Technical, economic and environmental optimization of the renewable hydrogen production chain for use in ammonia production: A case study

Supplementary Material S1 - Objective function terms

$$CPM_{r,p} = \mathrm{RC}_{r,p} * OC_r \qquad r \forall\in R, p \forall\in P \qquad \text{(S1)}$$

The terms presented in the equations are described as follows: $CPM_{r,p}$ – acquisition cost of resource r used in location p; $\mathrm{RC}_{r,p}$- total amount of resource r that is consumed in location p per year; OC_r - purchase price of resource r.

$$COP_{u,p} = Inv_{u,p} * OME \qquad \text{u } \forall\in \text{ U, p } \forall\in \text{ P} \qquad \text{(S2)}$$

The terms are described as follows: $COP_{u,p}$- Operating cost of unit u in location p; $Inv_{u,p}$- Annualized investment of unit u in location p and OME is Operation and Maintenance Expenses Factor (0.25).

$$REV_{r,p} = RS_{r,p} * MP_r \qquad r \forall\in R, p \forall\in P \qquad \text{(S3)}$$

The terms used are: $REV_{r,p}$ - Sales revenue of product r in location p; $RS_{r,p}$- total amount of resource r that is consumed in location p per year; MP_r - sale price of the resource r.

$$CTR_{p,p',r,mo} = transfOutModal_{r,p,p',mo}.dist_{p',p}\, modCost_{r,mo} \quad \forall r \in R, \forall p, p' \in P, \forall mo \in Mo \quad \text{(S4)}$$

The terms used are: $CTR_{r,p,p',mo}$- Transportation cost of resource r from location p to location p´ by modal mo; $transfOutModal_{r,p,p',mo}$ - amount of resource r that is transported from location p to p´ by modal mo; $dist_{p',p}$ - distance between location p' and location p; $modCost_{r,mo}$ - transport unit cost of resource r by the type of modal mo.

Supplementary Material S2 – Constraints

Mass balance constraints

$$\mathrm{RC}_{r,p} + \sum_u prod_{u,r,p} fop + \sum_{p'} transfIn_{r,p',p} =$$

$$\sum_u cons_{r,u,p} fop + RS_{r,p} + \sum_{p'} transfOut_{r,p,p'} \qquad r \forall\in R, p \forall\in P \quad \text{(S5)}$$

The terms presented in the equations are described as: $prod_{u,r,p}$ - quantity produced hourly in location p, of the resource r in unit u; $transfIn_{r,p',p}$ - amount of resource r that is transported from location p'

to location p; $transfOut_{r,p,p'}$ - amount of resource r that is transported from location p to location p'; fop – number of operating hours per year (ammonia plant operates 7446 hours/year) and $cons_{r,u,p}$- quantity consumed hourly of resource r in unit u in location p.

$$\mathrm{IAR_{u,r}w_{u,p}} - \mathrm{cons_{r,u,p}} = 0 \qquad \mathrm{u} \forall\in \mathrm{U}, \mathrm{r} \forall\in \mathrm{R}, \mathrm{p} \forall\in \mathrm{P} \qquad \text{(S6)}$$

$$\mathrm{OAR_{u,r}w_{u,p}} - \mathrm{prod_{r,u,p}} = 0 \qquad \forall \mathrm{u} \in \mathrm{U}, \mathrm{r} \forall\in \mathrm{R}, \mathrm{p} \forall\in \mathrm{P} \qquad \text{(S7)}$$

The definition of the terms used in the equations are: $\mathrm{IAR_{u,r}}$ - input parameter of a resource r in unit u; $\mathrm{OAR_{u,r}}$ - output parameter of a resource r in unit u; and $\mathrm{w_{u,p}}$ - capacity variable of unit u in location p.

Availability and demand constraints

$$RC_{r,p} \leq available_{r,p} \qquad \forall\, r \in R \qquad \text{(S8)}$$

$$RS_{r,p} \leq demand_{r,p} \qquad \forall\, r \in R \qquad \text{(S9)}$$

The terms used in the equations are defined as follows: $available_{r,p}$- represents the availability of resource r in location p; $demand_{r,p}$ - demand of resource r in location p.

Emissions balance constraints

$$TAE = \sum_p \sum_r RC_{r,p} * FE_r + \sum_p \sum_{p'} \sum_r \sum_{mo} transfOutModal_{p,p',r,mo} * dist_{p',p} * EFmod_{r,mo} \quad \text{(S10)}$$

Here is the definition of the terms used in the equations: TAE – total annual emissions; FE_r- emission factor of resource r; $transfOutModal_{p,p',r,mo}$- amount of resource r transport by modal mo from location p to location p'; $EFmod_{r,mo}$ – CO_2 emissions from transport of resource r by mo modal.

Transportation constraints

$$\text{transf}\, In_{r,p',p} = \sum_{mo} transfInModal_{r,p',p,mo} \qquad \forall\, r \in R, \forall\, p, p' \in P, \forall\, mo \in Mo \qquad \text{(S11)}$$

$$transfOut_{r,p,p'} = \sum_{mo} transfOutModal_{r,p,p',mo} \quad \forall\, r \in R, \forall\, p, p' \in P, \forall\, mo \in Mo \qquad \text{(S12)}$$

$$transfOutModal_{r,p,p',mo} = transfInModal_{r,p',p,mo} \quad \forall\, r \in R, \forall\, p, p\text{^}' \in P, \forall\, mo \in Mo \qquad \text{(S13)}$$

where:

$transfIn_{r,p',p}$ - total amount of resource r transported from location p' to location p ;
$transfInModal_{r,p',p,mo}$ – amount of resource r transported location p' and p by modal mo.

Decision variables

$$CapMin_{u,L} \cdot y_{u,L,p} \leq w_{u,L,p} \leq CapMax_{u,L} \cdot y_{u,L,p} \quad \text{(S14)}$$

$$\sum_L y_{u,L,p} = y_{u,p} \quad \text{(S15)}$$

$$\sum_L w_{u,L,p} = w_{u,p} \quad \text{(S16)}$$

The definition of the terms used in the equations are defined in: $CapMax_{u,L}$ - represents the maximum capacity of the production unit u at level L and $CapMin_{u,L}$ - the minimum capacity of the production unit u and level L; $w_{u,L,p}$ – capacity variable of unit u in location p at level L; $y_{u,p}$- binary variable (0 and 1), activation or non-activation of unit u in location p.

Supplementary Material S3- Physical models

Physical model of Ethanol_ESR technology

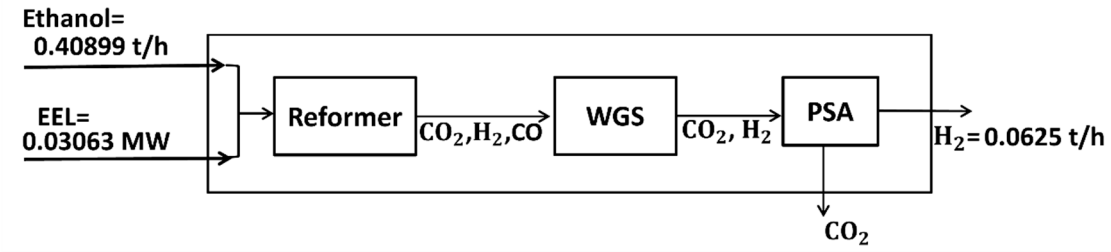


Figure S1 - Simplified process diagram for hydrogen production via electricity-assisted ethanol reforming (Ethanol_ESR).

Physical model of GS_WGS technology

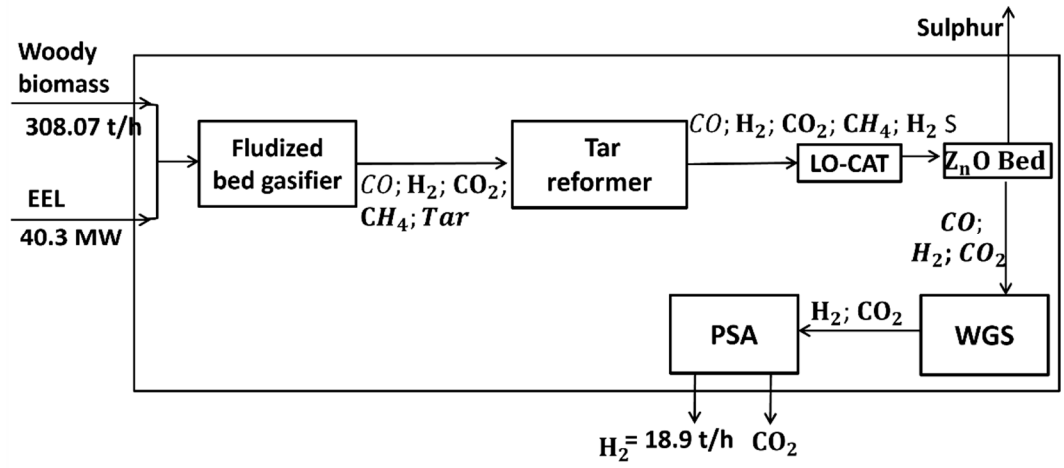


Figure S2 – Diagram of the physical model of the GS_WGS route for hydrogen production via woody biomass gasification. The process comprises fluidised bed gasification, tar reforming, contaminant removal by LO-CAT and ZnO, water-gas shift (WGS) and PSA purification. The plant operates at a flow rate of 308.07 t/h of dry biomass and produces 18.9 t/h of hydrogen. Data based on Salkuyeh, Saville and MacLean (2018).

Physical model of PEM technology

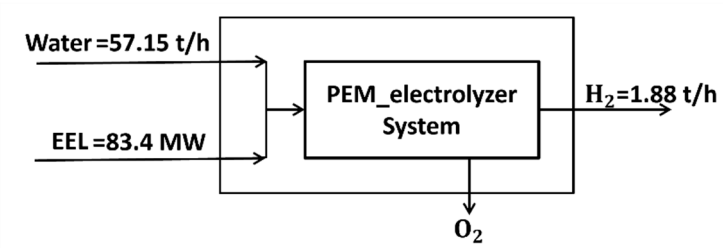


Figure S3. Schematic of electrolysis technology (PEM)

Physical model of the Vinasse technology_BD_SMR

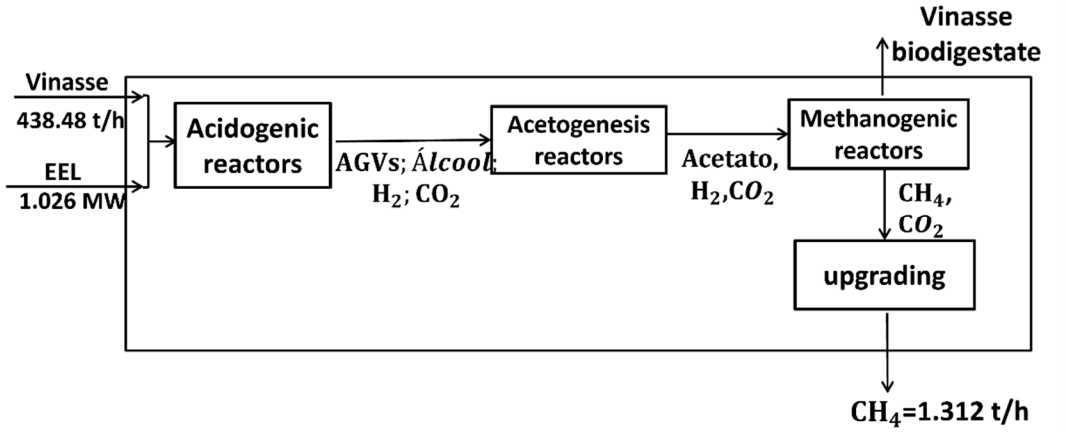


Figure S4. Schematic diagram of biomethane production from vinasse by anaerobic digestion.

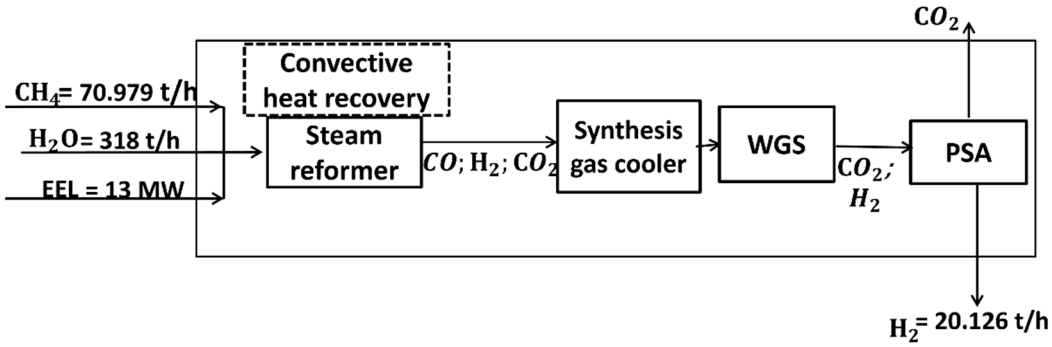


Figure S5. Schematic diagram of the steam reforming process of biomethane for hydrogen production, with convective heat recovery. The process uses 70.979 t/h of CH_4, 318 t/h of H_2O and 13 MW of net electrical energy (EEL), passing through the stages of steam reforming, synthesis gas cooling, water-gas shift (WGS) reaction and pressure swing adsorption (PSA) purification, resulting in the production of 20.126 t/h of H_2 and the release of CO_2.

Physical model of the air separation unit

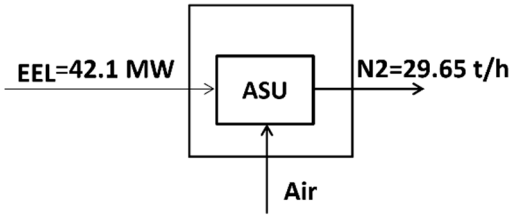


Figure S6. Technological scheme for obtaining nitrogen

Physical model of the ammonia synthesis unit

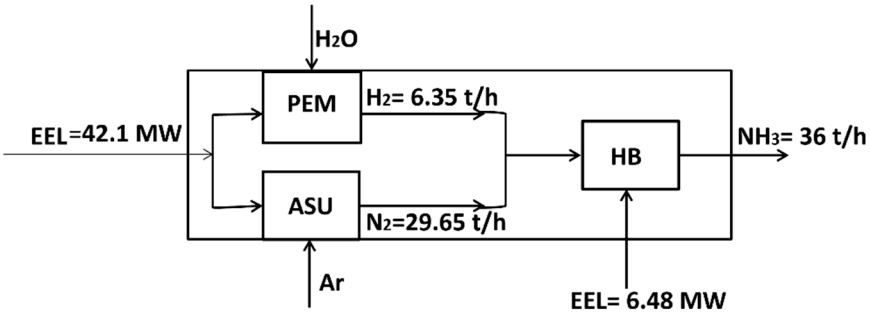


Figure S7. Production scheme for obtaining ammonia

Supplementary Material S4 – Investment equations

Adjustment of invested capital based on the scale factor

$$CA_{u,p} = Co_u \cdot (W_u)^{\propto} \quad \text{(S17)}$$

Where: $CA_{u,p,L}$ – Adjusted investiment cost of unit u for level L (M$); Co_u- Reference investment cost in unit u (M$); W_u - Capacity scale variable in relation to the reference capacity equal to 1, for unit u; α - Scaling factor (0.5 to 0.7, according to the equipment).

Annualised investment cost equation

$$Inv_{u,p} = \sum_p \sum_u CA_{u,p,L} \cdot CAF \quad \text{(S18)}$$

Where: $Inv_{u,p}$- Annualized investment of unit u in location p; $CA_{u,p,L}$ - Investiment cost of unit u for level L (M$) in location p; CAF - is the capital annualization factor.

capital annualization factor equation

$$CAF = \frac{i \cdot (1+i)^n}{(1+i)^n - 1} \quad \text{(S19)}$$

Where: i - is the discount rate, which is 6%; n - is the useful life of the plant (20 years).

The coefficients of the linearized equations

$$CA_{u,p,L} = capCostA_{u,L} \cdot w_{u,L,p} + capCostB_{u,p,L} \quad \text{(S20)}$$

Where: $CA_{u,p,L}$ - Investiment cost of unit u for level L (million USD) in location p; $capCostA_{u,L}$ - Slope coeficient for unit u for level L; $capCostB_{u,L}$ - Intercept coefficient for unit u for level L.

Supplementary Material S5. Linearisation coefficients

Unit	Level	w. Max.	w. Min.	capCostA (million USD)	capCostB (million USD)
Electrolysis_PEM	L1	0.4	0.1	200.02	10.50
Electrolysis_PEM	L2	1.1	0.5	157.00	30.00
Electrolysis_PEM	L3	1000	1.2	201.44	0
ASU	L1	0.4	0.1	28.601	7.39
ASU	L2	1.8	0.5	13.75	15.48
ASU	L3	5.2	1.9	7.79	27.18
GS_WGS	L1	0.68	0.2	683.14	187.41
GS_WGS	L2	1	0.7	519.96	292.12
GS_WGS	L3	1000	1.01	812.09	0
Haber-Bosch	L1	0.4	0.1	125.52	31.16
Haber-Bosch	L2	1.8	0.5	61.22	66.23
Haber-Bosch	L3	5.2	1.81	35.08	117.58
SMR_CH4	L1	0.4	0.1	506.85	53.36
SMR_CH4	L2	1.8	0.5	330.21	152.30
SMR_CH4	L3	5	1.9	238.64	333.40
SMR_CH4	L4	1000	5.1	305.31	0
Vinasse_BD_SMR	L1	0.35	0.1	1.99	13.62
Vinasse_BD_SMR	L2	1.4	0.36	4,.90	8.01
Vinasse_BD_SMR	L3	1.5	1.41	6.39	6.50
Vinasse_BD_SMR	L4	1000	1.51	10.72	0

Ethanol_ESR	L1	0.4	0.1	3.43	0.36
Ethanol_ESR	L2	1.8	0.5	2.23	1.03
Ethanol_ESR	L3	6	1.9	1.55	2.44
Ethanol_ESR	L4	1000	6.1	1.96	0