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De-carbonized Hydrogen and Electricity from Natural Gas

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Large Scale Production of H_2 from Fossil Fuels

Four Related Papers Prepared Under Princeton University's Carbon Mitigation Initiative Presented Here

	Natural Gas	**Coal & Residuals**
CO_2 Venting	Almost all H_2 produced today	Refineries, chemicals, NH_3 production in China 2) "Conventional technology"
CO_2 Capture	**1) FTR vs. ATR with CC**	2) "Conventional technology" 3) Membrane reactors 4) Overview

Background

- Production of hydrogen from natural gas is widespread in the refining and chemical industry
- In many cases, co-produced electricity is zero or negative
- CO_2 made available at moderate concentrations and pressures (partial pressure 5-15 bar)
- CO_2 is generally vented (production of urea is a notable exception)
- A number of well-established, mature technologies are commercially available to co-produce hydrogen, electricity and CO_2

Purpose of this study

- Understand thermodynamic and technological issues
- Assess performances achievable with commercially available technologies
- Understand trade-offs among hydrogen, electricity and CO_2 production
- Build a reference for comparisons with alternative feedstocks (particularly coal) and advanced technologies
- Following step: assess costs

Basic Assumptions

- Large scale plants: approx. 600 MW (LHV) of nat gas input, H2 output 300-450 MW (LHV)
- Stand-alone plants: no steam or chemical integration with adjoining process
- Feedstock is "commercial" nat gas with enough sulfur and paraffins to require de-sulfurization and pre-reforming
- Two steam reforming technologies: oxygen-blown, Auto-Thermal Reforming (ATR) and Fired Tubular Reforming (FTR)
- Two power plant options: "conventional" Rankine Steam Cycle (SC) and Combined Cycle (CC)
- CO2 venting vs CO2 capture by amine chemical absorption
- Total of eight plant configurations

More Basic Assumptions

- All configurations feature:
  - hydrogenation and sulfur removal at 380°C
  - saturator to preheat and humidify gas to be reformed
  - no quench boiler downstream of FTR
  - 2-stage Water-Gas Shift (~400-450°C and ~200-230°C)
- Size of ATR with CC determined by choice of gas turbine:
  - medium-power output, heavy-duty, Siemens V64.3a (corresponds to GE "F" technology, approx 70 MW when fired on nat gas)
- Same natural gas input for all other configurations
- Pure H2 separated by Pressure Swing Absorption (PSA)
- H2 delivered at 60 bar, CO2 delivered at 150 bar
- ATR at 70 bar, 950°C
- FTR at 25 bar, 850°C

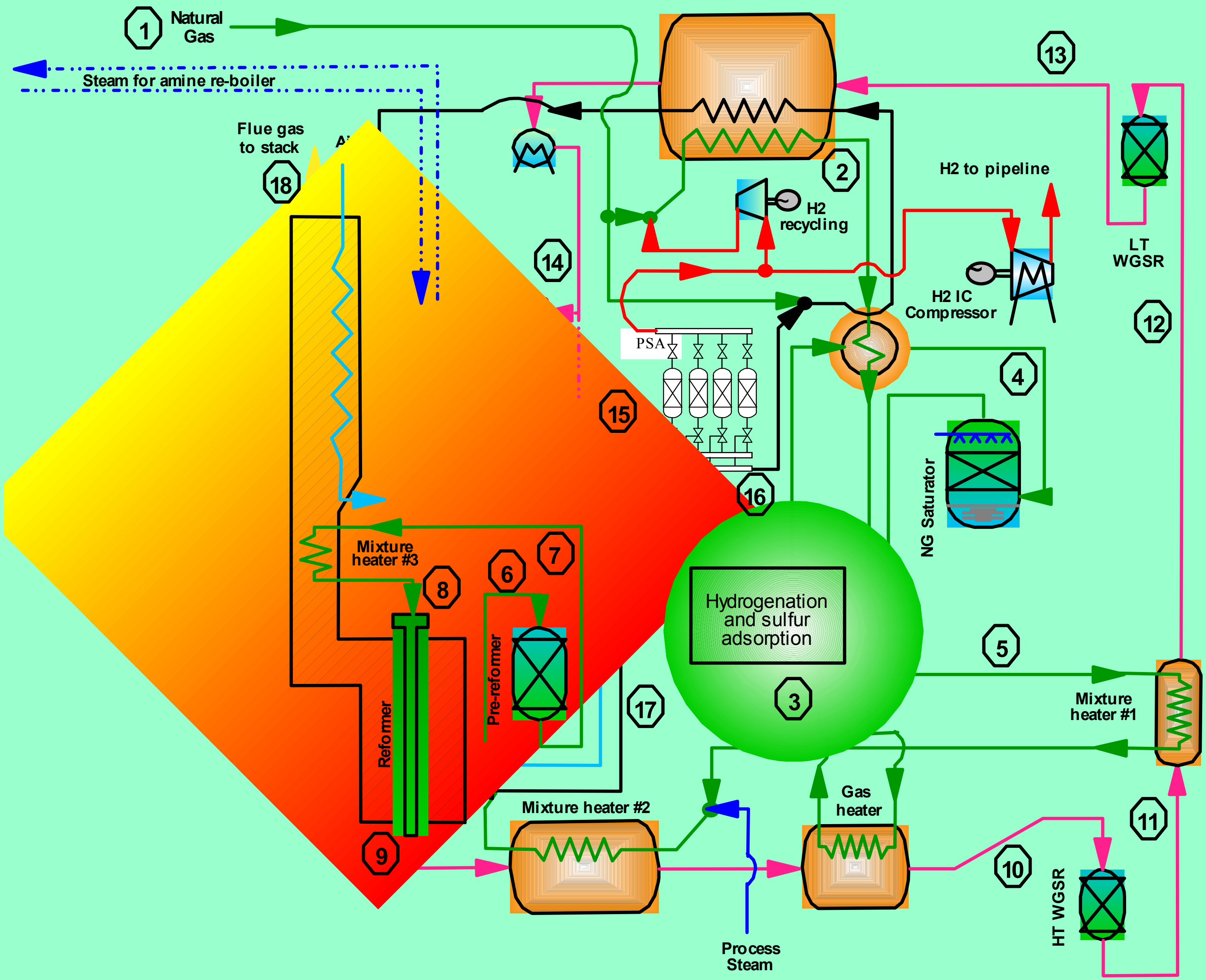
Fired Tubular Reforming

- **Steam Reforming and WGS**
  - ↗ **$CH_4 + H_2O + 206.158\ kJ/mol_{CH4} \rightarrow CO + 3\ H_2$**
  - ↗ **$CO + H_2O \rightarrow CO_2 + H_2 + 44.447\ kJ/mol_C$**
- **Nickel-base catalyst within super-alloy tubes heated by radiation in a furnace fed with purge gas (+ nat gas)**
- **Creep/life of reformer tubes limits operating T and P**

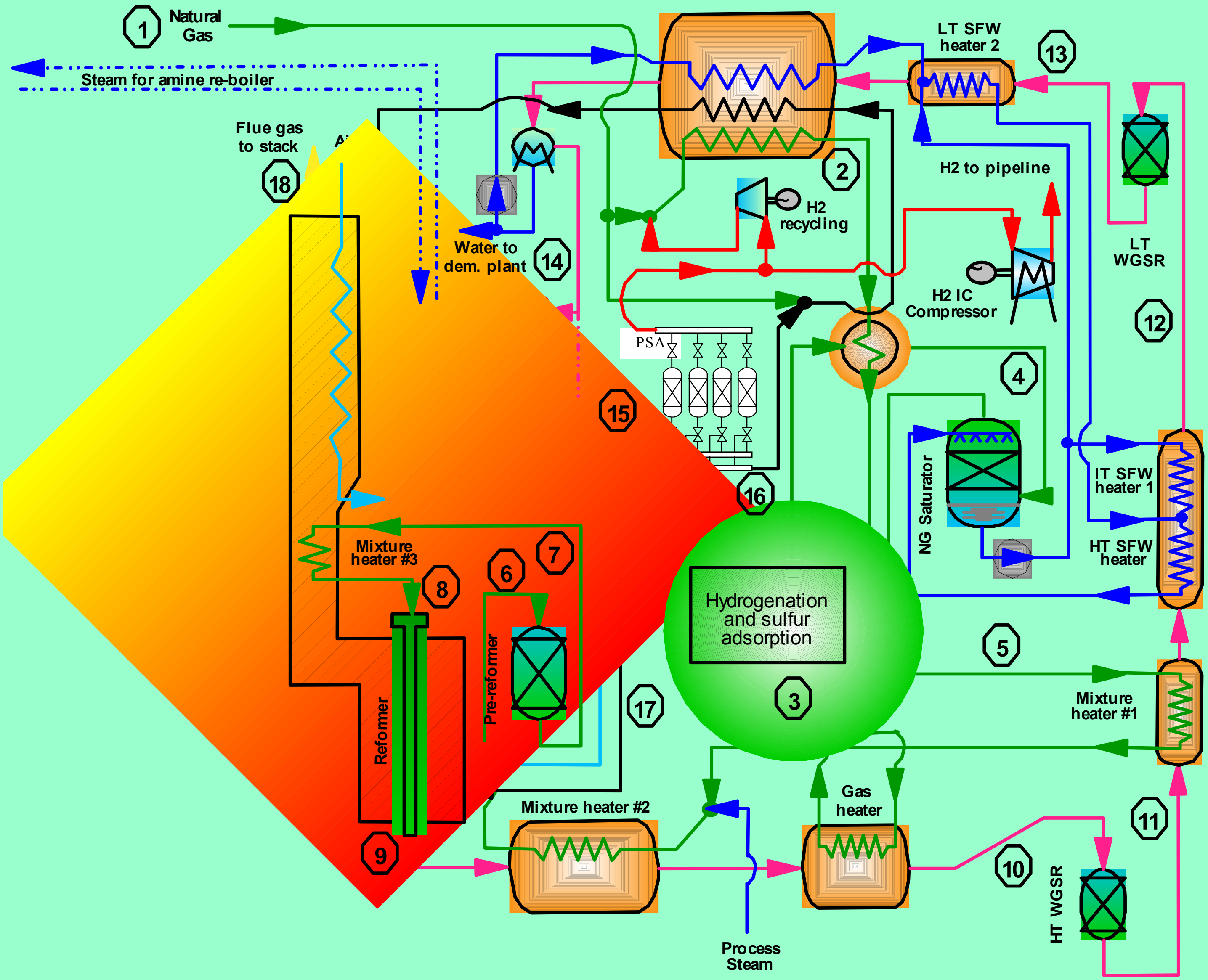
Auto-Thermal Reforming

- Partial oxidation + WGS reaction
  - $CH_4 + 0.5\ O_2 \rightarrow CO + 2\ H_2 + 35.670\ kJ/mol_{CH4}$
  - $CO + H_2O \rightarrow CO_2 + H_2 + 44.447\ kJ/mol_{C}$
  - $CH_4 + H_2O + 206.158\ kJ/mol_{CH4} \rightarrow CO + 3\ H_2$
- Nickel-base catalyst in adiabatic vessel
- No heat transfer surface → can operate at higher T and P

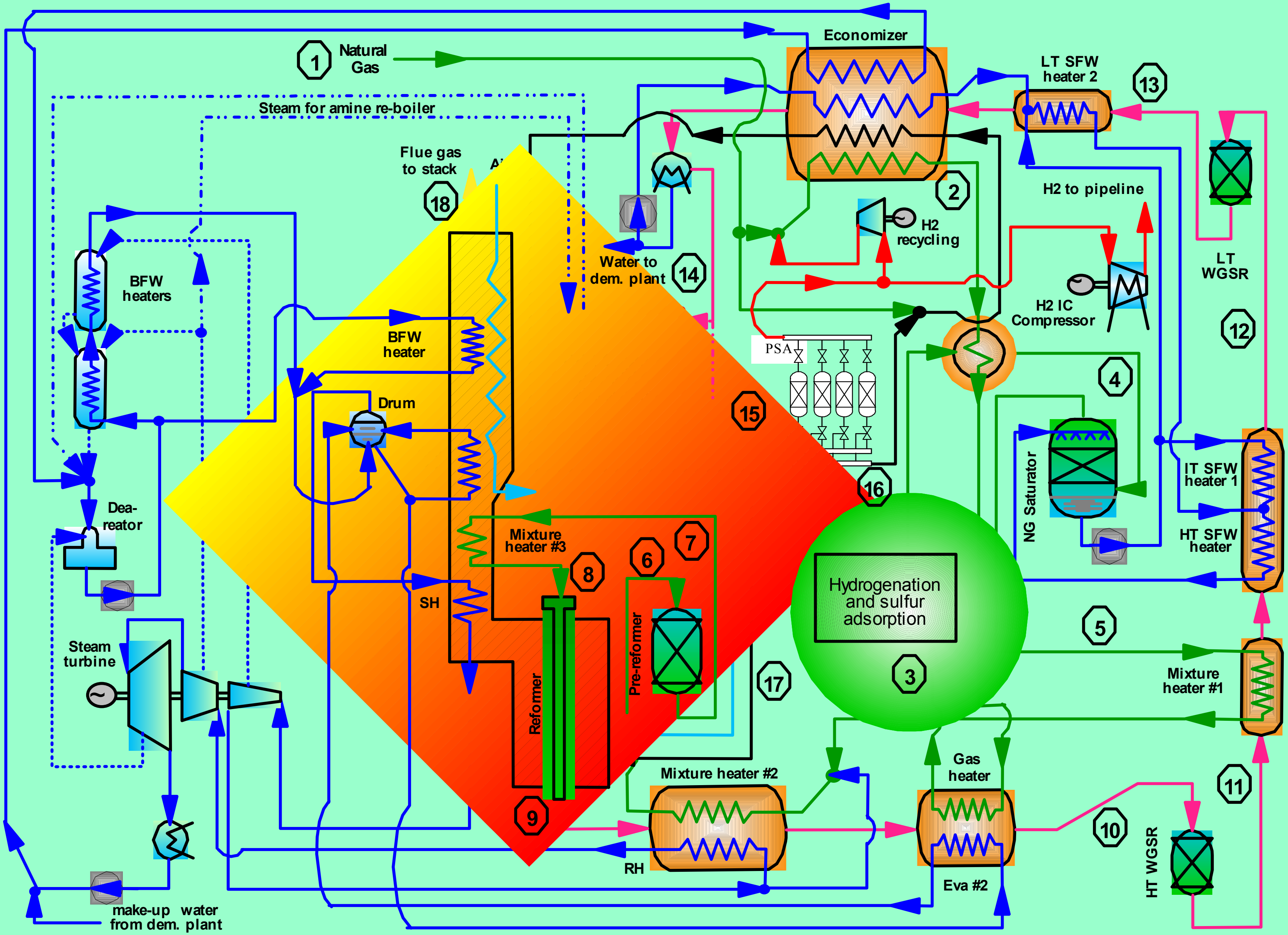
FTR + Steam Cycle: Reformer



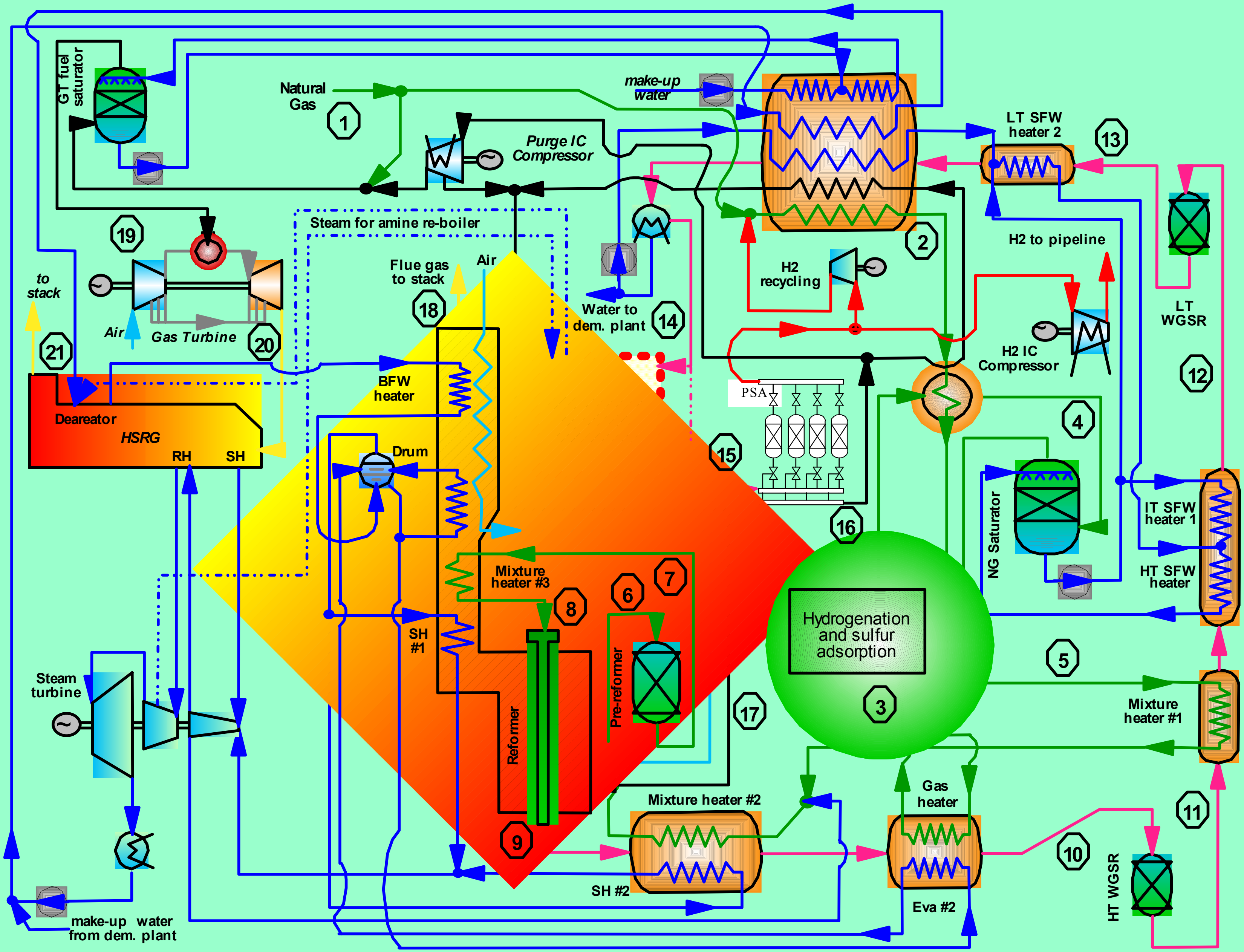
FTR + Steam Cycle: Reformer + Saturators



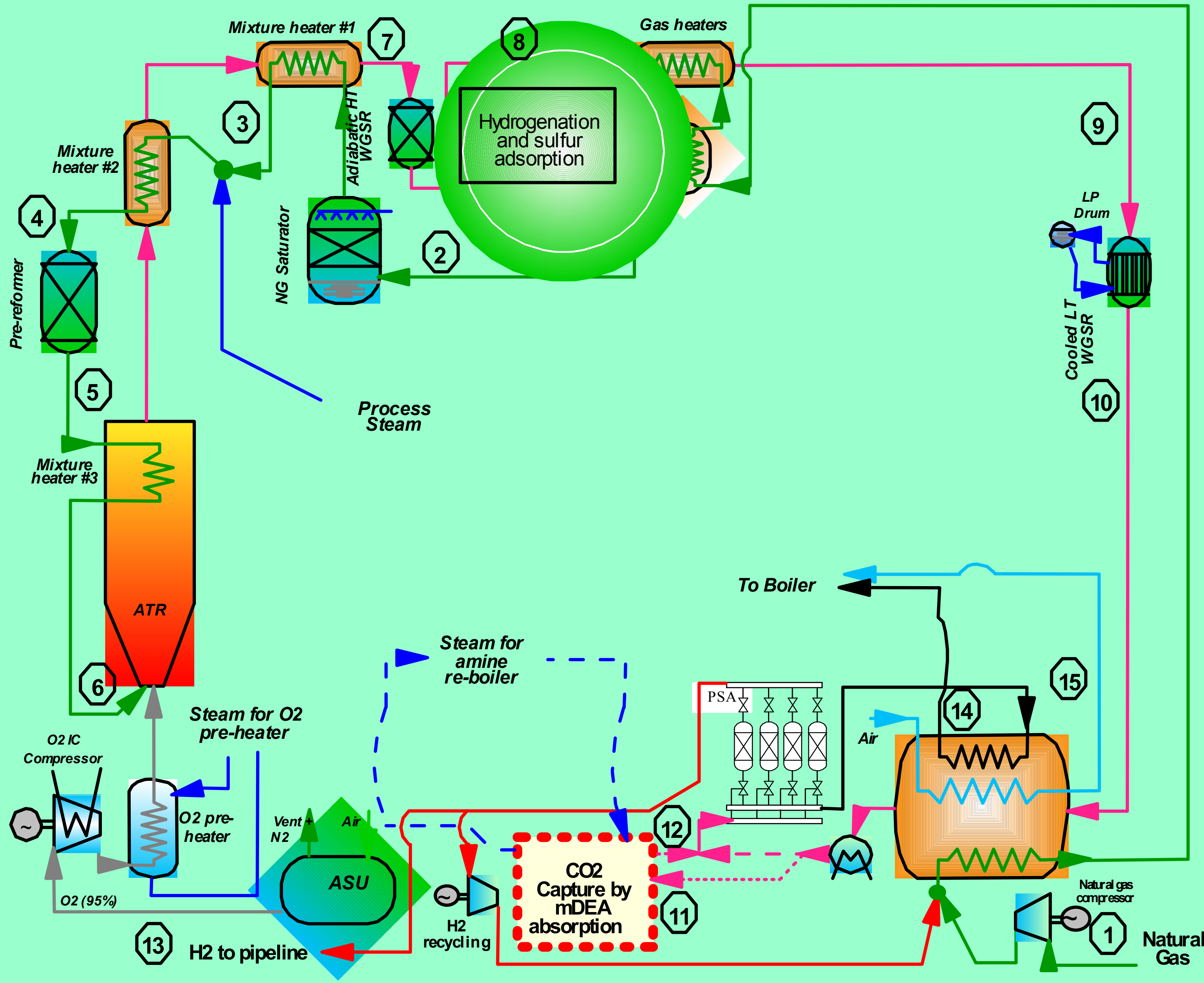
FTR + Steam Cycle: whole system



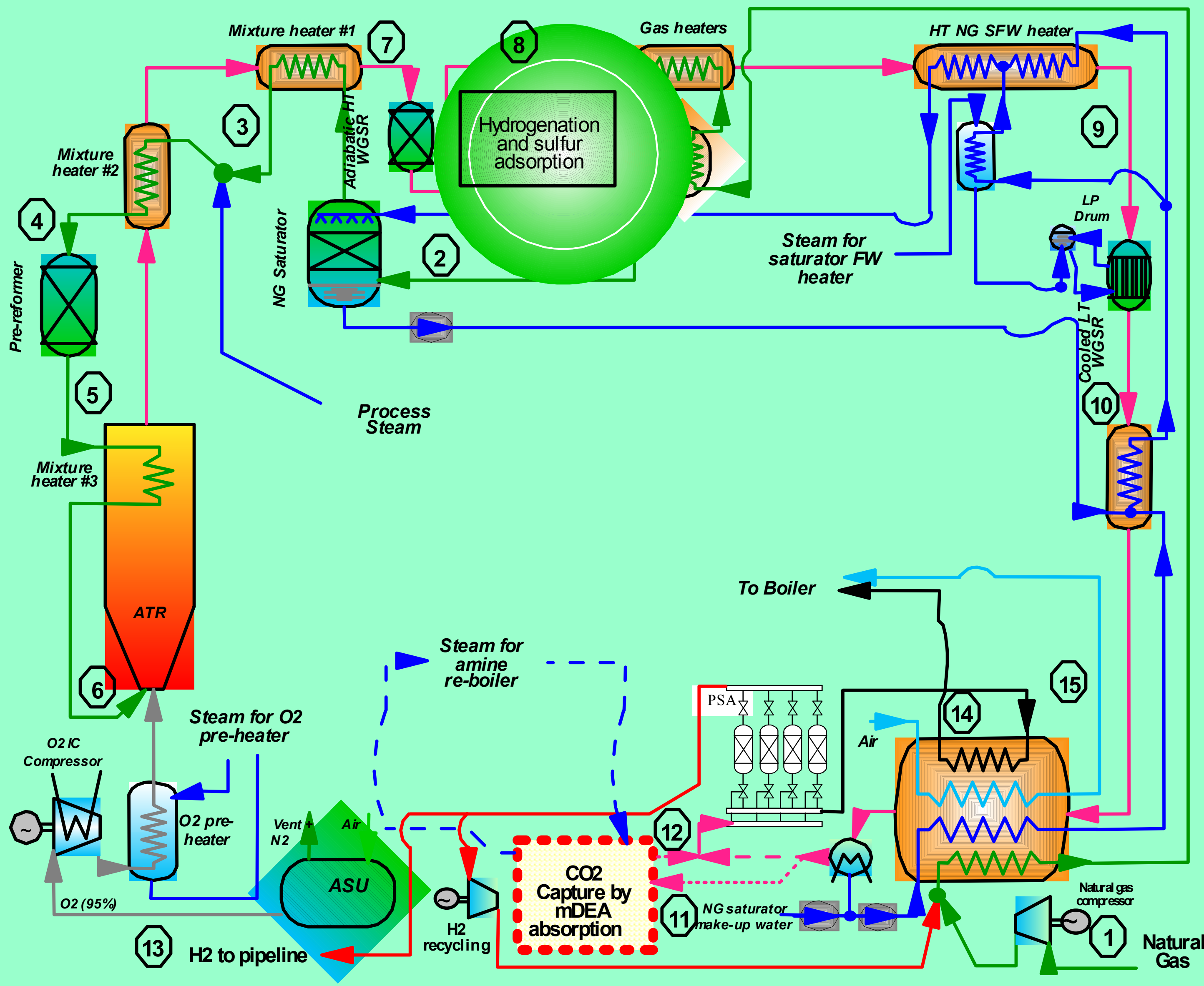
FTR + Combined Cycle: whole system



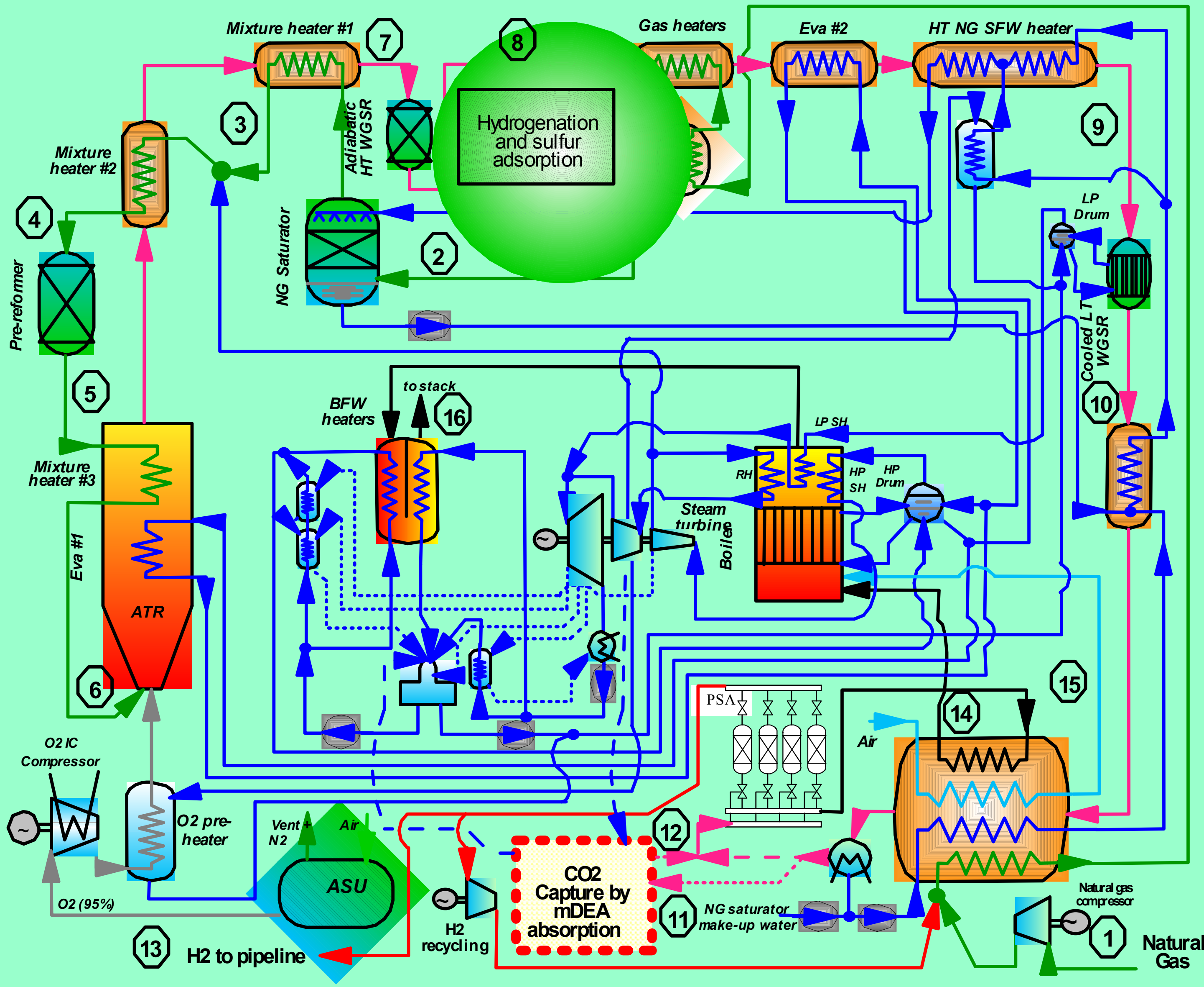
ATR + Combined Cycle: Reformer



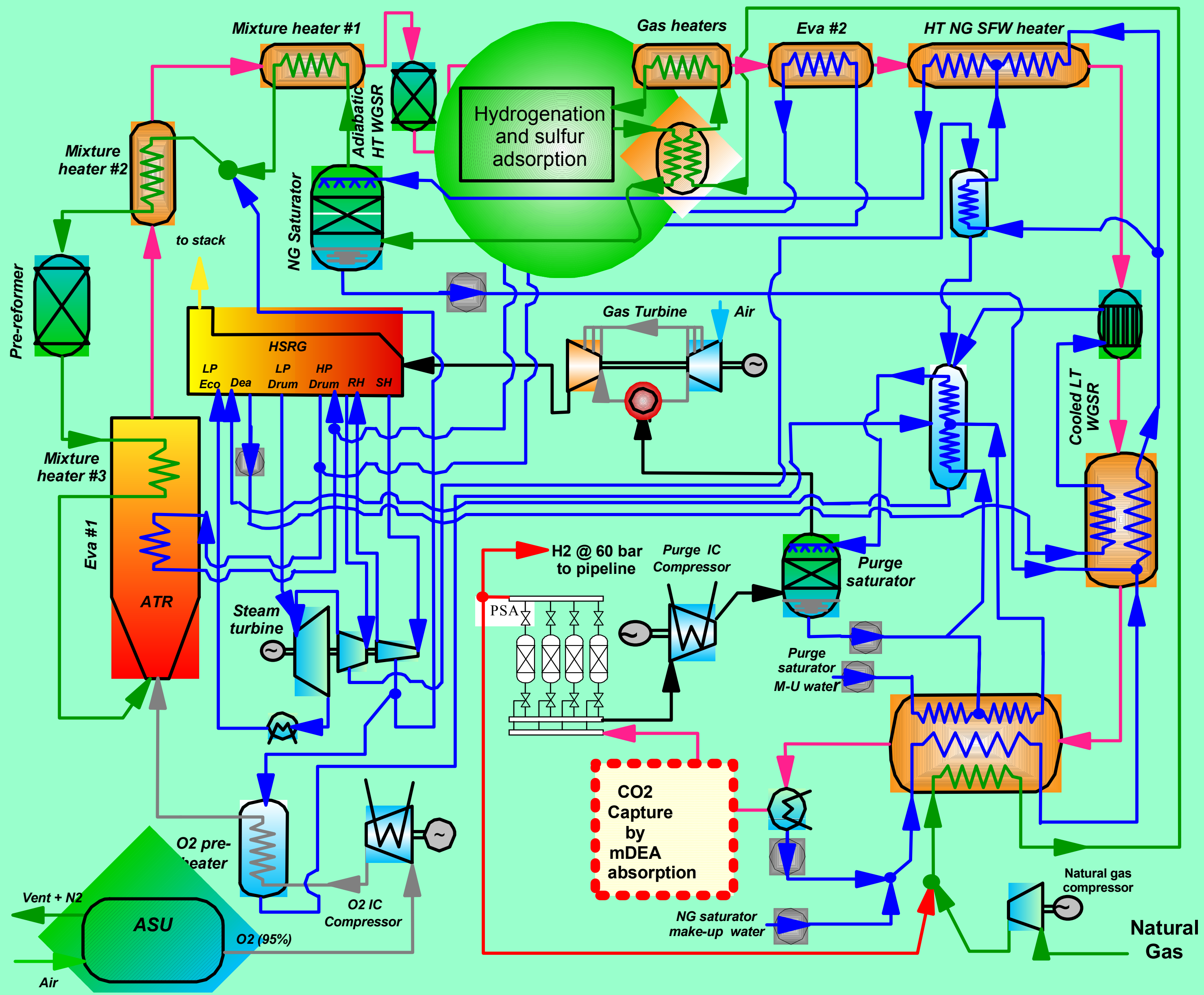
ATR + Combined Cycle: Reformer + Saturators



ATR + Steam Cycle: whole system



ATR + Combined Cycle: whole system



Heat and Mass Balances

- Code developed at Politecnico di Milano and Princeton to predict the performances of power cycles, including:
  - chemical reactions (→ gasification, steam reforming)
  - heat/mass transfer (→ saturation)
  - some distillation process (→ cryogenic Air Separation)
- Model accounts for most relevant factors affecting cycle performance:
  - scale
  - gas turbine cooling
  - turbomachinery similarity parameters
  - chemical conversion efficiencies
- Accuracy of performance estimates has been verified for a number of state-of-the-art technologies

Case study: IEA Study on FTR

			Reference Case*	Our Simulation
Assumptions	Natural Gas Input	MW_{LHV}	369.7	369.7
	Reforming Temperature	ºC	850	850
	Reforming Pressure	bar	25.4	25.4
	Steam/Carbon		3.00	3.00
	Fraction of NG Input to Burners	%	1.73	1.73
	H_2 in gas fed to Hydrogenator	%	2.00	2.00
	Hydrogenation Temperature	ºC	380	380
	Pre-reformer Inlet Temperature	ºC	620	620
	Reformer Inlet Temperature	ºC	670	670
	WGSR Inlet Temperature	ºC	~320	320
	PSA Separation Efficiency	%	88.0	88.0
	H_2 Compressor Inlet Pressure	bar	22.4	22.4
Results	Pre-reformer Outlet Temperature	ºC	~520	520
	CH_4 at Reformer Outlet	%	4.24	4.23
	WGSR Outlet Temperature	ºC	392	388
	CO at WGSR Outlet	%	1.98	1.98
	H_2 Production Efficiency	$\%_{LHV}$	76.0	75.7
	Gross Electric Efficiency	$\%_{LHV}$	1.94	1.97
	Net Electric Efficiency	$\%_{LHV}$	~0	0.43

*** Ref. Case: Foster Wheeler Report # PH2/2, march 1996, prepared for IEA**

Some relevant assumptions

- 10% vol. recycle H_2 to de-sulfurization unit
- FTR heat input controlled either by nat gas (7.5 % of input to burners) or by compressed purge gas
- HP steam generated at 110 bar, 540°C
- Reactor conversion efficiencies:
  - Pre-reformer: 10°C approach to equilibrium
  - FTR: CH_4 conversion 88.5% of full equilibrium
  - ATR and LT WGS: full equilibrium
  - HT WGS: CO conversion 97% of full equilibrium
- Pressure Swing Absorption
  - 35°C, purge gas at 1.3 bar
  - 88% H_2 separation efficiency
- Amine chemical absorption for CO_2 removal
  - 100 ppm CO_2 in gas exiting the absorber
  - stripper fed with 2.1 bar steam bled from steam turbine
  - 1 MJ steam/kg CO_2 removed
  - auxiliary + CO_2 compression work 440 kJ/kg CO_2 removed

Rationale of calculation scheme

- Set steam/carbon ratio
- Pre-heat nat gas to de-sulfurization temperature with gas-gas regenerator and heat from reformed gas
- Humidify nat gas as much as possible with saturator
- Add steam bled from steam turbine as needed
- Pre-heat to 620°C
- Pre-reform and then further pre-heat to 670°C with reformed gas
- Arrange steam cycle so to warrant Tgas ≤ 1100°C at inlet of superheater and reheater

Results

Electricity vs Hydrogen production - NO CO2 capture

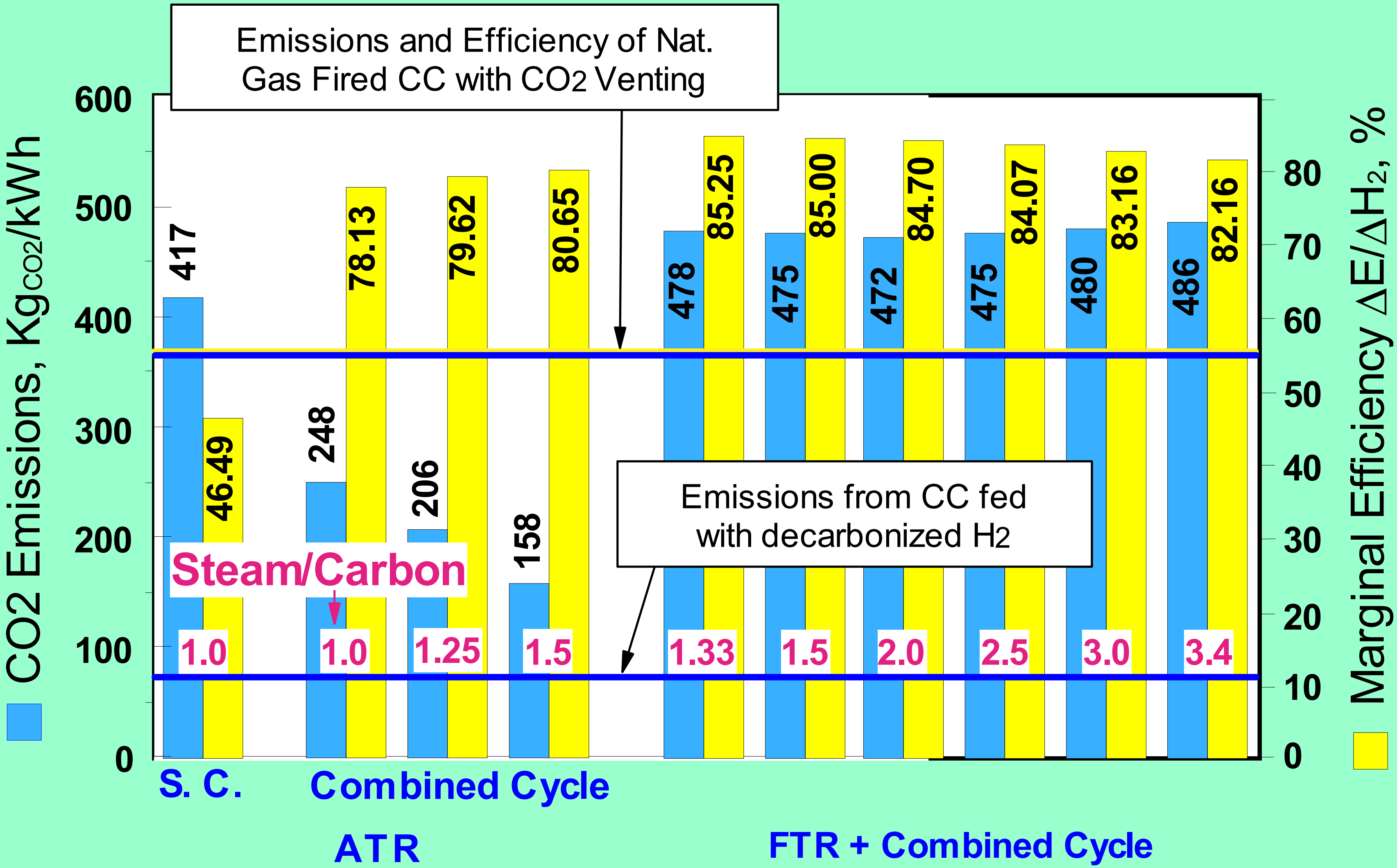
		NO CO2 capture				
		FTR	ATR		FTR	
		Reference Case	Steam Cycle	Combined Cycle	Steam Cycle	Combined Cycle
Steam to Carbon Ratio:		3	1	1	3	2
NG Input	MW_{LHV}	369.70	573.57	573.57	573.57	573.57
Gas turbine output	$\%_{LHV}$	-	-	13.19	-	11.71
Steam turbine output	$\%_{LHV}$	1.94	14.41	7.39	4.29	9.20
ASU and gas compression	$\%_{LHV}$	n.a.	-2.44	-2.45	-1.32	-0.90
Auxiliaries	$\%_{LHV}$	n.a.	-0.65	-2.05	-0.35	-0.41
CO2 removal and compression	$\%_{LHV}$	-	-	-	-	-
Net El Output	$\%_{LHV}$	0.00	11.31	16.08	2.62	19.61
H2 output	$\%_{LHV}$	76.00	55.62	55.37	75.28	51.10
CO2 emissions	kg/s	20.59	31.95	31.95	31.95	31.95
DeltaE/DeltaH vs Ref. Case	**%**	-	**55.5**	**78.0**	**362.1**	**78.7**
CO2 emissions vs Ref. Case	kg/GJLHV	73.28	73.28	73.28	73.28	73.28
	g/kWh	-	**476**	**339**	**74**	**335**

Results

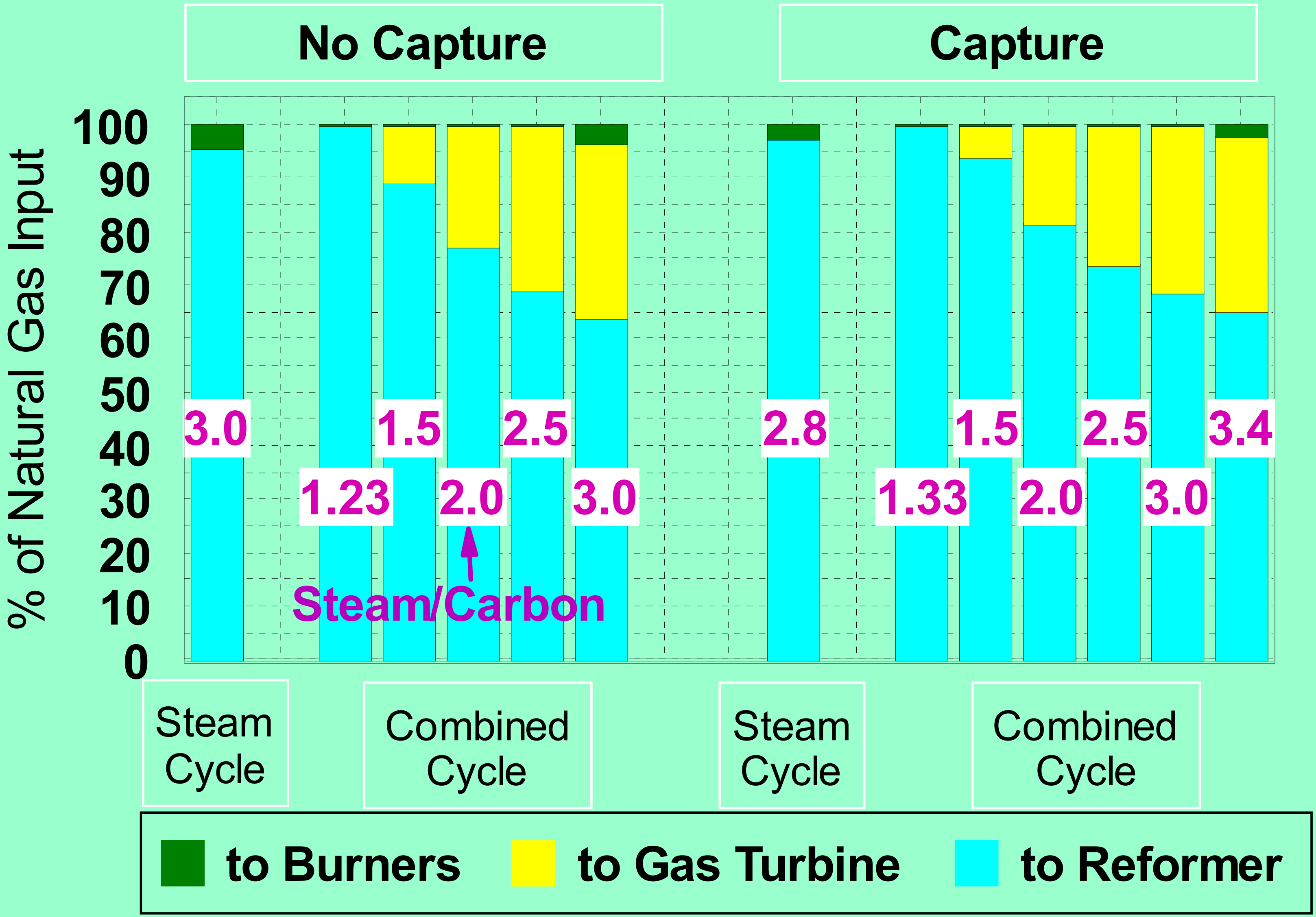
Electricity vs Hydrogen production - CO2 capture

		CO2 capture				
		FTR	**ATR**		**FTR**	
		Reference Case	**Steam Cycle**	**Combined Cycle**	**Steam Cycle**	**Combined Cycle**
Steam to Carbon Ratio:		3.3	1	1	2.8	2
NG Input	MW_{LHV}	383.61	573.57	529.87	573.57	573.57
Gas turbine output	$\%_{LHV}$	-	-	12.94	-	11.51
Steam turbine output	$\%_{LHV}$	4.05	13.07	6.30	3.93	7.38
ASU and gas compression	$\%_{LHV}$	n.a.	-2.45	-3.26	-1.25	-0.95
Auxiliaries	$\%_{LHV}$	n.a.	-0.65	-0.23	-0.52	-0.38
CO2 removal and compression	$\%_{LHV}$	n.a.	-1.76	-1.75	-1.65	-1.24
Net El Output	$\%_{LHV}$	0.00	8.22	14.01	0.52	16.32
H2 output	$\%_{LHV}$	73.30	55.62	55.37	74.55	54.03
CO2 emissions	kg/s	3.20	9.09	8.47	9.44	15.81
	% removed	85.0	71.5	71.3	70.4	50.5
DeltaE/DeltaH vs Ref. Case	**%**	-	**46.5**	**78.1**	**-41.3**	**84.7**
CO2 emissions vs Ref. Case	kg/GJLHV	11.38	11.38	11.38	11.38	11.38
	g/kWh	-	**417**	**249**	**5562**	**480**

Marginal Efficiency and CO2 emissions
Effect of Steam/Carbon ratio

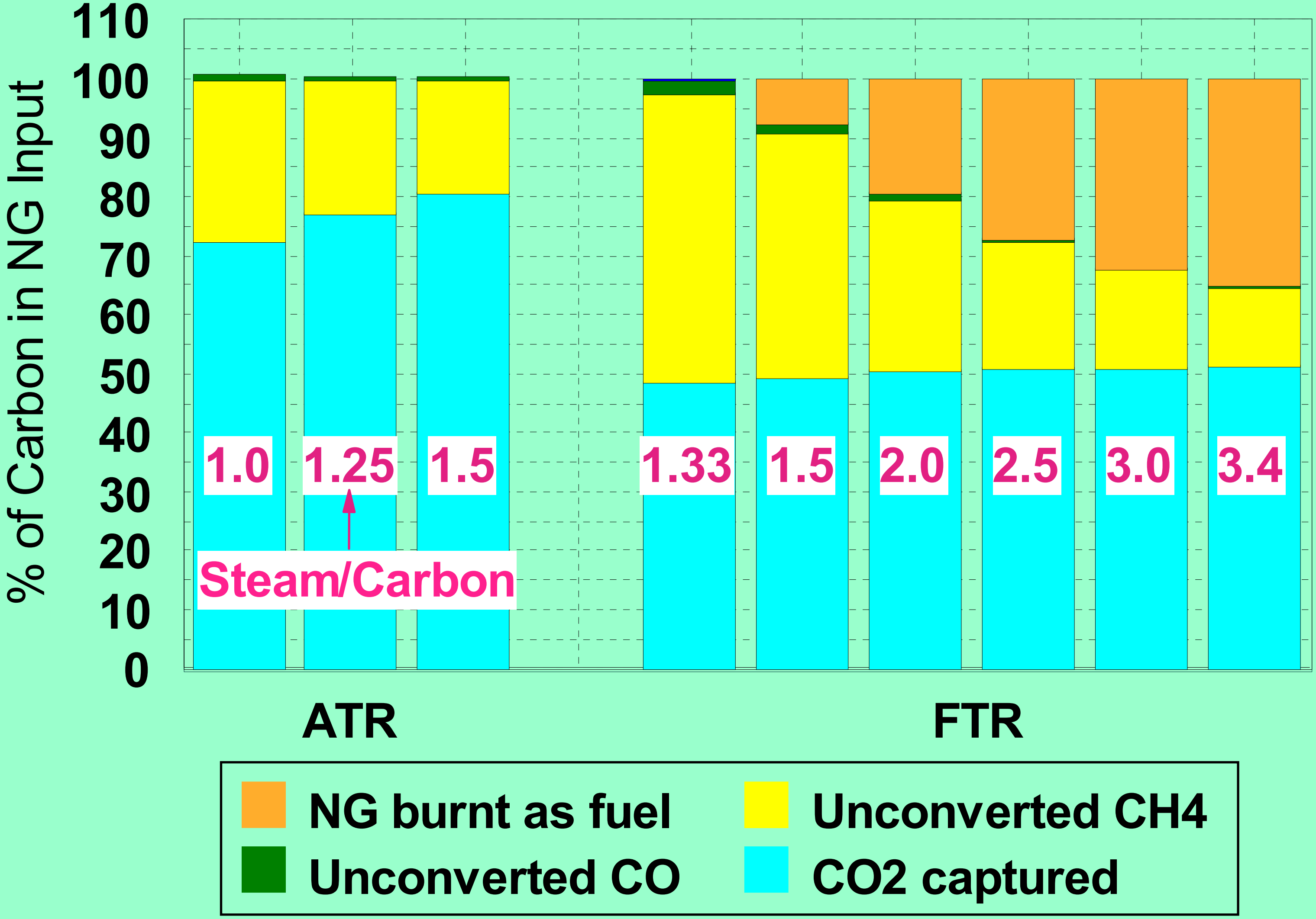


Natural Gas Input for FTR



Fate of carbon in NG feedstock

Combined Cycle with CO2 capture



Conclusions

- Co-production of electricity from nat gas reforming can be carried out at marginal efficiencies higher than 80%
- Highest E/H2 ratios and marginal efficiencies can be achieved by integrating the reformer with a Combined Cycle
- FTR+Combined Cycle can achieve relatively low carbon removal rates, unless E/H2 ratio is very low
- ATR+Combined Cycle can achieve carbon removal rates higher than 80% when operated with steam/carbon $\geq$ 1.5, with marginal electric efficiencies ~80%
- Configuration, design parameters and performance may vary substantially with the relative values of E, H2 and CO2
- Economics of ATR+Combined Cycles operated at high steam/carbon must be verified

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