Electronic supplementary information - Technical section

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Heat pipe reformer (HPR)

In this paragraph we introduce the HPR block. A schematic representation of the inlet and outlet material streams is shown in Figure 1.

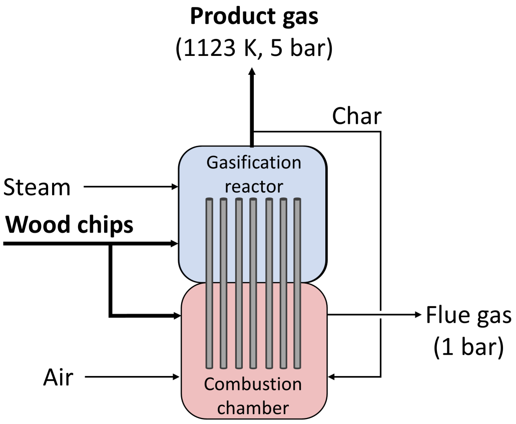


Figure 1: Schematic representation of a HPR gasifier.

Syngas

The composition of the syngas is taken from the work of Karl et al., Leimert et al. and Gallmetzer et al.? ? ? summarized in Table 1

Table 1: Product gas composition [mol%] of HPR gasifier.

	LB	BC	UB
H_2	46	44	44
CO	22	26	26
CO_2	22	18	18
CH_4	10	12	10
C_2H_4	0	0	2
H_2O	17.8	17.8	17.8

while the flow rate is calculated based on the amount needed to produce 1 MW of H_2; more specifically, a design specification in the Aspen Plus flowsheet is created and the syngas flow rate is automatically regulated to reach the production of 1 MW of H_2.

Wood inlet

The mass of wood needed is calculated based on the following assumptions:

- *Assumption 1*[1]*:* molar composition of wood (taken from EcoInvent):$CH_{1.48}O_{0.68}$, mass fraction composition C 49.4 wt%, H 6.1 wt% and O 44.5 wt%, $MW_{\mathrm{dBM}} = 24.3$ kg/mol.
- *Assumption 2*[1]*:* LHV = 18.9. MJ/kg
- *Assumption 3*[? ?] *:* amount of wood that goes to the combustor $\cong$ 33%
- *Assumption 4*[? ?] *:* gasifier efficiency (η_{G}) $\cong$ 70%

In order to close the carbon balance we have to reconcile the various experimental and match the assumptions listed above. The carbon mass balance is:

$$n^{C}_{PG} = n_{CO} + n_{\mathrm{CO_2}} + n_{\mathrm{CH_4}} + 2 \cdot n_{\mathrm{C_2H_4}} \tag{1}$$

$$n^{C}_{PG} = n^{C}_{\mathrm{wood}} - n^{C}_{char} - n^{C}_{comb} \tag{2}$$

$$n^{C}_{FG} = n^{C}_{char} + n^{C}_{comb} \tag{3}$$

where PG is the product gas, wood is the total input of wood into the system, comb is the portion of wood combusted with air and FG in the flue gas of the combustor. To close the mass balance we obtain that per MW of wood inlet, we have a certain amount of carbon in the form of char. This char is then combusted in the combustion chamber and therefore emitted as CO_2 within the flue gas. Table 2 summarizes the amount of char obtained for the three product gas compositions (LB, BS and UB)

Table 2

PG composition	Char[mol/hr]/Wood inlet [MW]
LB	50.7
BC	141.4
UB	2.8

Steam

Steam is co-produced from the down-stream process at P=44 bar and T=400°C.

The amount of steam fed into the gasifier is calculated following the procedure explained in Karl et al.[?] . The minimum steam demand for stoichiometric conversion S_{min} is calculated as:

$$S_{min} = (1-n)\frac{MW_{\mathrm{water}}}{MW_{\mathrm{wood}}} \tag{4}$$

where n is the stoichiometric amount of oxygen in the wood CH_nO_m, and MW is the molar weight. We obtain S_{min} is equal to 0.2365. The amount of steam expressed in mass is calculated as:

$$m_{\mathrm{steam}} = S_{min} \cdot \sigma \cdot m_{\mathrm{wood}} \tag{5}$$

where σ is the excess steam ratio (we took σ=3 as in Leimert et al.) and m_{wood} is the total wood inlet.

Air

The amount of air fed into the combustor is calculated following the procedure explained in Karl et al.[?] :

$$m_{air} = \frac{MW_{\mathrm{air}} \cdot \gamma \cdot m_{\mathrm{comb}}}{MW_{\mathrm{wood}} \cdot x_{\mathrm{O}_2}} \tag{6}$$

where γ is the excess air (we took γ=1.4 as in Karl et al.) and m_{comb} is the mass combusted and x_{O2} is the molar fraction of oxygen in air.

Flue gas

The mass of flue gas (FG) is calculated as:

$$m_{\mathrm{FG}} = m_{\mathrm{air}} + m_{\mathrm{comb}} \tag{7}$$

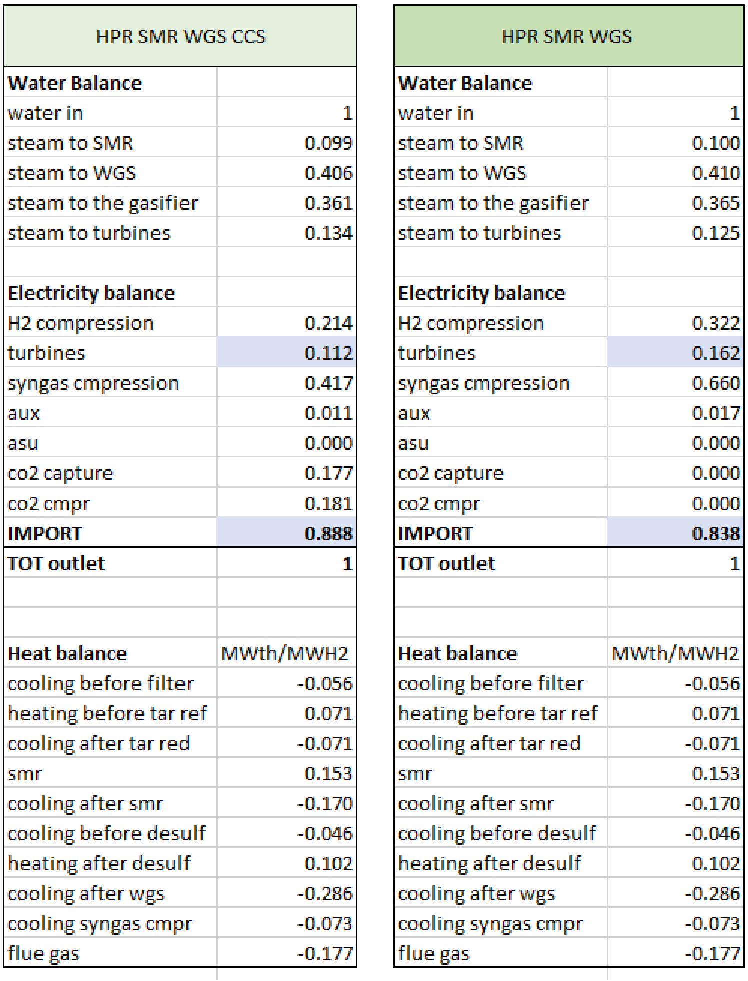
and the composition is retrieved based on the carbon balance and air input. The amount of CO_2 is calculated based on the moles of carbon present in the flue gas (n_{FG}^{C}). The FG composition obtained for the three product gas composition is summatized in Table 3.

Table 3: Flue gas composition [wt%] of HPR gasifier after gas cleaning.

	LB	BC	UB
CO_2	20	21	20
O_2	5	3	4
N_2	62	70	70
H_2O	13	6	6

Energy balance - LHV-based

In Figure 2 we report the water, electricity and heat balances.



HPR SMR WGS CCS	
Water Balance	
water in	1
steam to SMR	0.099
steam to WGS	0.406
steam to the gasifier	0.361
steam to turbines	0.134
Electricity balance	
H2 compression	0.214
turbines	0.112
syngas cmpression	0.417
aux	0.011
asu	0.000
co2 capture	0.177
co2 cmpr	0.181
IMPORT	**0.888**
TOT outlet	**1**
Heat balance	MWth/MWH2
cooling before filter	-0.056
heating before tar ref	0.071
cooling after tar red	-0.071
smr	0.153
cooling after smr	-0.170
cooling before desulf	-0.046
heating after desulf	0.102
cooling after wgs	-0.286
cooling syngas cmpr	-0.073
flue gas	-0.177

HPR SMR WGS	
Water Balance	
water in	1
steam to SMR	0.100
steam to WGS	0.410
steam to the gasifier	0.365
steam to turbines	0.125
Electricity balance	
H2 compression	0.322
turbines	0.162
syngas cmpression	0.660
aux	0.017
asu	0.000
co2 capture	0.000
co2 cmpr	0.000
IMPORT	**0.838**
TOT outlet	1
Heat balance	MWth/MWH2
cooling before filter	-0.056
heating before tar ref	0.071
cooling after tar red	-0.071
smr	0.153
cooling after smr	-0.170
cooling before desulf	-0.046
heating after desulf	0.102
cooling after wgs	-0.286
cooling syngas cmpr	-0.073
flue gas	-0.177

Figure 2: Water, electricity and heat balances of the HPR chains

Sorption enhanced reforming (SER) gasifier

In this section we introduce the oxySER conversion block. A schematic representation of the inlet and outlet material streams is shown in (Figure 3).

For this work, we chose to operate the combustor with oxygen instead of air (oxySER), therefore almost pure CO_2 can be recovered at outlet of the reactor.

The bed material considered is Limestone (type KS_W described in the report ERBA II[2]); its composition is summarized in Table 4

Syngas

The composition of the inlet syngas is taken from the literature (from the ERBAII final report[2]

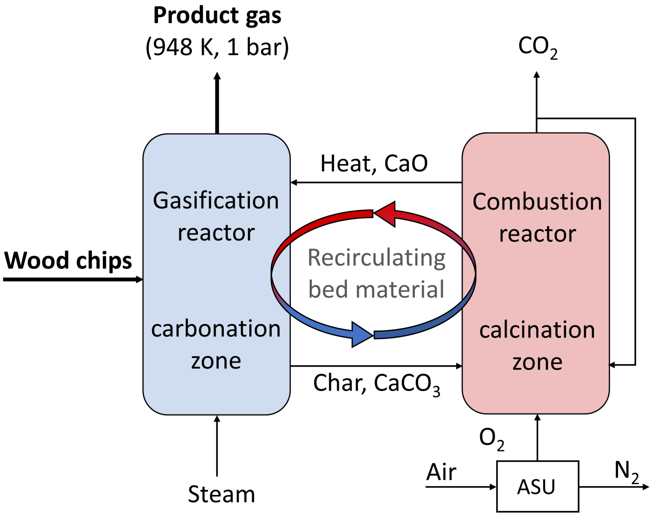


Figure 3: Schematic representation of a oxySER gasifier.

Table 4

Chemical composition	wt%
CaO	96.96
MgO	1.25
SiO_2	0.89
Al_2O_3	0.54
Fe_2O_3	0.36
Mass loss after calcination	44

and from Pfeifer et al.[?]) (see table 5). While the flow rate is calculated based on the amount needed to produce 1 MW of H_2 (via design specification).

Wood inlet

Table 5: Product gas composition [mol%] of oxySER gasifier after gas cleaning.

	LB	BC	UB
H_2	64.1	66.7	69.5
CO	6.9	7.7	8.6
CO_2	11.6	8.7	5.6
CH_4	14.03	13.97	13.90
C_2H_4	1.2	1.0	0.8
C_2H_6	0.6	0.7	0.8
N_2	1.5	1.3	1.1

The mass of wood needed is calculated based on the following assumptions:

- *Assumption 1[1]:* molar composition of wood (taken from EcoInvent):$\mathrm{CH_{1.48}O_{0.68}}$, mass fraction composition C 49.4 wt%, H 6.1 wt% and O 44.5 wt%, $\mathrm{MW_{dBM}} = 24.3$ kg/mol.
- *Assumption 2[1]:* LHV = 18.9. MJ/kg
- *Assumption 3[2,3]:* amount of carbon that goes to the combustor (η_C) $\cong$ 63%

We express the ratio between the moles of carbon present in the flue gas and in the dry biomass fed into the gasifier:

$$\eta_C = 1 - \frac{\mathrm{n_C^{PG}}}{\mathrm{n_C^{wood}}}$$

$$\mathrm{n_C^{wood}} = \frac{0.1\mathrm{MJ/s} \cdot 3600\mathrm{s}}{18.9\mathrm{MJ/kg}} \cdot \frac{0.495}{12\mathrm{kg/kmol}}$$

$$= 0.785$$

$$\eta_C = [0.623^2, 0.624^3]$$

the value of $\mathrm{n_C^{PG}}$ is retrieved from the experimental data reported in the literature; using the data from the IEA final report[3] we get $\eta_C = 0.623$ and from the ERBAII project[2] $\eta_C = 0.624$; thus in our calculations we use a value of $\eta_C = 0.63$.

Steam

The amount of steam has been calculated as:

$$m_{\text{steam}} = 0.5 \cdot m_{\text{wood}} \tag{8}$$

Oxygen

The amount of oxygen fed is calculated based on the values reported in the literature[2]. Based on this value, we calculated how much oxygen per MW of wood input is required (parameter $\eta_{\mathrm{O_2,BM}}$):

$$\eta_{\mathrm{O_2,BM}} = \frac{m_{\text{air}} w_{\mathrm{O_2}}}{\mathrm{LHV}_{\text{wood}} m_{\text{wood}}} \tag{9}$$

where $\mathrm{w_{O2}}$ is the oxygen weight fraction in air. We obtain $\eta_{\mathrm{O_2,BM}} = 0.115$. The amount of oxygen burnt in the combustor is calculated as:

$$\mathrm{m_{O_2}} = \mathrm{LHV}_{\text{wood}} m_{\text{wood}} \cdot \eta_{\mathrm{O_2,BM}}$$

$\mathbf{CO_2}$-rich flue gas

The composition of the oxySER flue gas is taken from the literature (from Schweitzer et al.[?] and it is expressed as mass fraction ($\mathrm{w_i}$):

$$\mathrm{w_{CO_2}} = 0.7986$$

$$\mathrm{w_{O_2}} = 0.0527$$

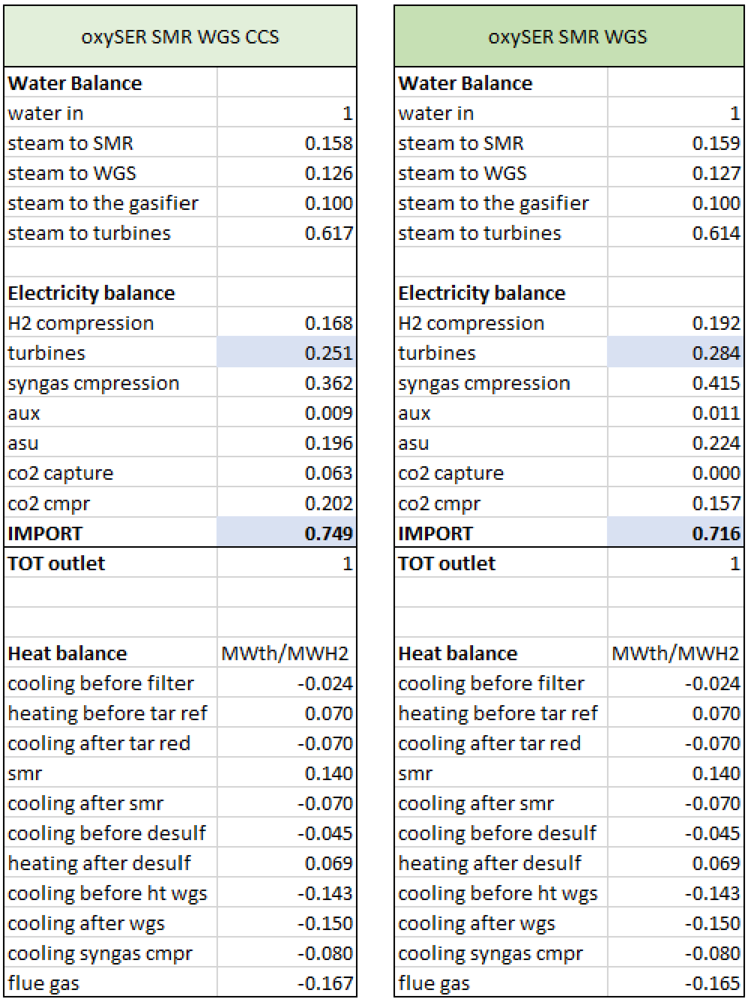
$$\mathrm{w_{H_2O}} = 0.1487$$

while the flow rate is calculated based on the assumption made on the amount of carbon burnt in the combustor (see paragraph wood inlet, where we define the amount of $\mathrm{CO_2}$ present in the flue gas $\mathrm{m_{CO_2}^{FG}}$)):

$$\mathrm{m_{tot^{FG}}} = \frac{\mathrm{m_{CO_2}^{FG}}}{\mathrm{w_{CO_2}}}$$

Energy balance - LHV-based

In Figure 4 we report the water, electricity and heat balances.



oxySER SMR WGS CCS	
Water Balance	
water in	1
steam to SMR	0.158
steam to WGS	0.126
steam to the gasifier	0.100
steam to turbines	0.617
Electricity balance	
H2 compression	0.168
turbines	0.251
syngas cmpression	0.362
aux	0.009
asu	0.196
co2 capture	0.063
co2 cmpr	0.202
IMPORT	**0.749**
TOT outlet	1
Heat balance	MWth/MWH2
cooling before filter	-0.024
heating before tar ref	0.070
cooling after tar red	-0.070
smr	0.140
cooling after smr	-0.070
cooling before desulf	-0.045
heating after desulf	0.069
cooling before ht wgs	-0.143
cooling after wgs	-0.150
cooling syngas cmpr	-0.080
flue gas	-0.167

oxySER SMR WGS	
Water Balance	
water in	1
steam to SMR	0.159
steam to WGS	0.127
steam to the gasifier	0.100
steam to turbines	0.614
Electricity balance	
H2 compression	0.192
turbines	0.284
syngas cmpression	0.415
aux	0.011
asu	0.224
co2 capture	0.000
co2 cmpr	0.157
IMPORT	**0.716**
TOT outlet	1
Heat balance	MWth/MWH2
cooling before filter	-0.024
heating before tar ref	0.070
cooling after tar red	-0.070
smr	0.140
cooling after smr	-0.070
cooling before desulf	-0.045
heating after desulf	0.069
cooling before ht wgs	-0.143
cooling after wgs	-0.150
cooling syngas cmpr	-0.080
flue gas	-0.165

Figure 4: Water, electricity and heat balances of the oxySER chains

Entrained Flow (EF) gasifier

The entrained flow biomass gasifier is modelled in Aspen Plus following what described in Meerman et al.[4]. A schematic representation of the gasifier output and input stream is shown in Figure 5

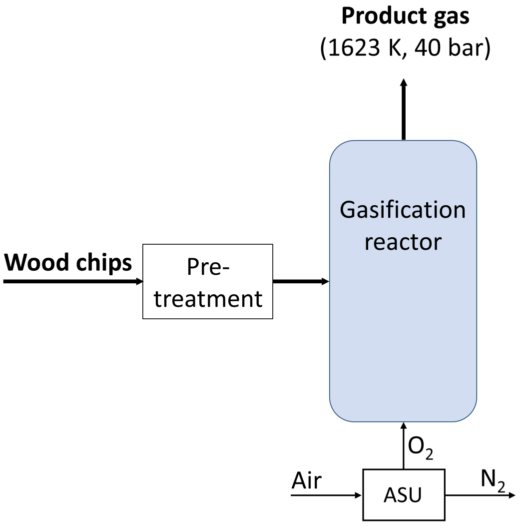


Figure 5: Schematic representation of an EF gasifier. For this type of technology before feeding a biomass pre-treatment is needed (pre-drying, torrefaction and pulverisation of the wood chips)

Wood chips

In the case of an EF gasifier, the pre-tratment of wood is necessary. To emulate the torrefaction process, wet biomass is heated to 260°C with subsequent reduction of the water content to 3 wt.%. Heat is provided from the product gas cooling section. The modelling of the reaction mechanisms occurs in a decomposition reactor (RYield reactor)[4]. Reactions are not modelled in detail but biomass is converted to reference state, whereas the energy required for breaking the molecular bonds is fed to the gasifier. The electricity consumption needed for the biomass pre-treatment are taken from different sources: drying and torrefaction from Manouchehrinejad et al.[5] (drying inlet moisture content 30-50 wt%, outlet moisture content 15-10 wt%, electric energy consumption 0.14 MJ/kg, thermal energy consumption 2.67 $\mathrm{MJ_{th}}$/kg; torrefaction outlet moisture content 3-2 wt%, electric energy consumption for torrefaction 0.15 MJ/kg, and 0.02 MJ/kg for tor cooling, thermal energy consumption 0.67 $\mathrm{MJ_{th}}$/kg) and for pulverization from Tremel et al.[6] (electric energy consumption 36 kWh/t; range of values found in the literature 25-45 kWh/t[4,5]). The wood has to be pressurized before being fed into the entrained flow reactor; the technology selected is the hydraulic screw piston feeding system, and the electricity consumption of the biomass pressurization process is calculated based on the coefficient retrieved from Meerman et al. (42.5 kWh/t).[4] We are aware that the coefficients used might not be precise and these assumptions could affect the overall performance of the production chain. Therefore, we performed a sensitivity analysis on the electricity consumption of the pre-treatment section and of the biomass pressurization and feeding system by decreasing and increasing it by 20 pp. We also performed a sensitivity analysis on the percentage of dry mass lost due to torrefaction; in this case, the range of values selected comes from the work of Berman et al..[?] The amount of wood fed into the gasifier is calculated such that at the end 1MW of hydrogen is obtained.

Syngas

The obtained syngas composition after the gas cleaning is expressed as mole fraction (see table 6).

Oxygen

Oxygen is produced from an air separation unit. We assume the same energy requirements as in out previous work[7]. We compress it before feeding into the gasification reactor. The oxygen

Table 6: Product gas molar composition [mol%] EF gasifier after gas cleaning.

$$\begin{array}{lcrlcr} x_{H_2} & = & 28.89 & x_{CO} & = & 55.45 \\ x_{CO_2} & = & 14.07 & x_{CH_4} & = & 0 \\ x_{C_2H_4} & = & 0 & x_{C_2H_6} & = & 0 \\ x_{N_2} & = & 0.37 & & & \\ x_{Ar} & = & 1.22 & & & \end{array}$$

pressure is 1.2 times the pressure of the reactor:

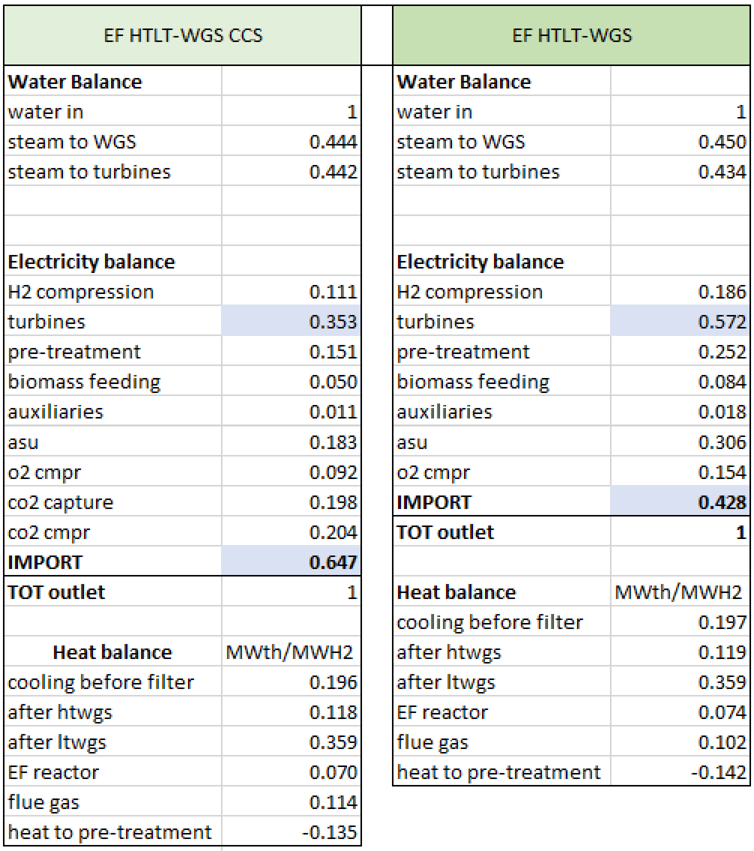
$$\begin{aligned} P_{EF} &= 40\text{bar} \\ P_{O_2} &= 1.2 \cdot P_{EF} \\ &= 48\text{bar} \end{aligned}$$

Energy balance - LHV-based

In Table 7 we report the energy balance of the EF chain on LHV-basis, while in Figure 6 we report the water, electricity and heat balances.

Wood input	1.8422	MW
Wood after pre-treatment	1.7545	MW
Product gas after gas cleaning	1.2408	MW
Gas before the HT-WGS	1.2475	MW
Gas after the LT-WGS	1.1233	MW
Hydrogen recycle stream	0.0065	MW
Hydrogen product	1	MW

Table 7: EF energy balance



EF HTLT-WGS CCS	
Water Balance	
water in	1
steam to WGS	0.444
steam to turbines	0.442
Electricity balance	
H2 compression	0.111
turbines	0.353
pre-treatment	0.151
biomass feeding	0.050
auxiliaries	0.011
asu	0.183
o2 cmpr	0.092
co2 capture	0.198
co2 cmpr	0.204
IMPORT	**0.647**
TOT outlet	1
Heat balance	MWth/MWH2
cooling before filter	0.196
after htwgs	0.118
after ltwgs	0.359
EF reactor	0.070
flue gas	0.114
heat to pre-treatment	-0.135

EF HTLT-WGS	
Water Balance	
water in	1
steam to WGS	0.450
steam to turbines	0.434
Electricity balance	
H2 compression	0.186
turbines	0.572
pre-treatment	0.252
biomass feeding	0.084
auxiliaries	0.018
asu	0.306
o2 cmpr	0.154
IMPORT	**0.428**
TOT outlet	**1**
Heat balance	MWth/MWH2
cooling before filter	0.197
after htwgs	0.119
after ltwgs	0.359
EF reactor	0.074
flue gas	0.102
heat to pre-treatment	-0.142

Figure 6: Water, electricity and heat balances of the ef chains

Carbon balance

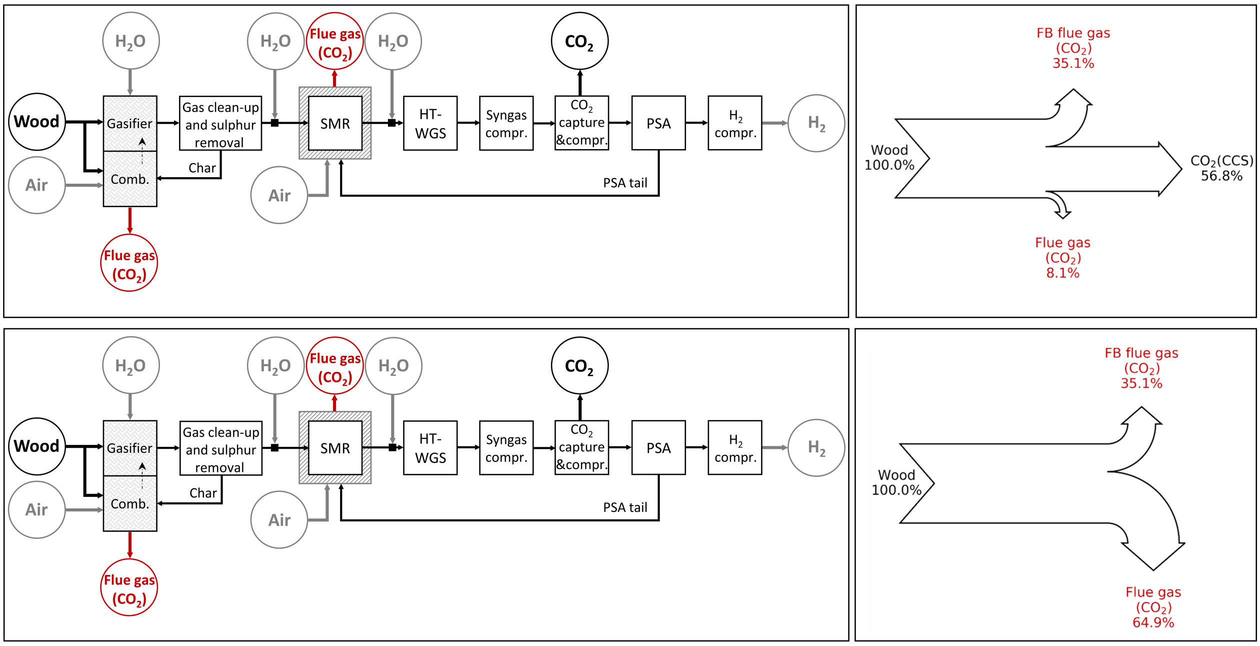


Figure 7: On the left: Schematic process schemes of the HPR chain with and without CCS; on the right: Sankey diagram of the carbon balance.

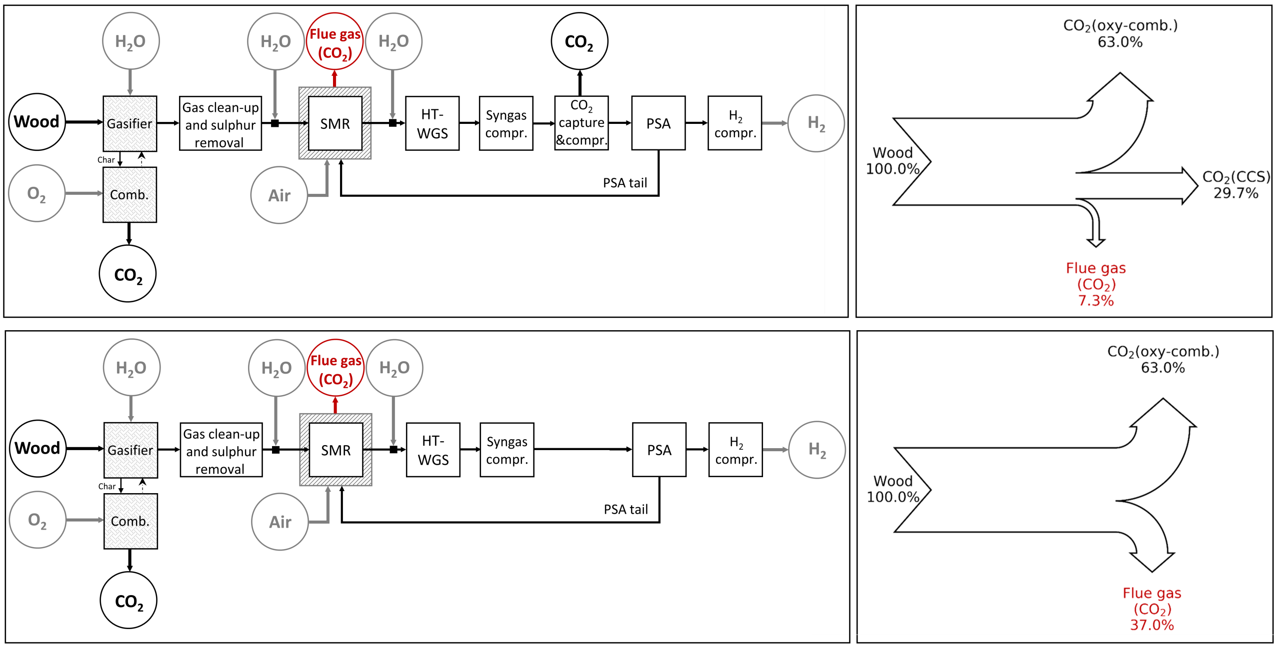


Figure 8: On the left: Schematic process schemes of the oxySER chain with and without CCS; on the right: Sankey diagram of the carbon balance.

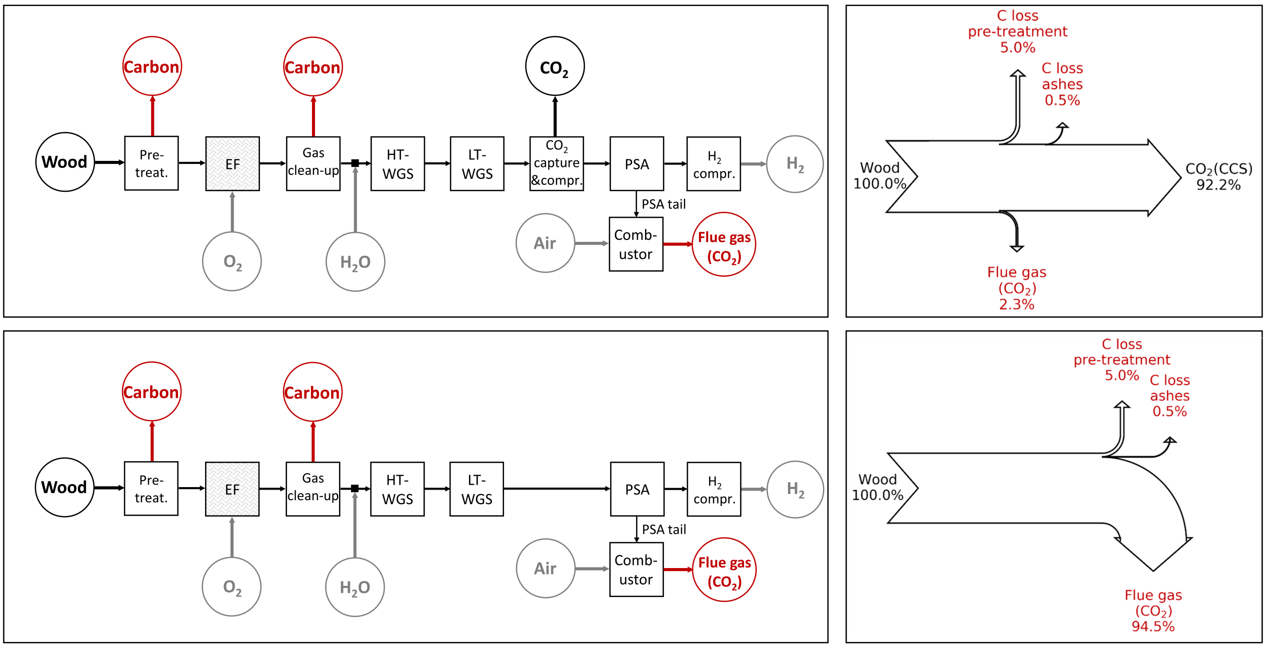


Figure 9: On the left: Schematic process schemes of the EF chain with and without CCS; on the right: Sankey diagram of the carbon balance.

Block 2: SMR

We modelled the steam methane reformer using the RGibbs unit in Aspen Plus, which uses Gibbs free energy minimization with phase splitting to calculate equilibrium, where the option to calculate phase equilibrium and chemical equilibrium was selected. The modelling of this reactor is in agreement with the work done by Foster and Wheeler published in the IEAGHG report on hydrogen production.[8] The reformer reactor is operated at 1185 K; the heat required is provided via heat from a furnace where the PSA tail gas is burnt with air (see detailed flowsheet explained in Antonini and Treyer et al.[7] for more information about the heat integration of the hydrogen production plant). The molar steam to carbon ratio at the inlet of the SMR is set to 2.6. By operating the SMR as described above, we obtain a methane conversion for both HPR and oxySER cases of 99%.

Block 3: WGS

The water-gas-shift section is composed by a single high-temperature WGS reactor unless specified (see EF chain with HT and LT shifts) and it is modelled at equilibrium following the temperature approach. The inlet temperature is set at 560 K and 469 K respectively for HT and LT WGS, and the molar steam to reactive carbon (CO and CH_4) ratio at the inlet of the HT WGS reactor is set to 3.1.

Block 4: pre-combustion CO_2 capture plant

The same detail simulation of an MDEA-based CO_2 capture plant used in Antonini and Treyer et al.[7] is employed; the MDEA concentration in the solvent is 50 wt%, the used CO_2 to MDEA molar ratio at the inlet of the absorber (CO_2 in the gas inlet stream, MDEA in the lean streams) is 0.30. For the HPR and oxySER cases the raw hydrogen is compressed before entering the capture unit at 26 bar; while for the EF the all process occurs hat high pressure and before the capture unit the raw hydrogen stream has a pressure of 34 bar. We consider a CO_2 capture rate of the unit of 98%. The specific equivalent work required to capture CO_2 is 0.68 $\mathrm{MJ/kg_{CO_2}}$ for the HPR and oxySER configurations, and 0.70 $\mathrm{MJ/kg_{CO_2}}$ for the EF one.

Block 5: PSA

An hydrogen recovery of 90% and purity of 99.97% are considered. The same assumptions made in our previous publication[7] are considered.

Steam cycle and power generation

Process water enters the system at 280 K and 1 bar. in the first step is pumped to a given pressure $\mathrm{P_{pump}}$ which is calculated based on the final pressure targeted at the inlet of the turbine section (44 bar) and the sum of the pressure drops along the steam cycle

$$\mathrm{P_{pump}} = 44 + \sum \Delta P \tag{10}$$

Here we consider a pressure drop of 3% per heat exchanger. We assign the following specification to the following blocks: economizer $\mathrm{T_{out}}$=333 K and liquid only, evaporator vapor fraction=1, Super-heater exit temperature=673 K; The process steam needed in the conversion process (i.e. gasification, SMR, WGS) is split before the turbine section, thus we use superheated steam at 44 bar and 673 K. We modelled a two-turbines system with an isoentropic efficiency 75% and a mechanical efficiency of 95%. The high pressure turbine has an in inlet pressure of 44 bar and a discharge pressure of 4.4 bar. While the low-pressure (LP) turbine has a discharge pressure of 0.048 bar (condensing turbine). After the LP turbine we condense and pump the water out of the co-generation plant.

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