task of the prereformer is to **react all higher hydrocarbon** impurities to methane, **thus protecting** the main reformer catalyst
- Advantages:
  - oriented to reaction of higher hydrocarbons
  - increased main reformer catalyst life time
  - lower steam/hydrocarbon ratio is possible in the reformer
- Typical operating temperature: 400-520°C
- Purified natural gas is mixed with high pressure steam upstream the prereformer (45 barg, 450 °C).

Second step: **Reforming** with steam



B. Reforming

- In the reforming part the methane feed is **converted to synthesis gas**, which is mainly comprised of hydrogen and carbon-monoxide
- Additional components in the reactor effluent: carbon dioxide, unreacted methane, steam
- Reaction parameters:
  - temperature: 800 – 890 °C
  - Pressure: 25 - 30 barg
  - steam/hydrocarbon ratio: 2 - 4.5
- **Reforming reactions are always endothermic**

Reforming **chemistry and catalysis**

- Methane reforming (steam reforming) is strongly endothermic

$$\mathbf{CH_4 + H_2O \leftrightarrow CO + 3H_2}$$

$$C_nH_m + nH_2O \leftrightarrow nCO + (n+m/2)H_2$$

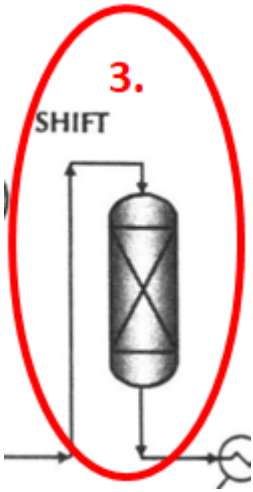
- Industrial catalysts: NiO/support

  Active metal: Ni - robust, high activity, less sensitive to potential catalyst poisons, most widely used

Catalyst support requirements: good heat and pressure resistance, **acidic sites not allowed** (cracking will occur) e.g.: magnesium-aluminium-oxide, α-aluminium-oxide, calcium-aluminium-oxide

Picture from Jonhson Matthey[13]

Third step: **water-gas shift reaction**



- In the shift reactor the carbon-monoxide is transformed into carbon-dioxide, thus **maximising the hydrogen yield** (water-gas shift reaction)

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

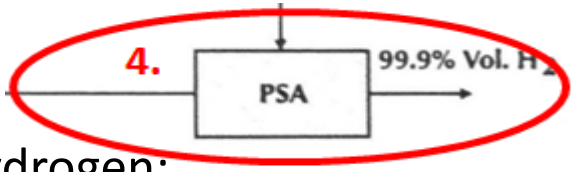
- Operating temperature:
  - LTS: 200-240 °C
  - HTS: 310-450 °C
- **Shift catalyst** are oxides of the following metals:
  - High temperature catalyst: **Fe/Cr**, Fe is being the active component, Cr to provide structural support
  - Low temperature catalyst: **Cu/Zn**, Cu is being the active component, Zn to prevent sintering

- **Waste heat removal** of flue gas. Flue gas, leaving the radiation section of reformer takes significant amount of heat. Major part of this heat may be regained with the heat exchanger bundles placed in the convection zone of the reformer. With this reuse together with the heat absorbed in the reformer bundles, **90% of the heating value** of the fuel gas may be utilised.

Picture from Jonhson Matthey[13]

Fourth step: **hydrogen purification**

- **Besides hydrogen**, the shift reactor effluent consists carbon-dioxide and some carbon-monoxide, nitrogen and methane too.

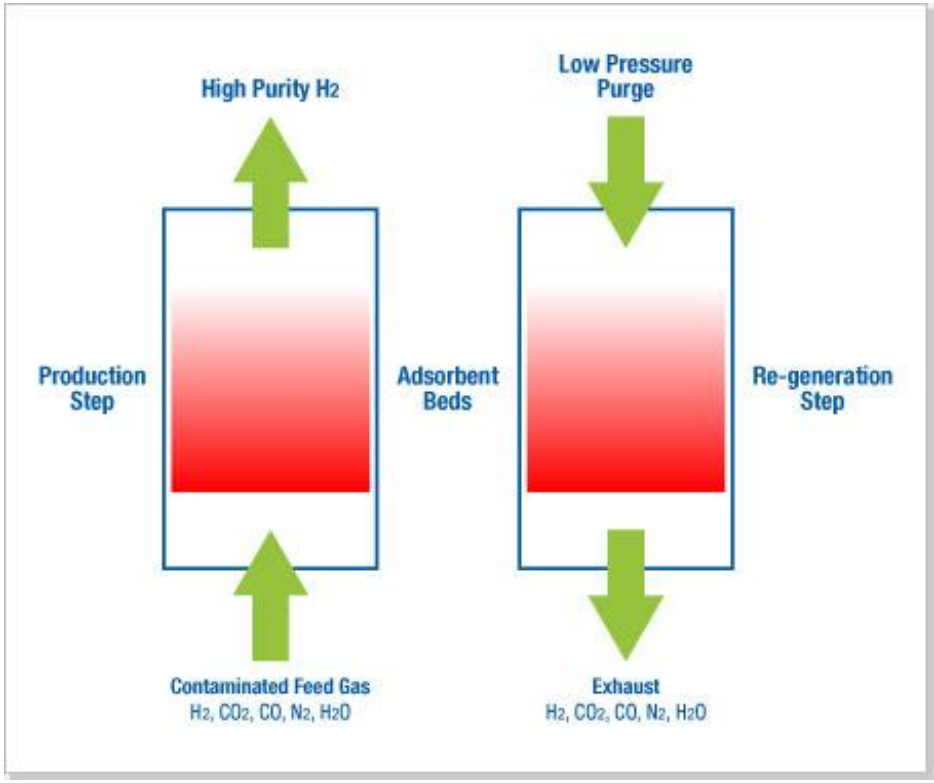


- There are **three main method** for the purification of hydrogen:

PSA	Cryogenic	Membrane
Big unit footstep	Small unit footstep	Small unit footstep
Medium CAPEX	High CAPEX	Low CAPEX
Very low OPEX	High OPEX	Low OPEX
H_2 >99 mol %	**H_2 ~ 93 mol %**	**H_2 ~ 98 mol %**
High H_2 loss	**Low H_2 loss**	Medium H_2 loss
No perssure loss	Low perssure loss	High perssure loss

Pressure Swing Adsorption (PSA)

- Most widely used solution to reach very high purity
- Purity: 99.9< vol.%
- Multiple pairs of adsorbers are used (8-10-12 or more)
- Short cycle time: ~1 min
- The adsorber cycles are delayed to each other, in order to provide continuous product and exhaust gas flow

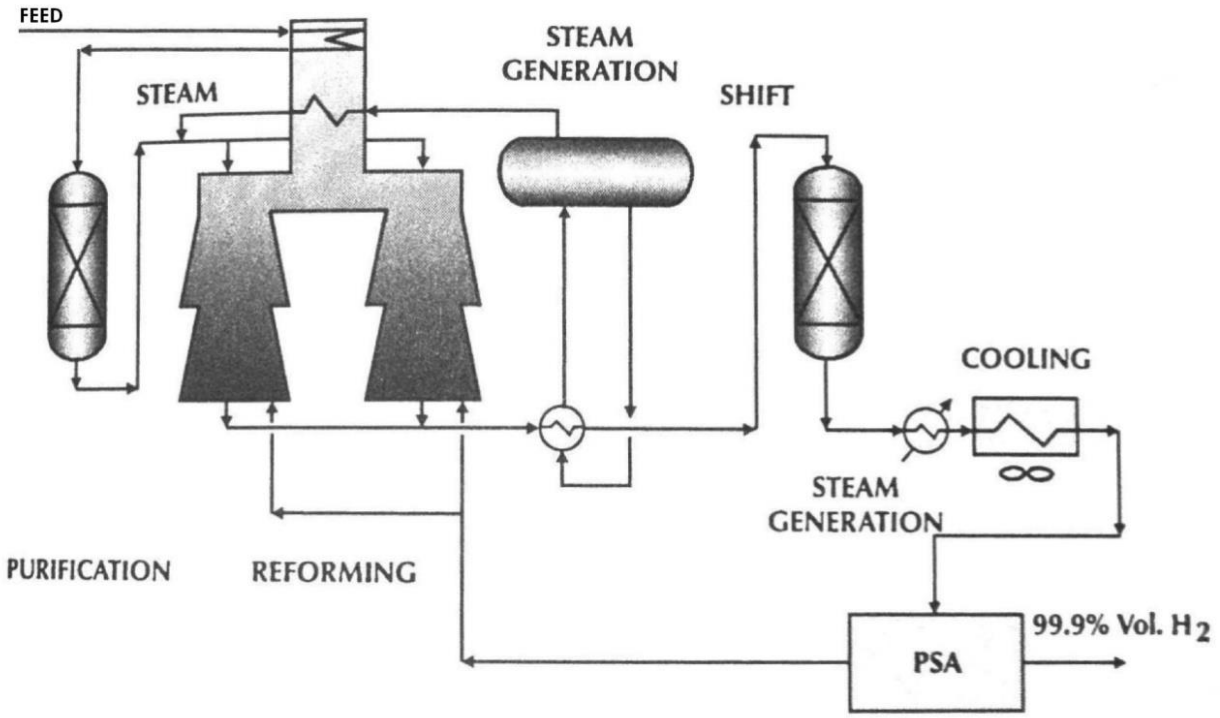


- Impurities may be desorbed via depressurisation
- H_2 recovery: 70-80%

Picture from Xebec Inc.[15]

Single slide summary: SMR-PSA

- **Aim:** production of high purity hydrogen gas
- **Feedstock:** natural gas + steam
- **Process parameters:** 800-900°C, 25-30 barg
- **Heat balance:** endothermic
- **Catalyst:** NiO/α-aluminium-oxide (main reactor)
- **Overall reaction equation:** $CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$
- **Products:** high purity hydrogen, fuel gas




The End

Suggested literature

1 IEA webpage: http://www.iea.org

2 IEA Gas Emergency Policy: https://www.iea.org/publications/freepublications/publication/gas_emergency_policy.pdf

3 Climate Home News: http://www.climatechangenews.com/2017/03/10/watchdog-suspends-azerbaijan-eu-gas-pipeline-loans-threatened/

4 STAR Refinery project: https://www.enerdata.net/publications/daily-energy-news/rosneft-will-supply-1-mtyear-oil-star-refinery-project-turkey.html

5 Everything about natural gas: http://naturalgas.org/

6 Energy consumption at home: http://www.foldgaz.hu/Oktatas.aspx

7 EIA International Energy Outlook 2016: http://www.eia.gov/forecasts/ieo/nat_gas.cfm

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