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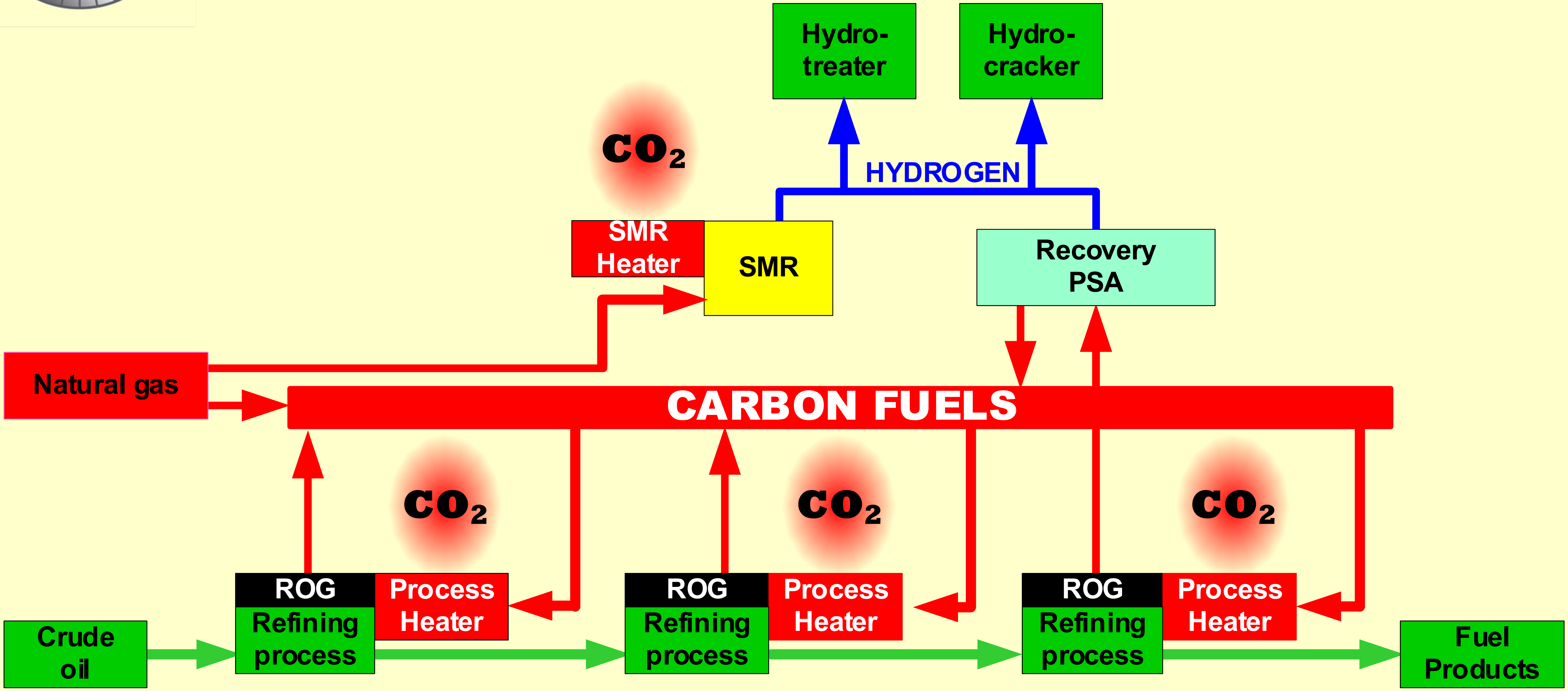
Z-Hydrogen to Decarbonize Refineries

Jon Feinstein and Sanjiv Ratan
ZoneFlow Reactor Technologies, LLC

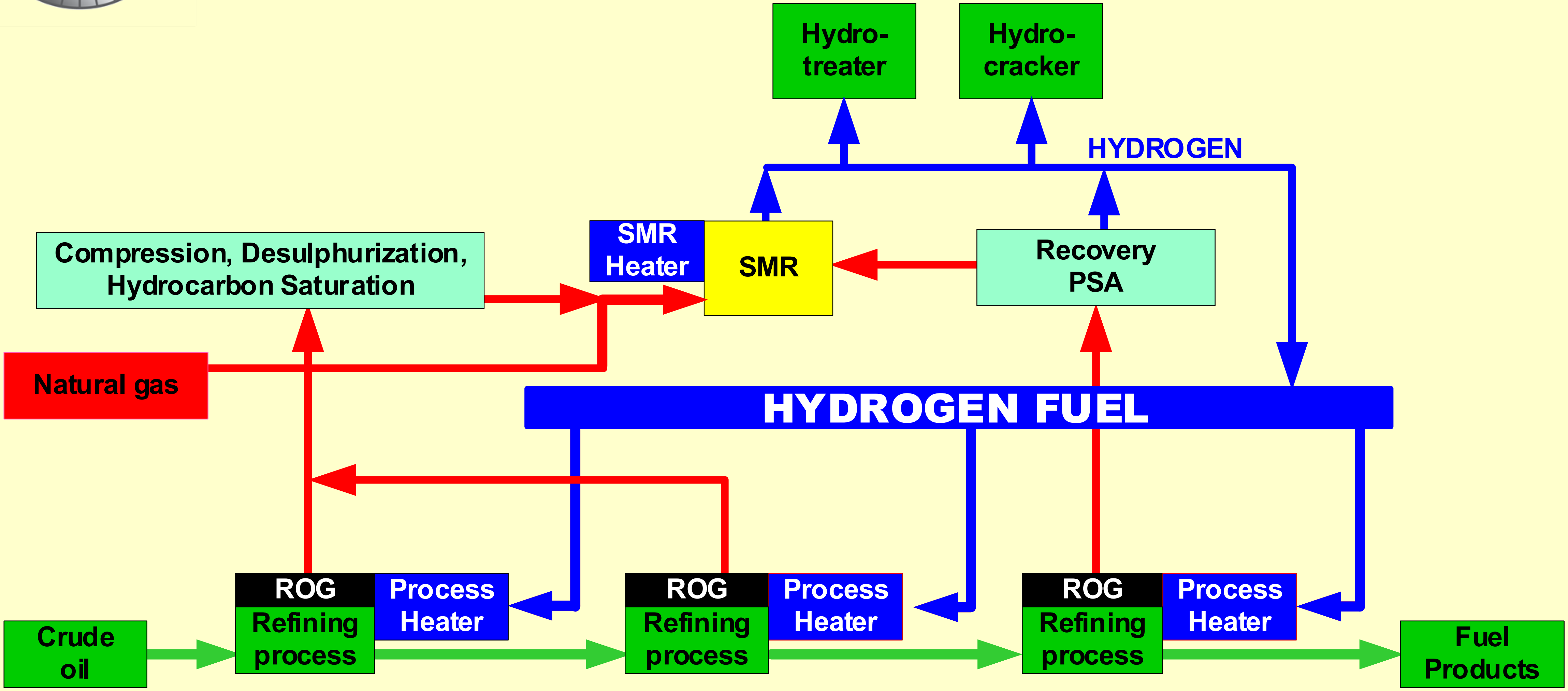
Refinery Decarbonization
Points to the Hydrogen Production Unit

- Refining creates 5% of the cradle-to-grave emissions from oil.
- Only the hydrogen production unit separates carbon from hydrogen (the clean fuel) at high CO_2 partial pressure.
- The hydrogen separation unit must play the central role in the decarbonization of refinery emissions.

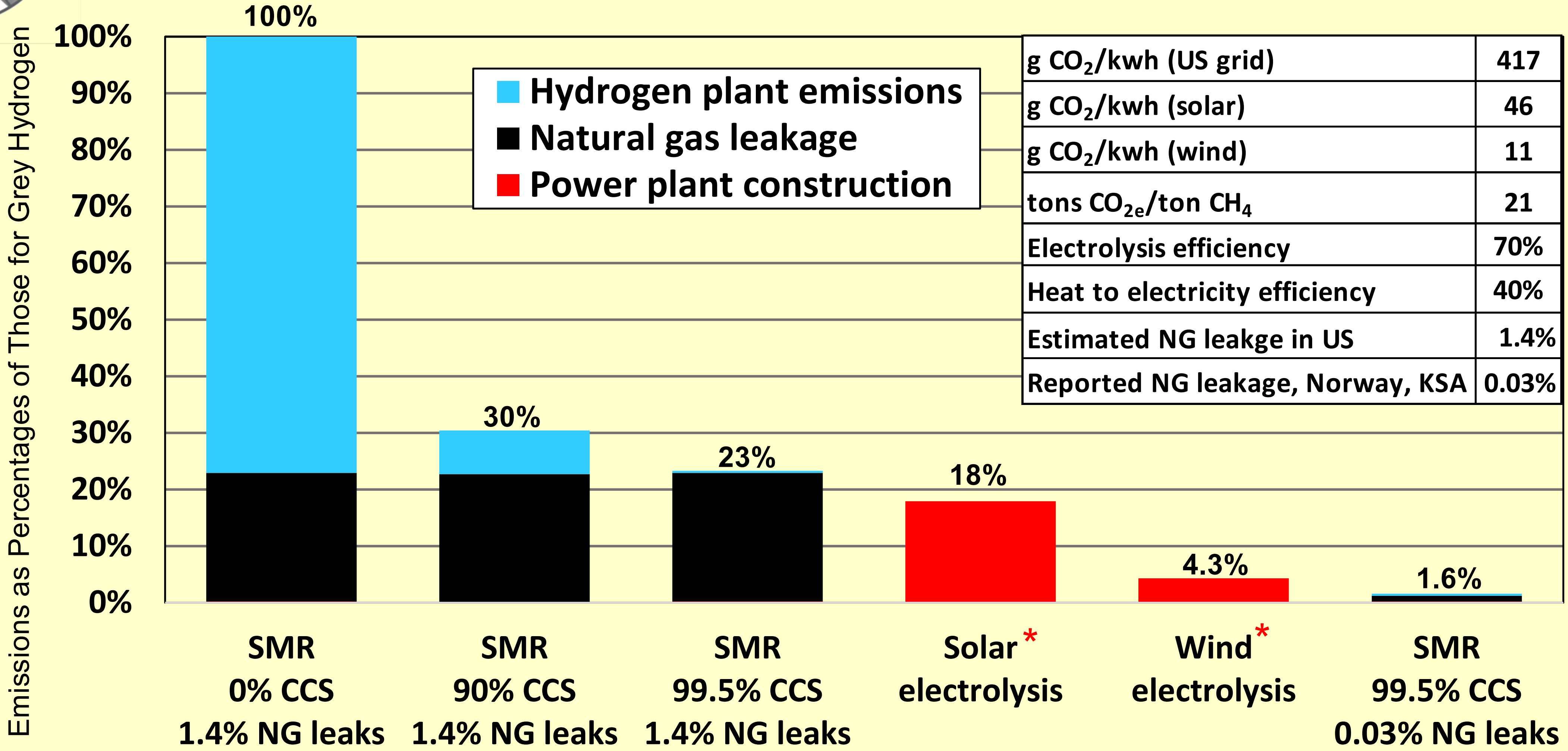
Refinery-Off-Gases Used as Fuel in Scattered Process Heaters



Hydrogen Used as Fuel for Process Heaters



Life Cycle Analysis CO_{2e} Emissions Relative to Grey SMR Hydrogen

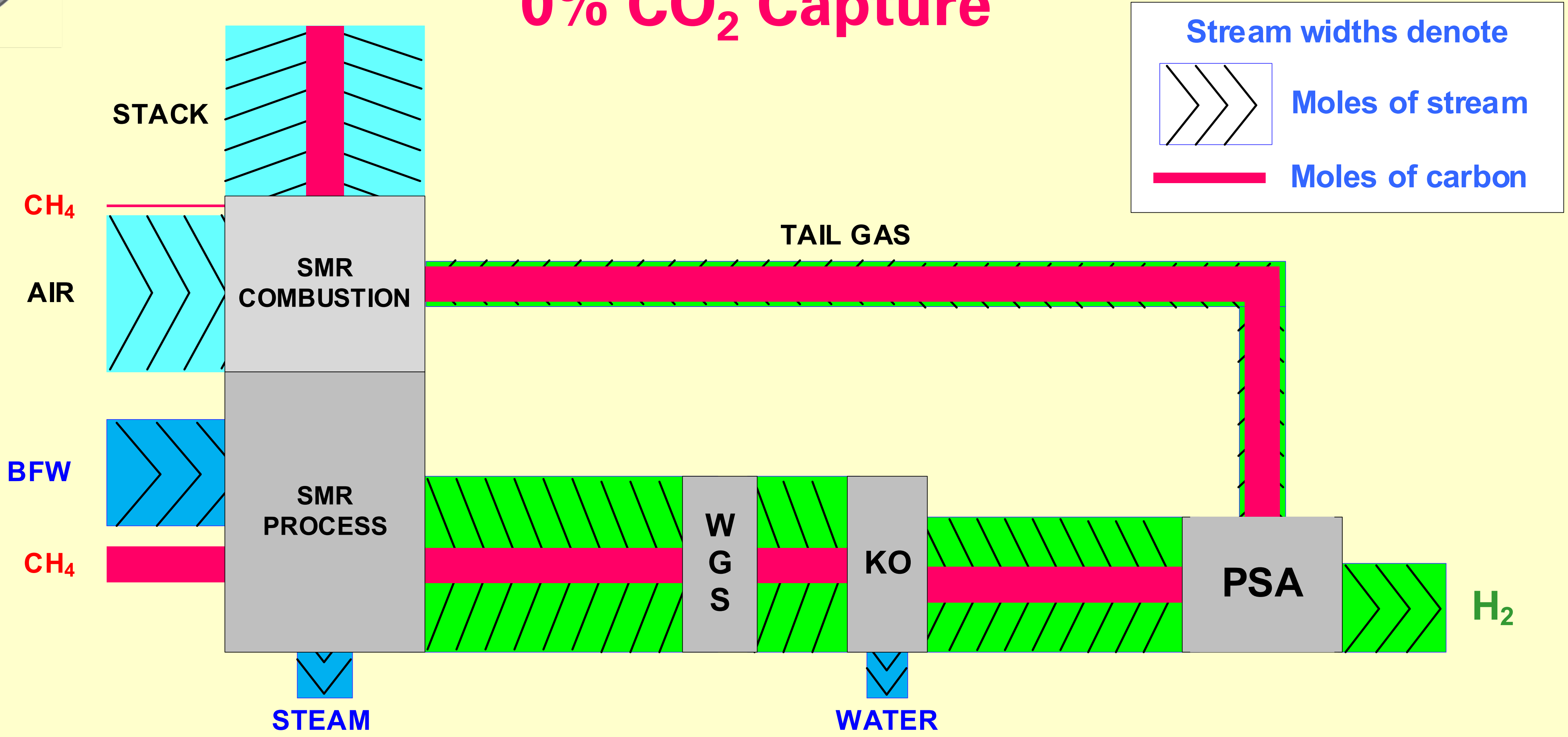


g CO_2/kwh (US grid)	417
g CO_2/kwh (solar)	46
g CO_2/kwh (wind)	11
tons CO_{2e}/ton CH_4	21
Electrolysis efficiency	70%
Heat to electricity efficiency	40%
Estimated NG leakge in US	1.4%
Reported NG leakage, Norway, KSA	0.03%

* with implausible assumption of 100% renewable power that is dispatchable

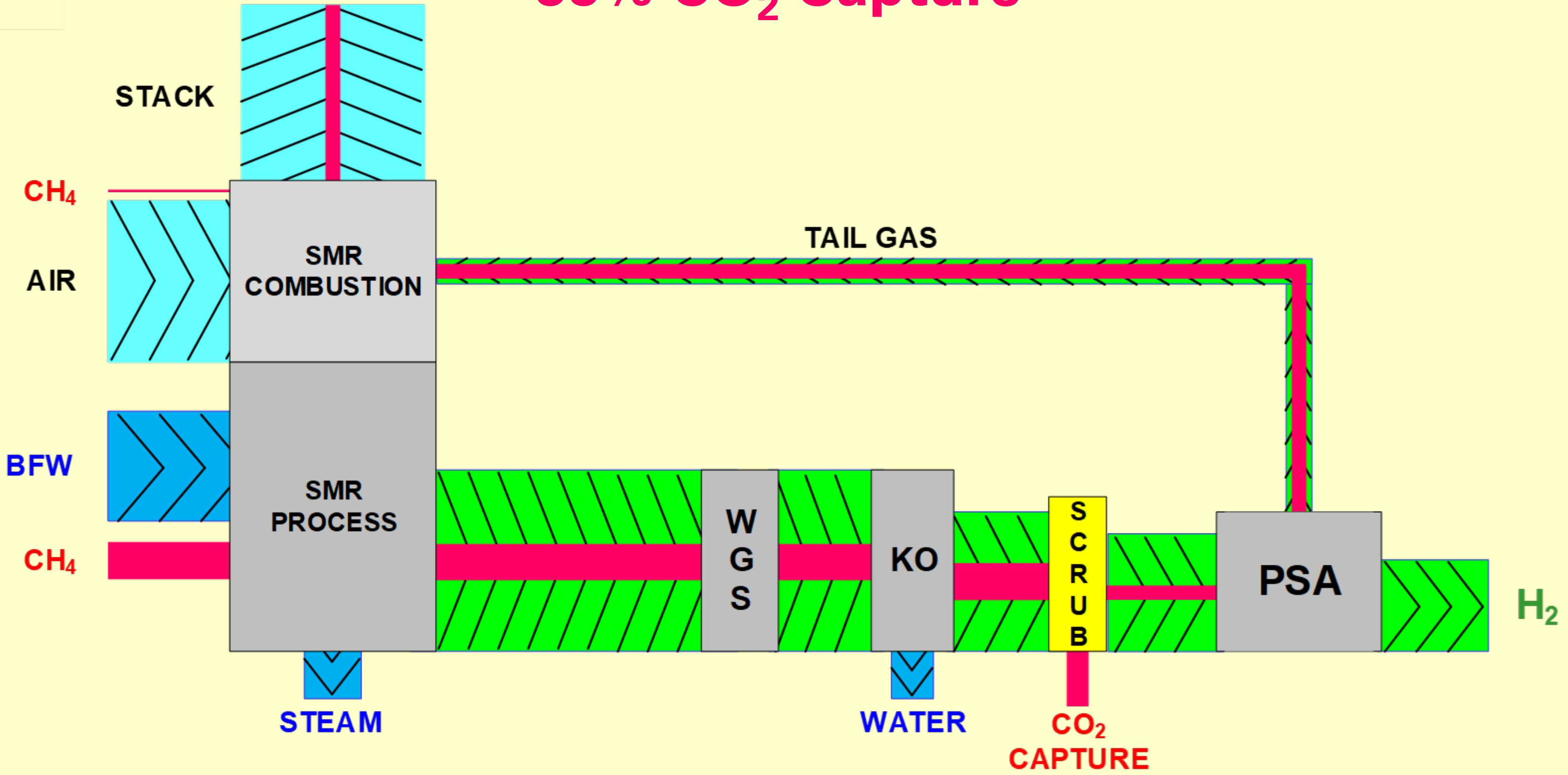
Grey H_2 SMR

0% CO_2 Capture



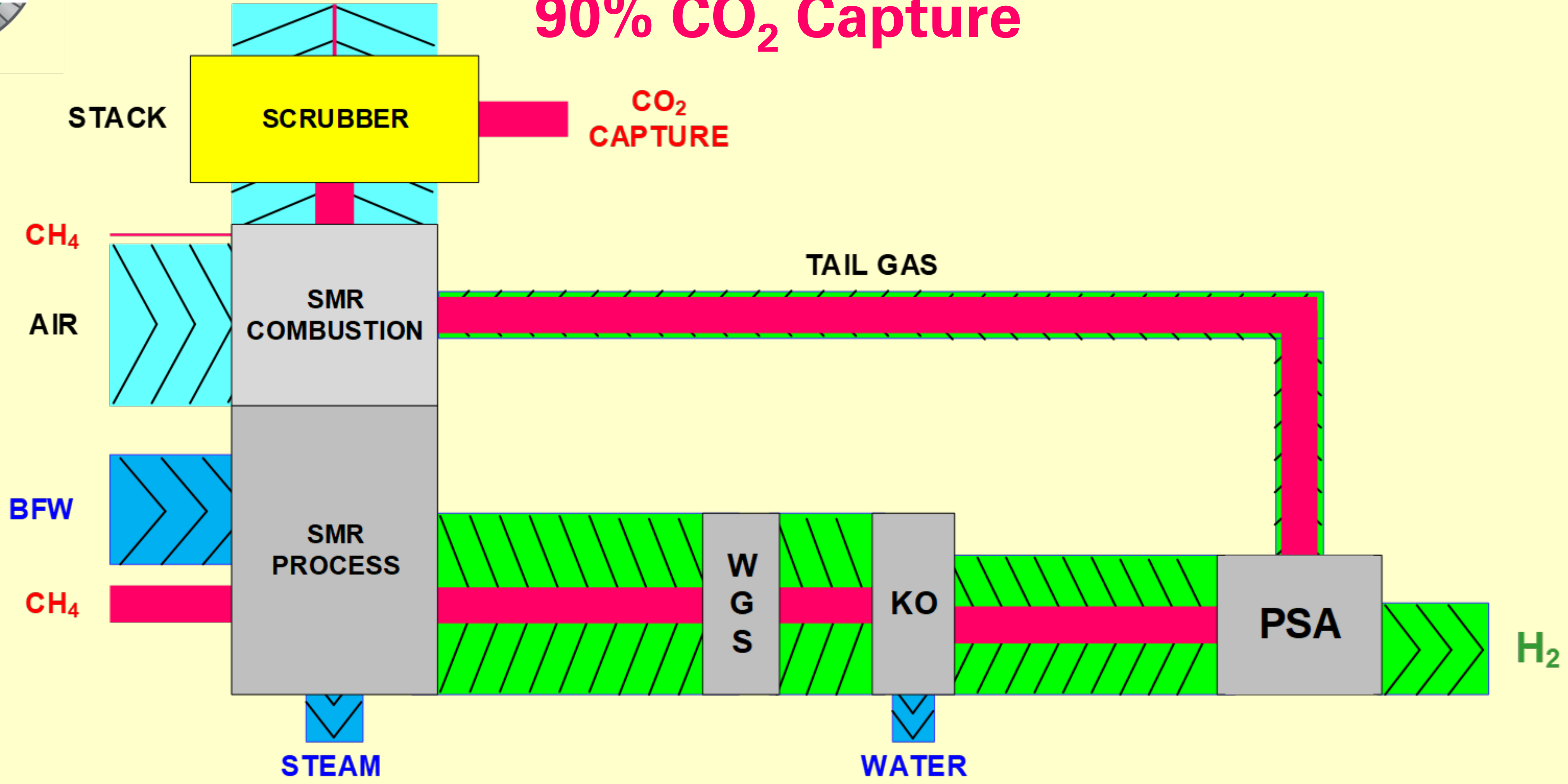
Pre-Combustion

55% CO_2 Capture



Post-Combustion

90% CO_2 Capture



Post-Combustion CO_2 Capture: Serious Drawbacks

- Must first remove NOx, SOx and particulates
- Large molar flow at atmospheric pressure entails
  - Low inlet partial pressure of CO_2
  - High energy consumption to push the gas through the system
  - Large equipment (2-3 times that for pre-combustion)
- Residual oxygen (from excess combustion air)
  - Degrades the solvents
  - Causes corrosion
- Alternatives to amines (VSA, chilled ammonia, chemical looping) are not economical either

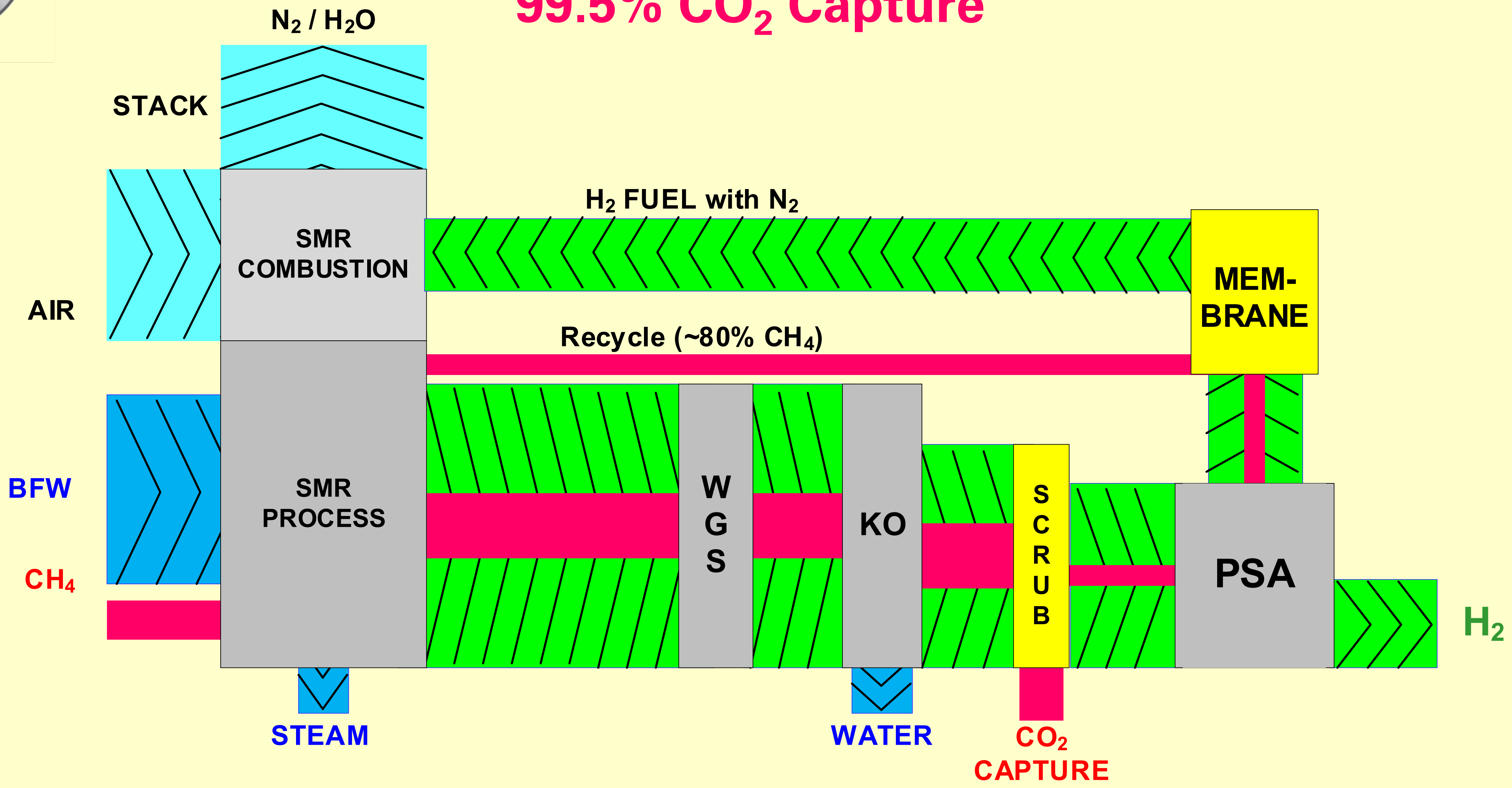
ATR Limitations

70% CO_2 avoidance

- ATR uses partial oxidation of natural gas with pure oxygen followed by steam reforming
- Oxygen separation from air is (electric) power-intensive, adding to the carbon footprint, even if 100% renewable (non-dispatchable).
- A fuel-fired heater is still needed for feed preheating which either emits carbon or requires expensive post-combustion carbon capture.
- Above factors lower the net CO_2 avoidance to 70% or less.
- ATR route for H_2 economical only at much larger capacities
- Not applicable for retrofitting the existing SMR-based H_2 plants in refineries.

Z-Hydrogen

99.5% CO_2 Capture



N_2 / H_2O

STACK

AIR

SMR COMBUSTION

H_2 FUEL with N_2

MEM-BRANE

Recycle (~80% CH_4)

BFW

CH_4

SMR PROCESS

W G S

KO

S C R U B

PSA

H_2

STEAM

WATER

CO_2 CAPTURE

Feedstock Conversion to Product

		Methane usage	Methane conversion	WGS conversion	PSA H_2 loss	Moles H_2 per mole CH_4	H_2 to fuel	Moles H_2 export per mole CH_4
Grey SMR	**Feedstock**	90%	70%	80%	11%	2.32	0%	**2.3**
	Fuel	10%						

Z-H_2	**Feedstock**	100%	100%	100%	0%	4.00	45%	**2.2**
	Fuel	0%						

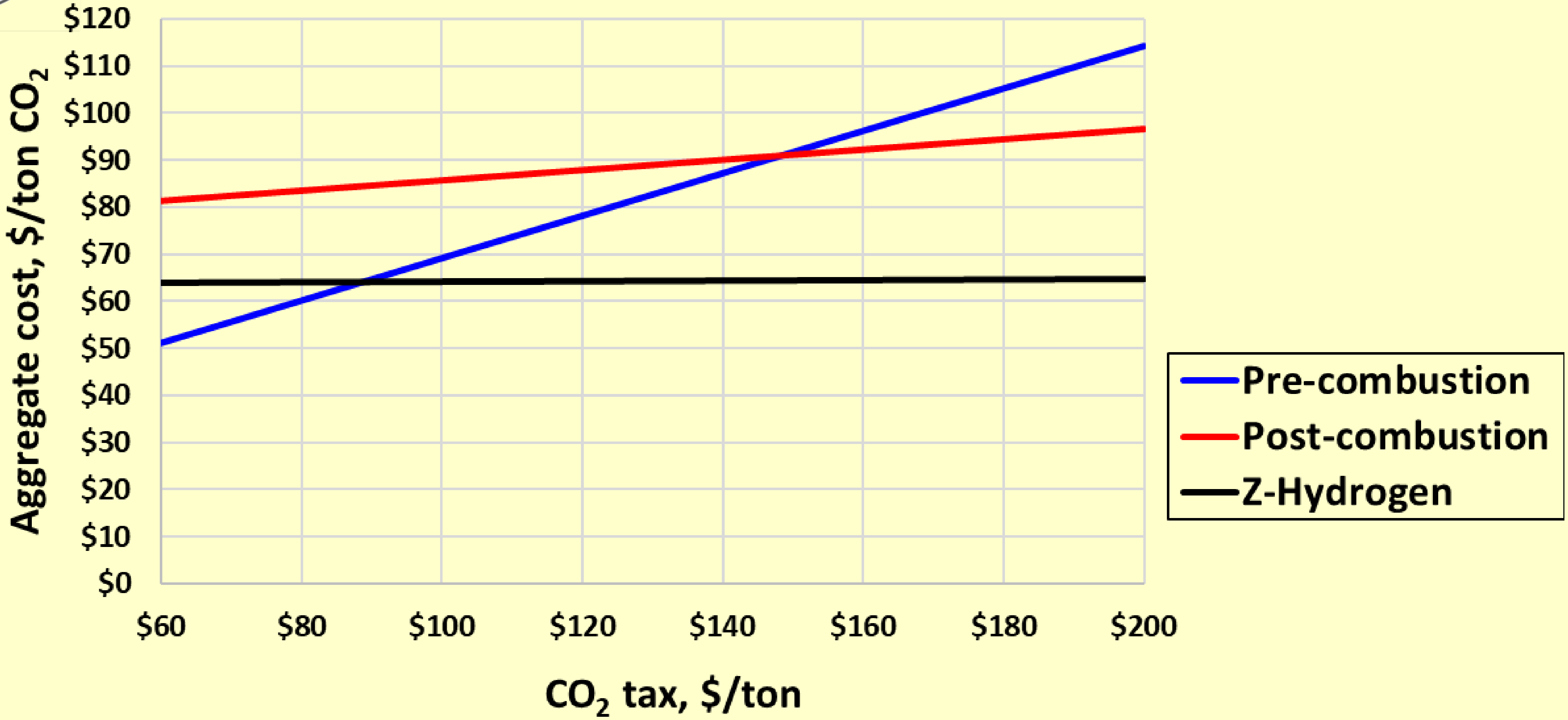
- **Net hydrogen export per unit of methane is about the same.**
- **Because only about 70% feedstock can convert per trip, the SMR must process about 50% more feed, affecting the capital cost.**

Options for Low Carbon Hydrogen

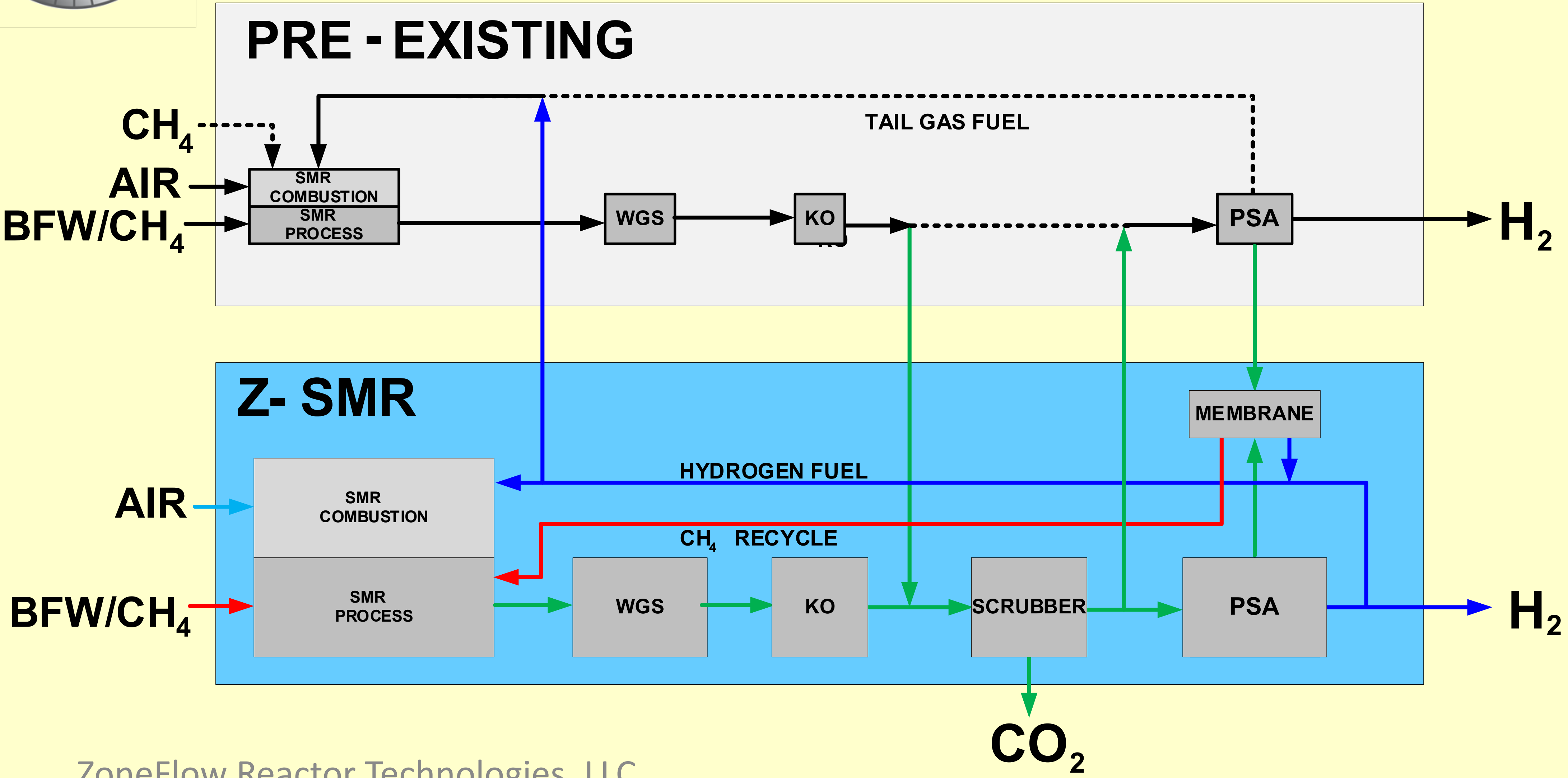
(CO$_2$ Avoidance and Incremental Costs Relative to Grey Hydrogen)

	Levelized costs, \$/ton CO$_2$ avoided				
Carbon capture	**SMR**	**CO$_2$ capture**	**Transport/ sequestration**	**Total**	**CO$_2$ avoidance**
Pre-combustion	\$0	\$34	\$10	\$44	55%
Post-combustion	\$0	\$74	\$10	\$84	89%
Z-Hydrogen	\$24	\$30	\$10	\$64	99.5%

Options for Low Carbon Hydrogen



Z-Hydrogen Decarbonization of a Refinery with Full Utilization of Existing SMR



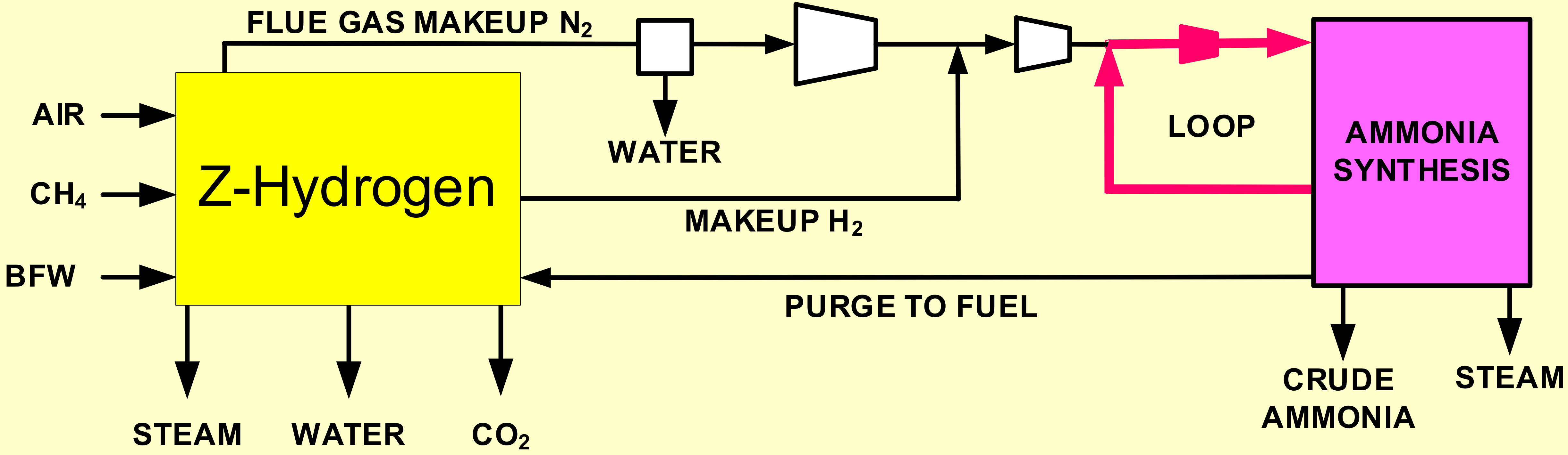
Z-Hydrogen Differentiators

- Lowest emissions
- Lowest cost at high % CO_2 avoidance
- Unmatched integration of proven and reliable pre-combustion CO_2 removal with SMR reconfiguration for highest CO_2 avoidance
- Market-ready - no new or "under development" CO_2 capture or other technology and related risks
- Effective redemption of existing SMR assets by retrofitting
- Optimal integrated utilization of steam for power, heat, and reactions
- Low land use

Z-Hydrogen Applications

- **Patents pending Z-H_2, Z-Ammonia, Z-Methanol and Z-GTL**
- **Refineries** use Z-Hydrogen SMRs to fuel all process heaters, lowering the GHG footprint of oil by 5%.
- **Ammonia** Combine PSA hydrogen with purified nitrogen from the SMR flue gas. Purge just carbon-free inerts (Ar) to burners.
- **Methanol and** GTL Monetize the excess hydrogen as fuel. Recycle the synthesis loop CH_4 and N_2 purges to transform carbon emissions to methanol and fuel products.

Z-Ammonia


FLUE GAS MAKEUP N_2
AIR
CH_4
BFW
Z-Hydrogen
WATER
MAKEUP H_2
LOOP
AMMONIA SYNTHESIS
PURGE TO FUEL
STEAM
WATER
CO_2
CRUDE AMMONIA
STEAM

Thank You !

For additional information, contact:

Jon Feinstein
Technology Director
jfeinstein@ZoneFlowTech.com
+1 914.471.2137

www.zoneflowtech.com

ZoneFlow Reactor Technologies, LLC