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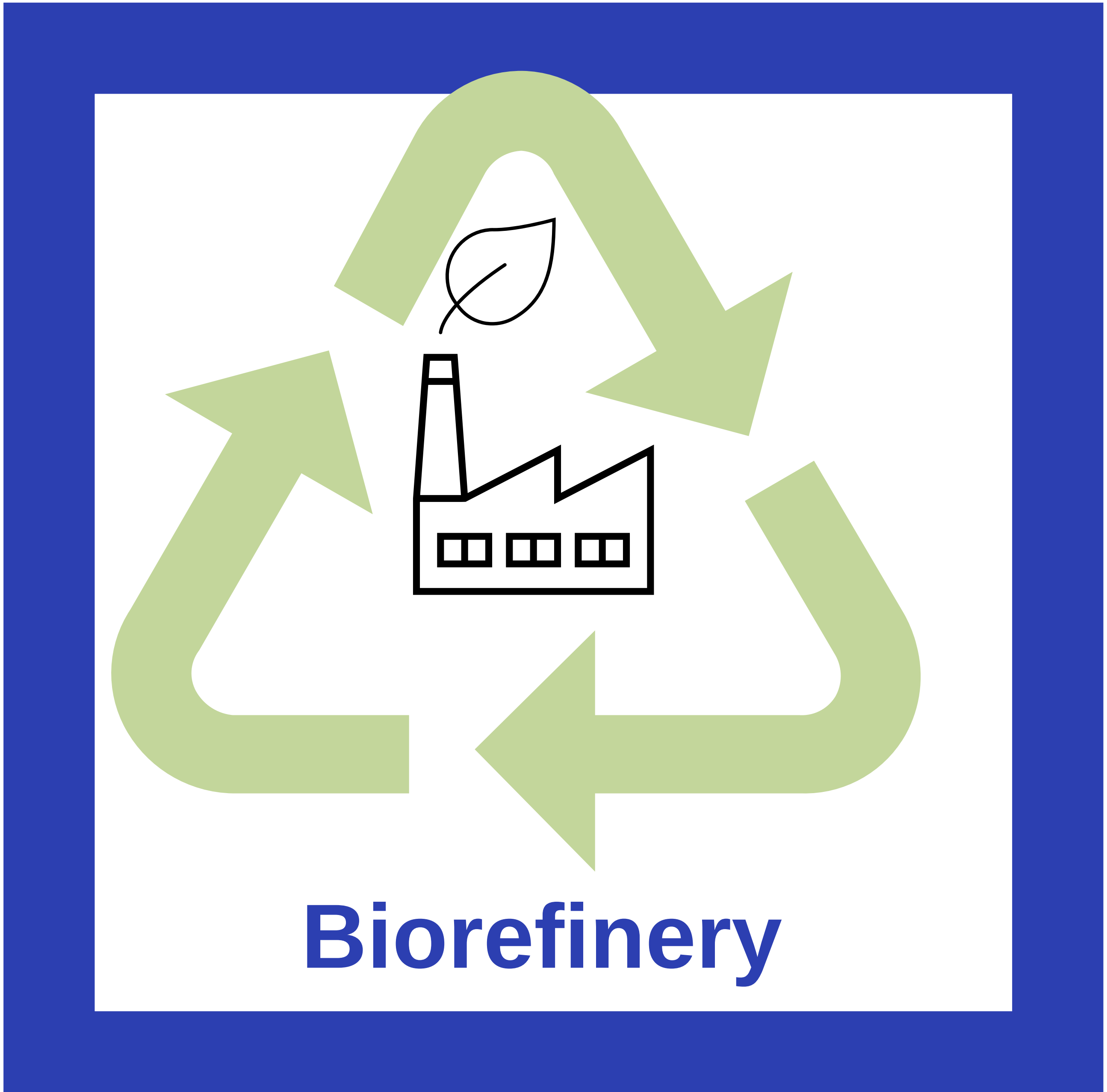
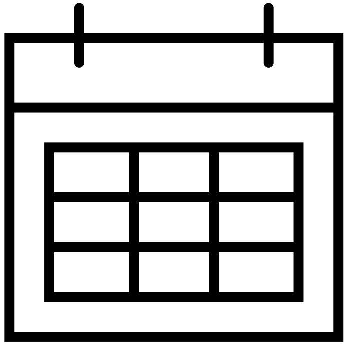
Eng Energy & Environment


Biorefinery

Information

Professor: Carla Silva (camsilva@ciencias.ulisboa.pt)



Wednesdays

16h-19h30

Room: 8.2.13

Information

Professor: Carla Silva (camsilva@ciencias.ulisboa.pt)

4 challenges!

Oral evaluation: discussing the challenges

Definition & examples

IEA Bioenergy

Technology Collaboration Programme

IEA Bioenergy Task 42
“‘Biorefineries”

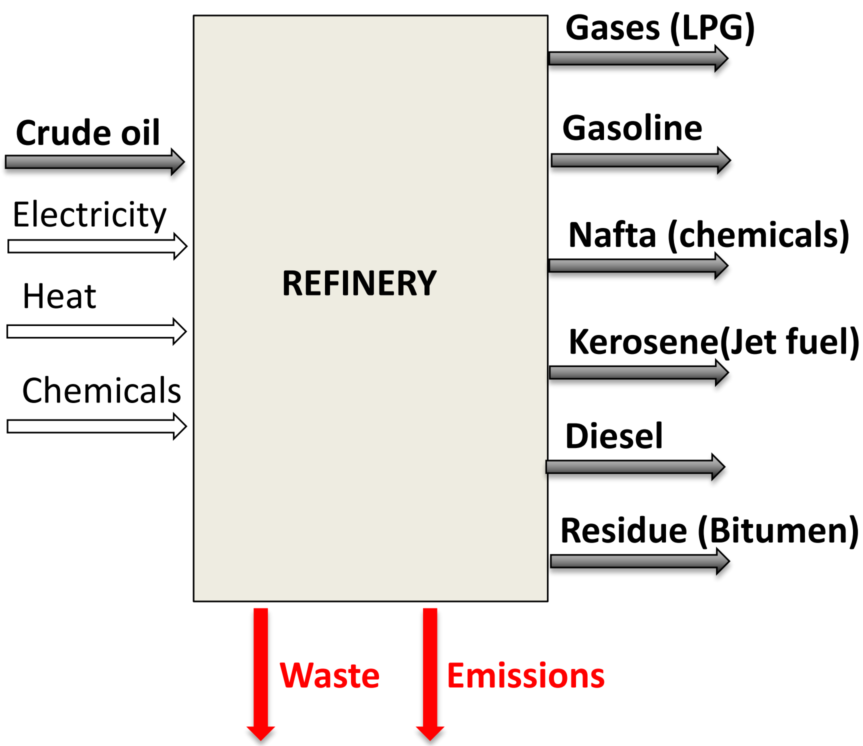
“‘Biorefining is the sustainable processing of biomass into a spectrum of marketable products and energy”.

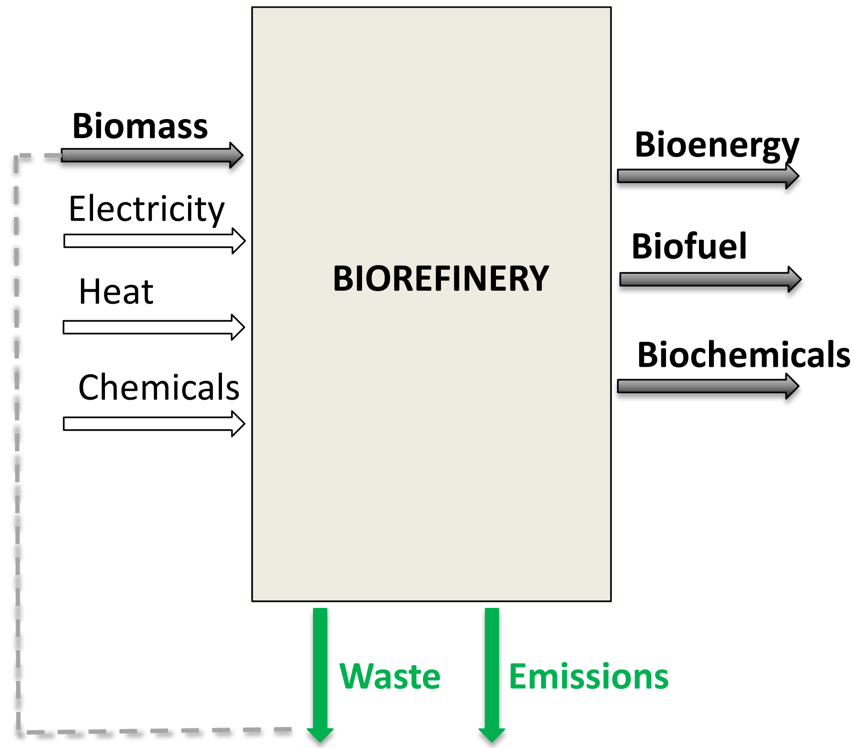
2007

Definition & examples

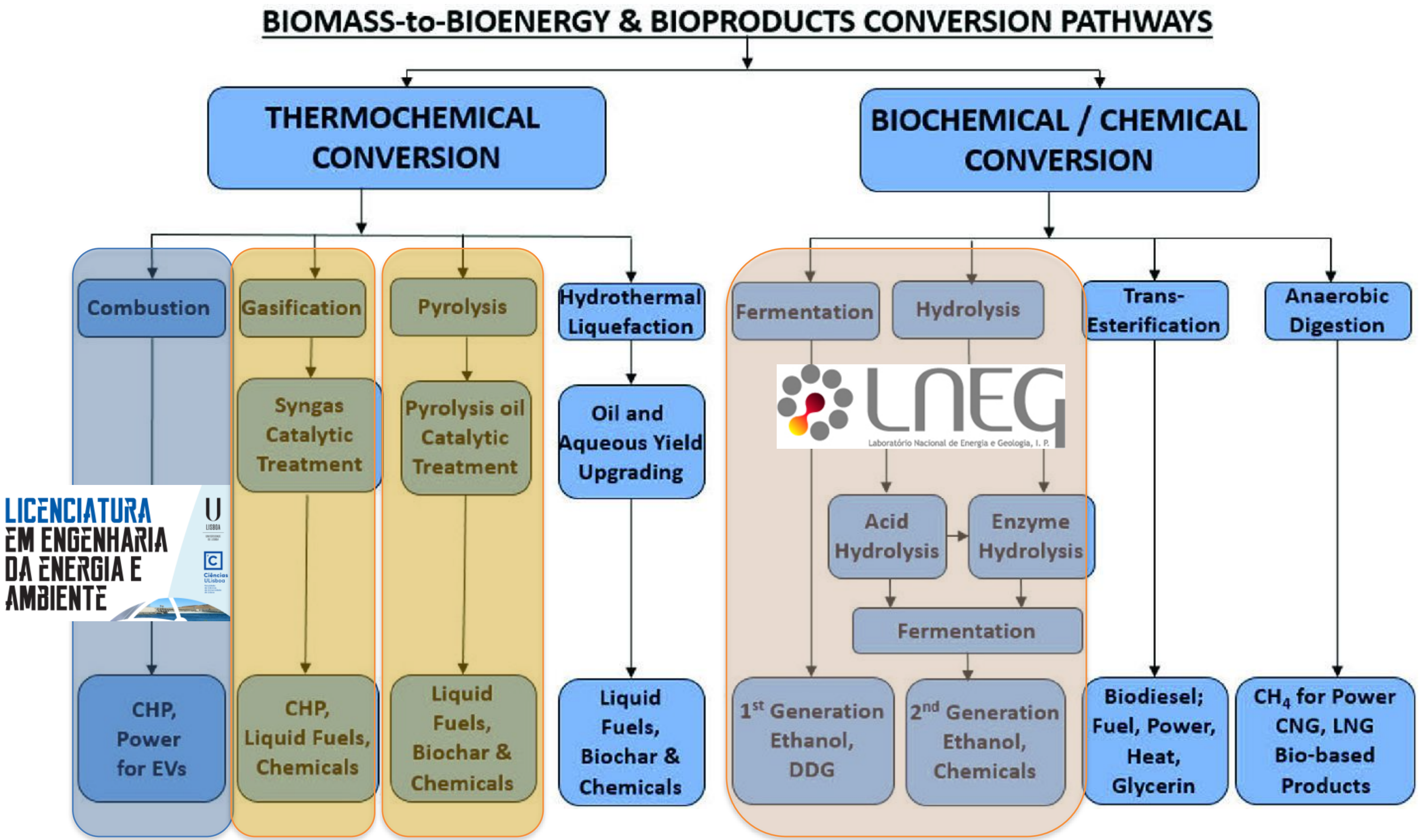
The biorefinery concept: Using biomass instead of oil for producing energy and chemicals, Energy Conversion and Management, Volume 51, Issue 7, 2010, Pages 1412-1421, ISSN 0196-8904, https://doi.org/10.1016/j.enconman.2010.01.015

Definition & examples



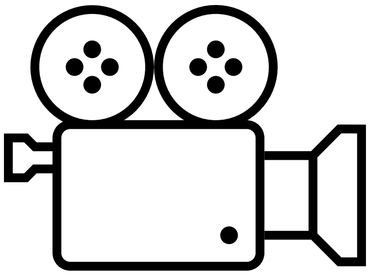


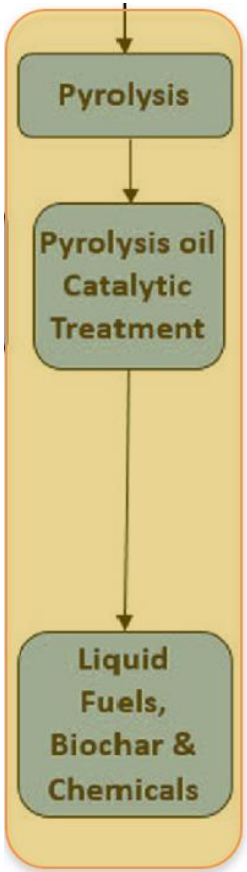
Processes – Conversion Technologies



Processes – Biochemical conversion

Pyrolysis products: **Biochar** and **Bio-oil**

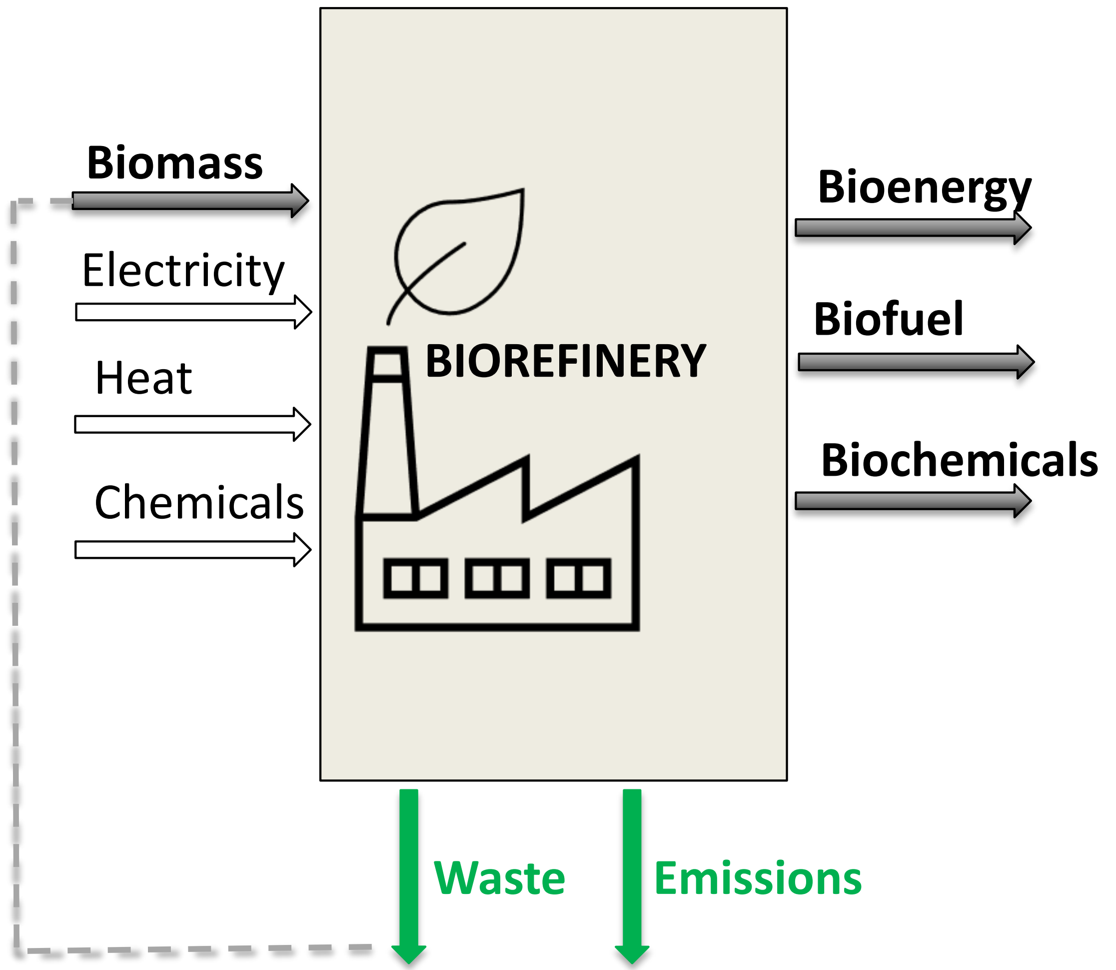




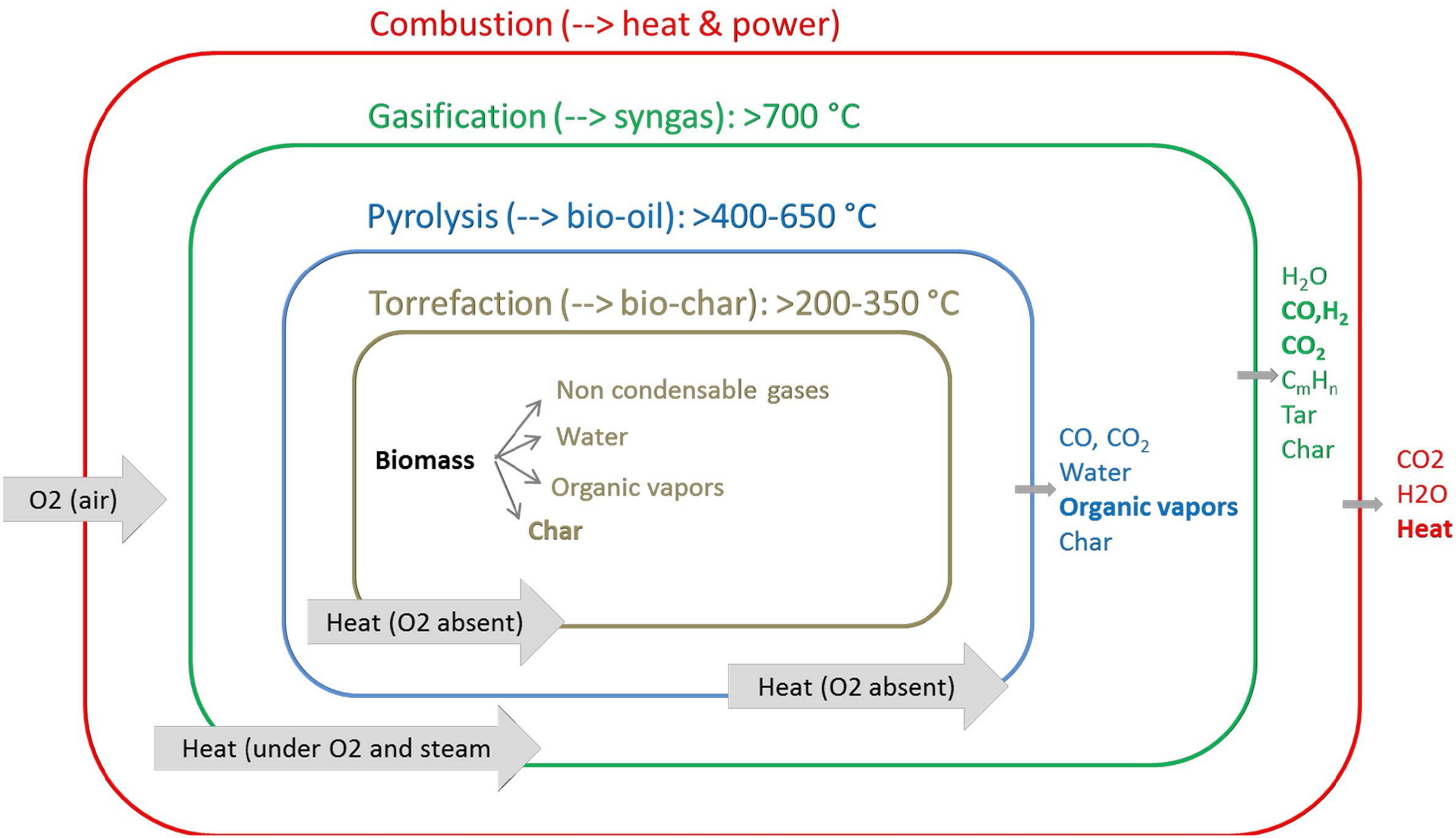
NOVA
NOVA SCHOOL OF SCIENCE & TECHNOLOGY

Processes

Collect and pre-treat: Decompose biomass in: Build products:

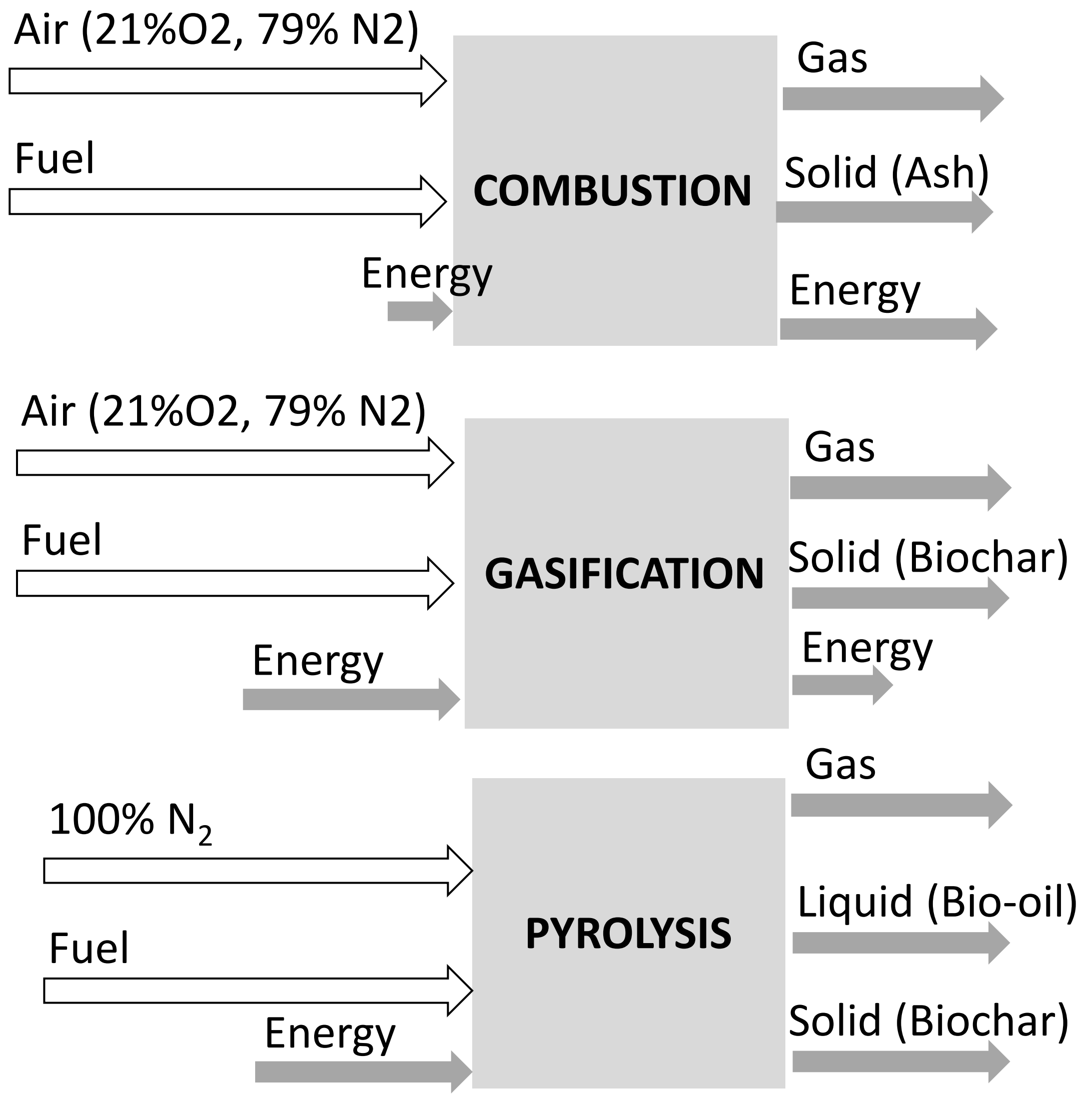


Thermochemical processes



•DOI: 10.1016/j.ejbt.2017.01.004

Thermochemical processes



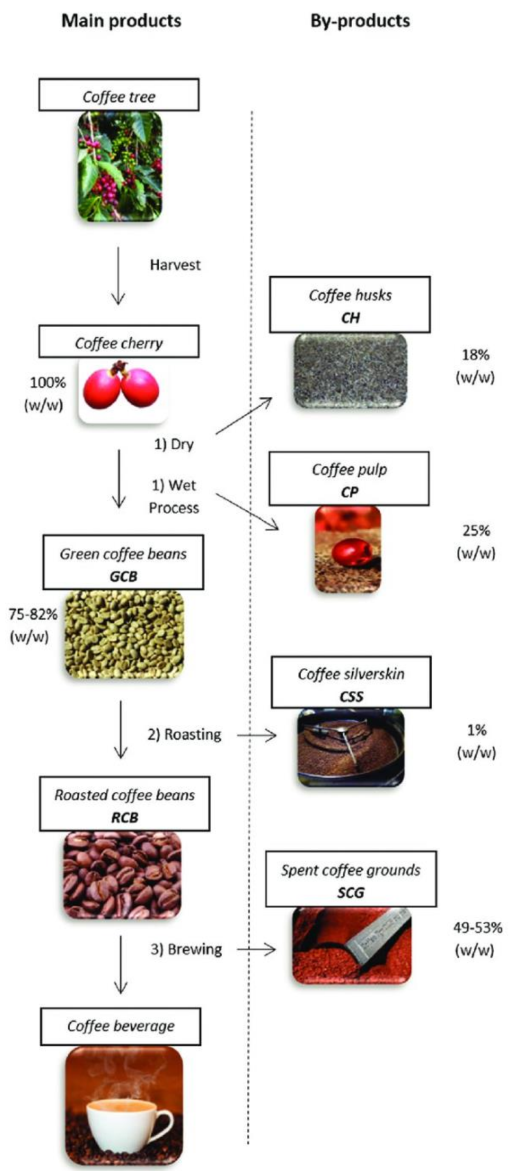
Thermochemical processes

https://doi.org/10.1016/j.wasman.2011.09.025

	Combustion	Gasification	Pyrolysis
Aim of the process	To maximize waste conversion to high temperature flue gases, mainly CO_2 and H_2O	To maximize waste conversion to high heating value fuel gases, mainly, CO, H_2, and CH_4	To maximize thermal decomposition of solid waste to gases and condensed phases
Operating conditions			
Reaction environment	Oxidizing environment, excess stoichiometric oxygen	Reducing, low oxygen	Zero oxygen
Reactant gas	Air	Usually air, could be oxygen enriched, or steam	None
Temperature	850–1,200 °C	500–1,500 °C, depending on specific process	500–800 °C
Pressure	Atmospheric	Atmospheric	Slight positive
Process output			
Produced gases	CO_2, H_2O	CO, H_2, CO_2, H_2O, CH_4	CO, H_2, CH_4, and other hydrocarbons
Pollutants/unwanted byproducts	SO_2, NOX, HCl, PCDD/F, particulates	H_2S, HCl, NH_3, HCN, tar, particulates	H_2S, HCl, NH_3, HCN, tar, particulates

Thermochemical processes

TORREFACTION



Heating no oxygen

CENTRO de CIÊNCIA do CAFÉ

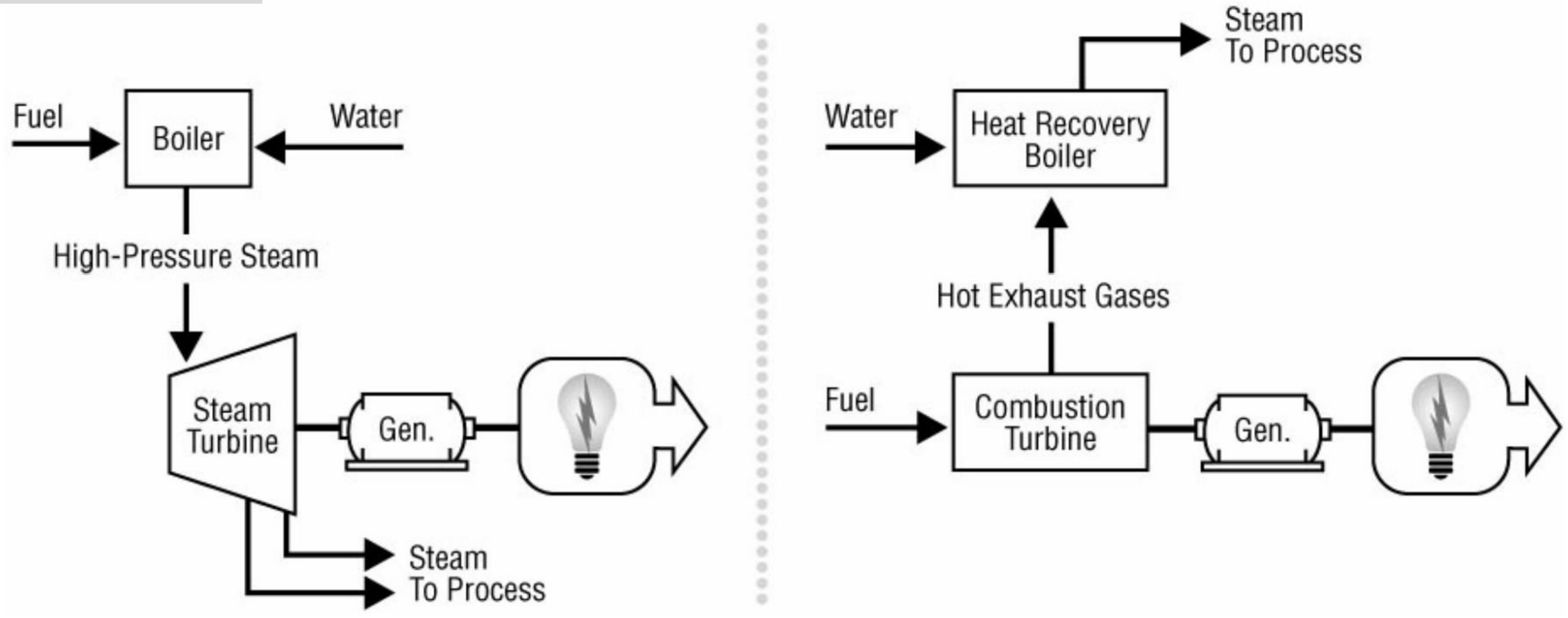
Herdade das Argamassas, 7370-171 Campo Maior

Thermochemical processes

COMBUSTION

STEAM (T=Temperature, P = Pressure)

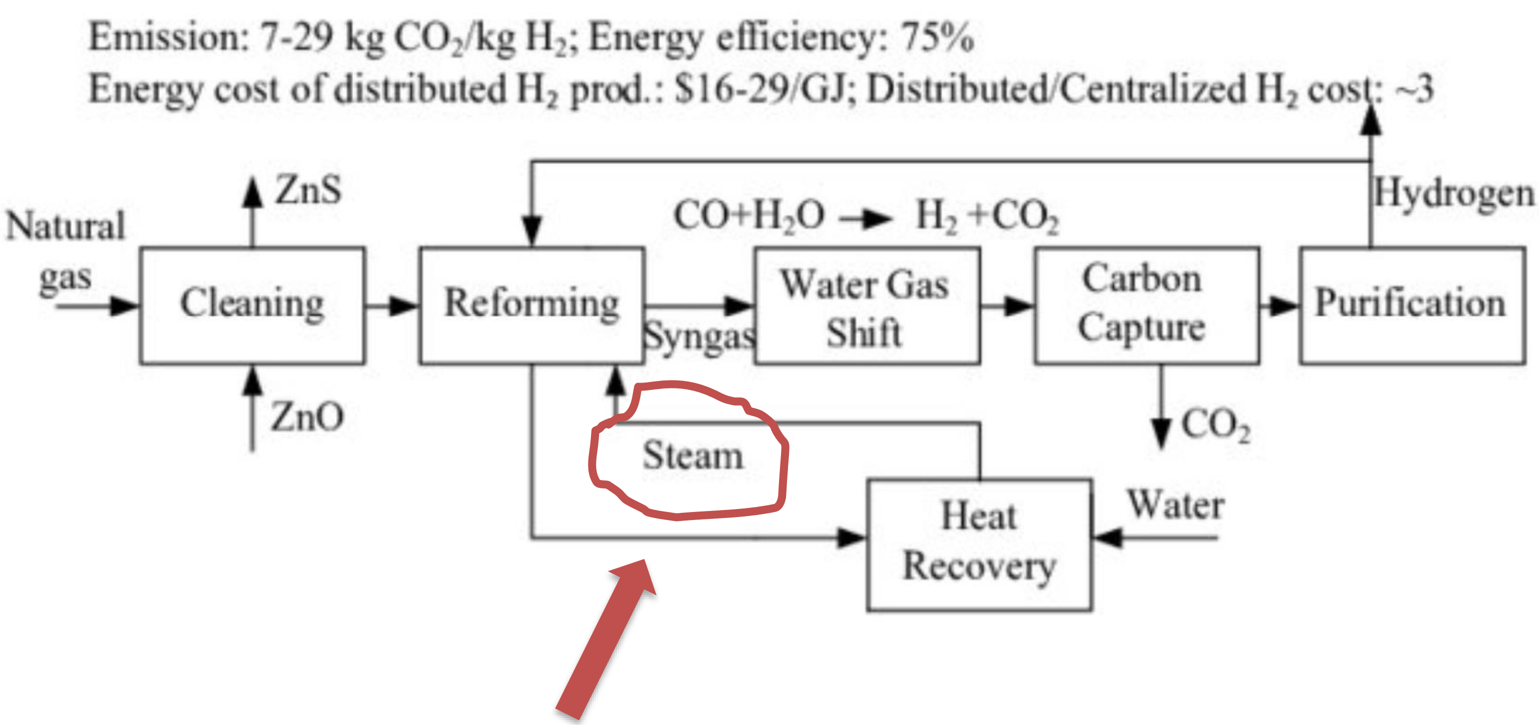
Figure 1. Typical CHP Configurations



Thermochemical processes

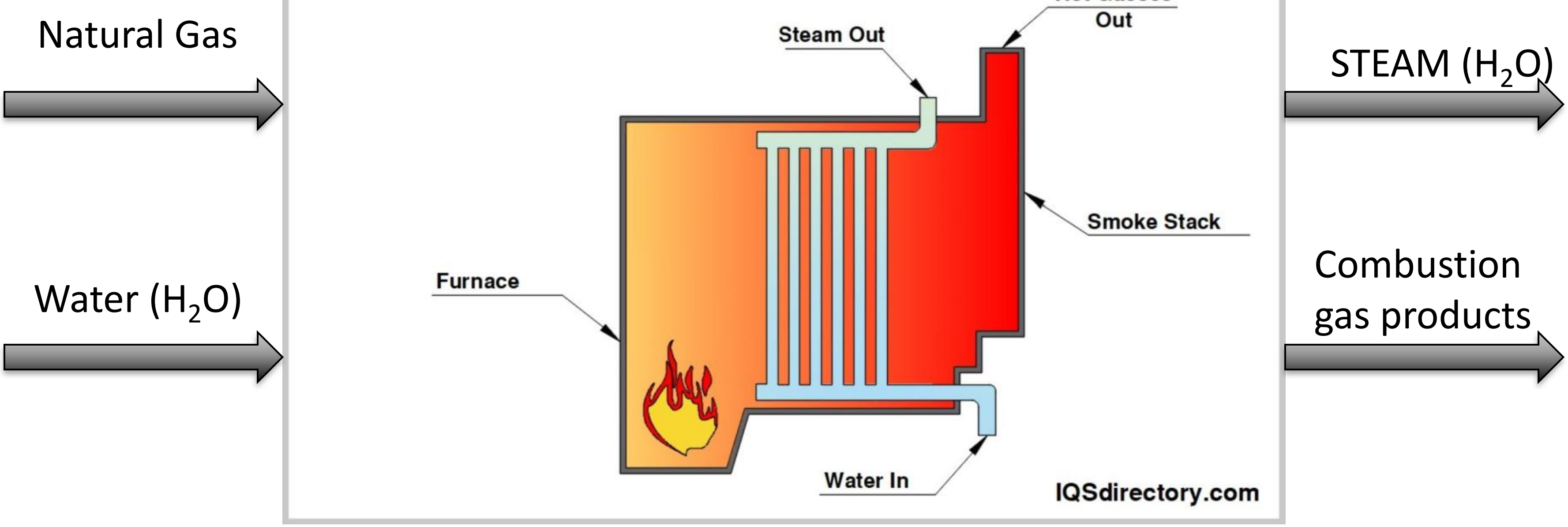
Hydrogen Production by Natural Gas

Matzen, Michael J.; Alhajji, Mahdi H.; and Demirel, Yasar, "Technoeconomics and Sustainability of Renewable Methanol and Ammonia Productions Using Wind Power-based Hydrogen" (2015). Yasar Demirel Publications.
http://digitalcommons.unl.edu/cbmedemirel/9



Thermochemical processes

Steam production by Natural Gas combustion



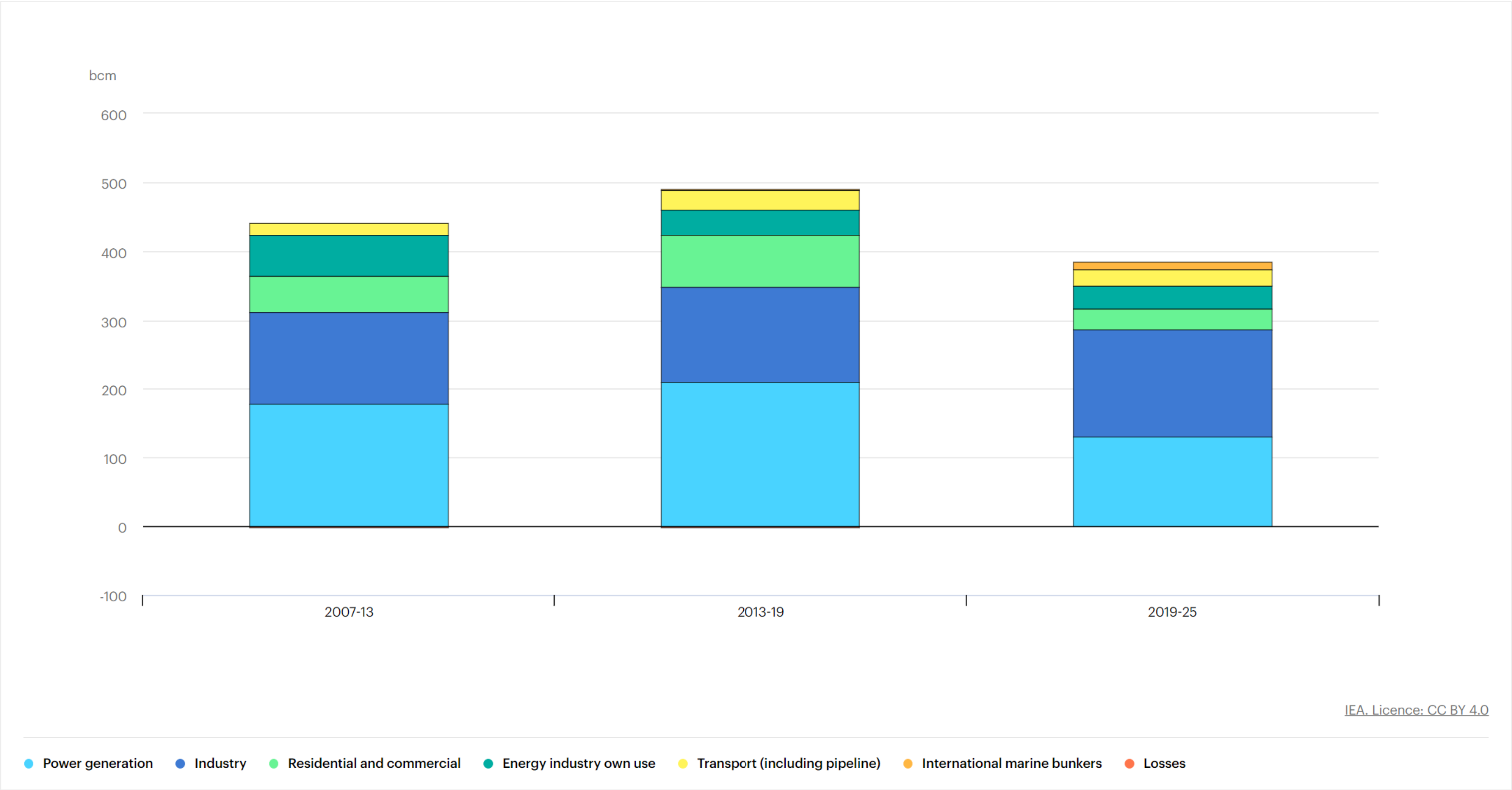
Thermochemical processes

Global natural gas demand per sector, 2007-2025

Last updated 26 Oct 2022

Download chart ↓

Cite Share



Thermochemical processes

IEA, Global natural gas demand per sector, 2007-2025, IEA, Paris https://www.iea.org/data-and-statistics/charts/global-natural-gas-demand-per-sector-2007-2025, IEA. Licence: CC BY 4.0

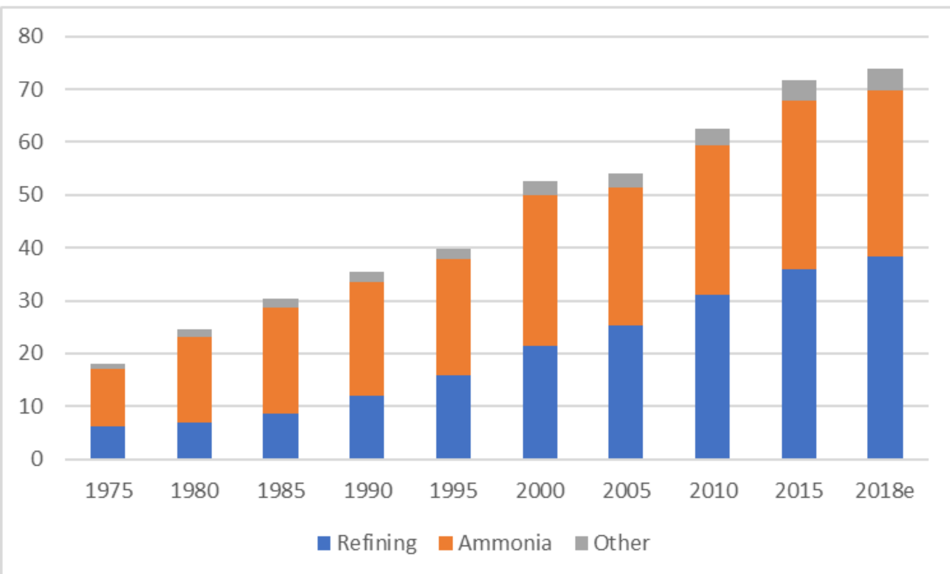
https://www.dgeg.gov.pt/pt/estatistica/energia/gas-natural/consumos/

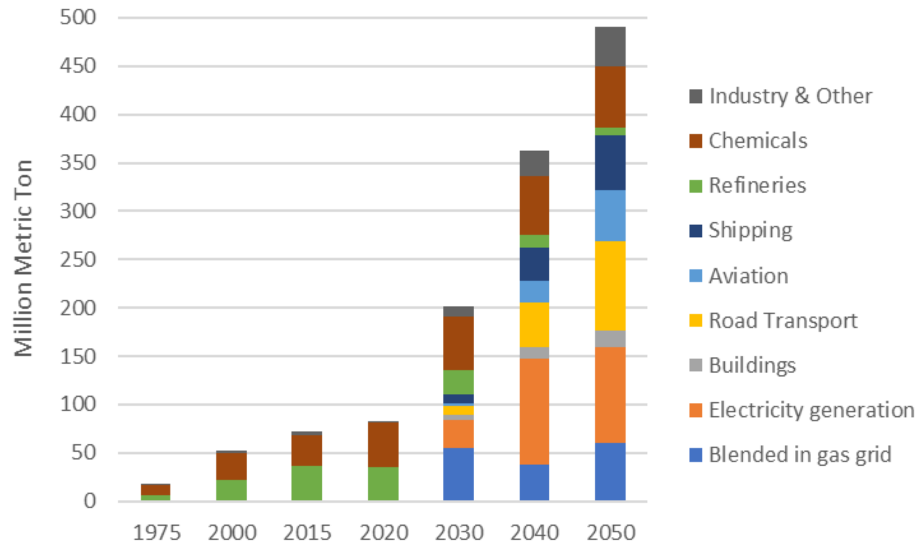
Thermochemical processes

https://studentenergy.org/production/steam-methane-reforming/

Thermochemical processes

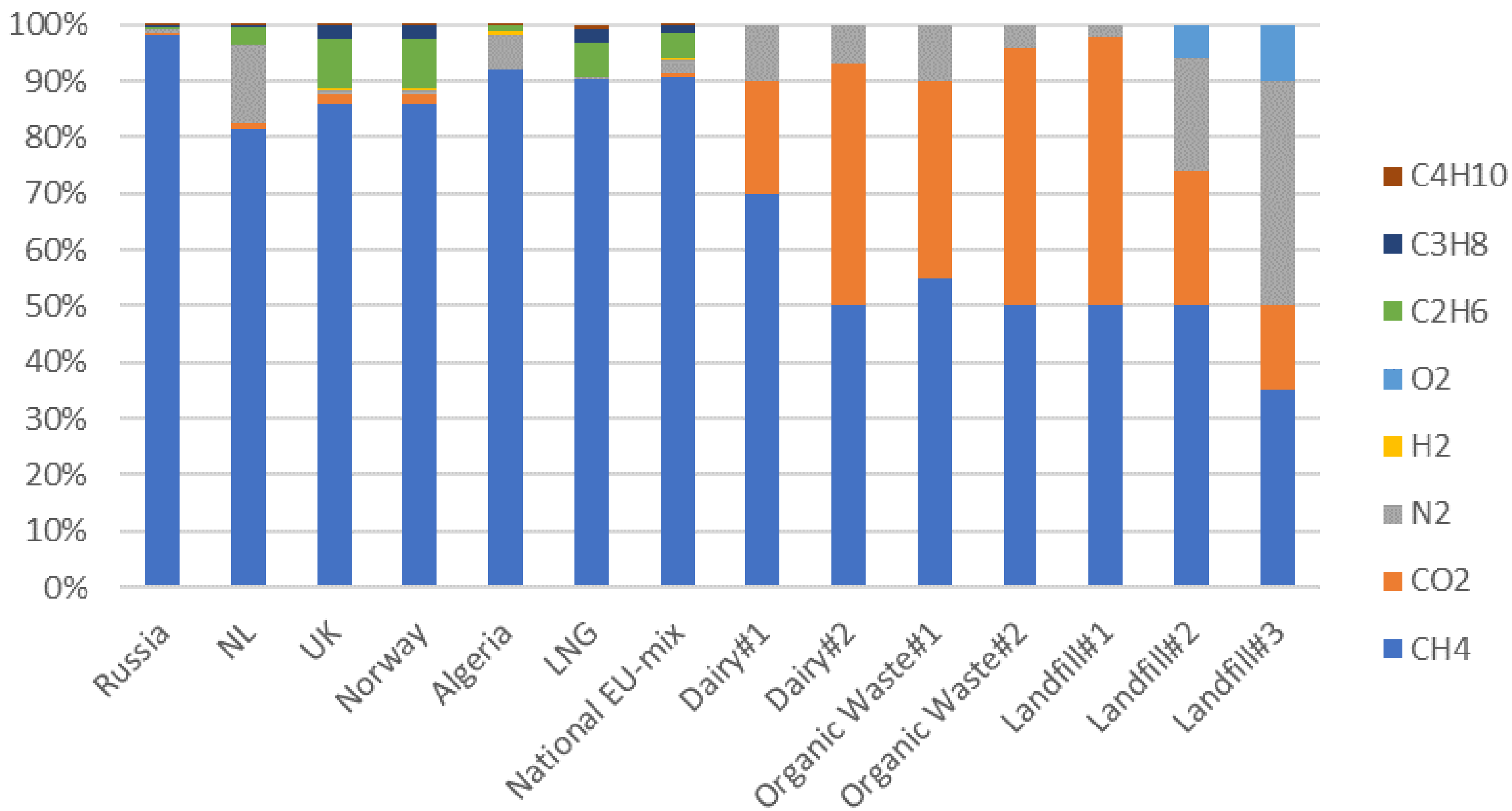
Pure H_2 demand.....





Thermochemical processes

CH_4 PRESENT IN…..Natural Gas Fossil Fuel & Biogas renewable Fuel



Prussi, M., Yugo, M., De Prada, L., Padella, M., Edwards, R., Lonza, L. JEC Well-to-Tank report v5, EUR 30269 EN, Publications Office of the European Union, Luxembourg, 2020, ISBN 978-92-76-19926-7, doi:10.2760/959137, JRC119036.

Thermochemical processes

Hydrogen Production by Natural Gas

A steam methane reformer (SMR) uses steam heat (H_2O), pressure, and a catalyst to convert methane (CH_4) into hydrogen ($3H_2$) and carbon monoxide (CO). For this reaction to occur, the temperature must be within 700–1,000°C, while the pressure can vary from 3 to 25 bar

$$CH_4 + H_2O \leftrightarrow CO + 3H_2$$

STEAM 750 °C

Thermochemical processes

Chemical equations that occurs in the SMR reactor:

$$CH_4 + H_2O \leftrightharpoons CO + 3H_2 \qquad [\Delta H = +206 \text{ kJ mol-1}]$$
$$CO + H_2O \leftrightharpoons CO_2 + H_2 \qquad [\Delta H = -41 \text{ kJ mol-1}]$$

Thermochemical processes

Example SMR reactor calculation (support excel file)

$$CH_4 + H_2O \leftrightarrows CO + 3H_2 \qquad [\Delta H = +206 \text{ kJ mol-1}]$$

$$CO + H_2O \leftrightarrows CO_2 + H_2 \qquad [\Delta H = -41 \text{ kJ mol-1}]$$

Thermochemical processes

How much $kgCH_4/kgH_2$, MJ/ kgH_2, $Lwater/ kgH_2$, $kgCO_2/kgH_2$ and $kgCO_2eq/kgH_2$

H_2O/CH_4 = 3

Ptotal = 15 bar

Treactor = 850 ºC

K_pReforming= exp [24.383-15405/T]

K_pShift= exp [2299/T-2.79]

T em ºC

Thermochemical processes

1st mass balance and input/output system table

2nd iterative procedure with Solver function

$CH_4 + H_2O \leftrightharpoons CO + 3H_2$ [ΔH = +206 kJ mol-1]

$CO + H_2O \leftrightharpoons CO_2 + H_2$ [ΔH = -41 kJ mol-1]

Thermochemical processes

Off-gas burning for energy….

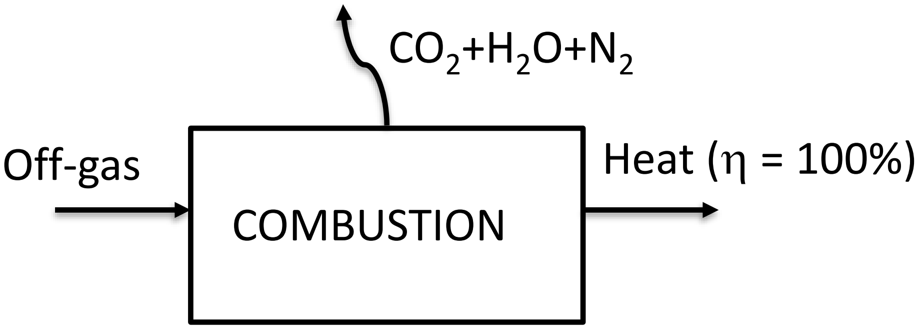
LHV (MJ/kg)= 38.2 mC + 84.9 mH−8mO

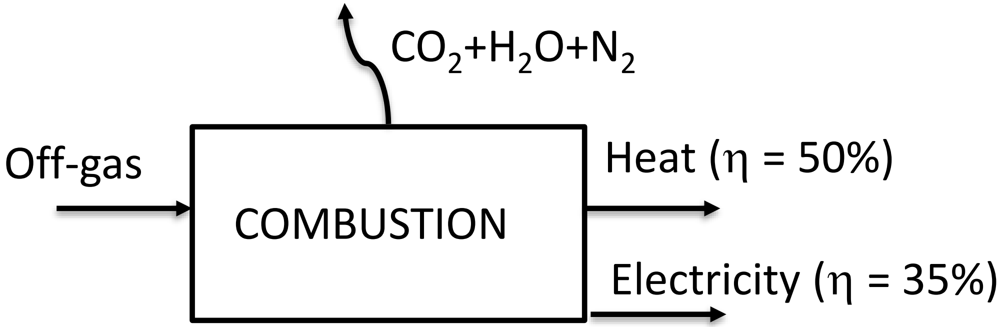
mC, mH and mO in %

S. Hosokai, K. Matsuoka, K. Kuramoto, and Y. Suzuki, “Modification of Dulong’s formula to estimate heating value of gas, liquid and solid fuels,” Fuel Process. Technol., vol. 152, pp. 399–405, Nov. 2016

Thermochemical processes

Off-gas burning for energy….

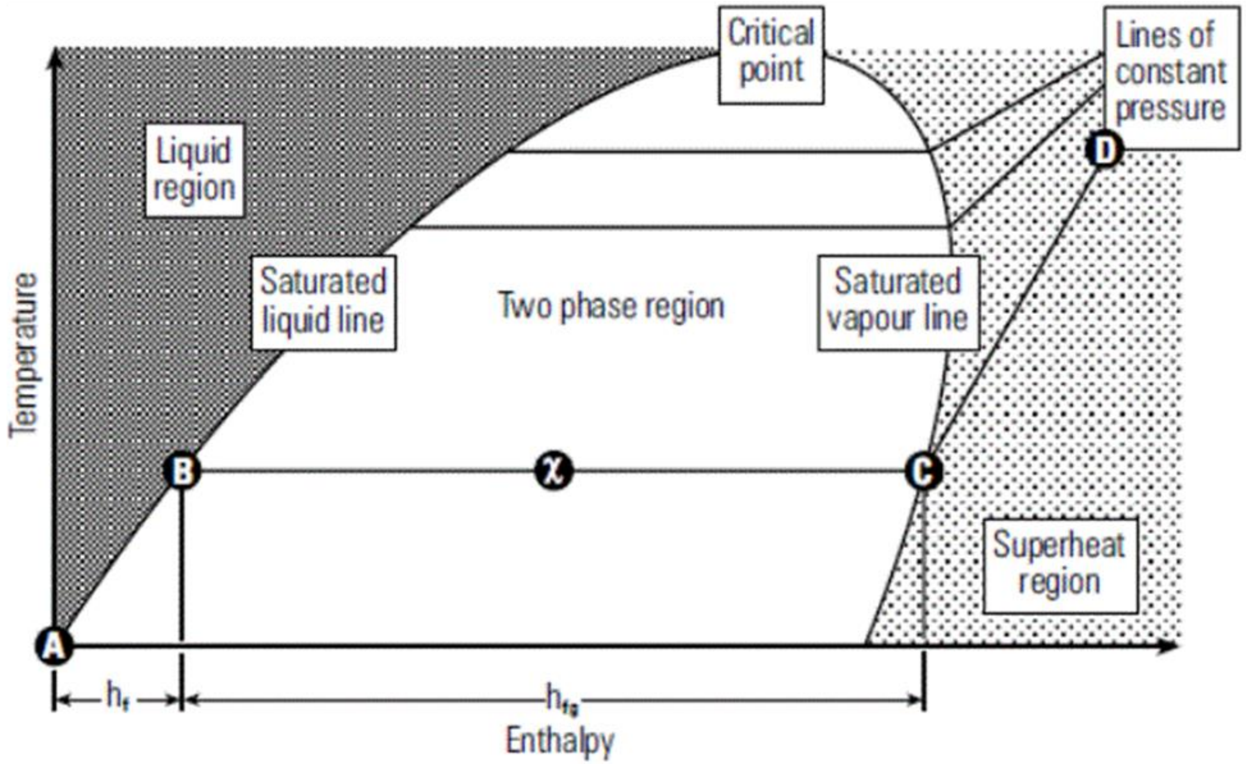




Thermochemical processes

STEAM (T=Temperature, P = Pressure)

Water



Water

H_2O

TABLE A-3 Properties of Saturated Water (Liquid–Vapor): Pressure Table

		Specific Volume m^3/kg		Internal Energy kJ/kg		Enthalpy kJ/kg			Entropy kJ/kg · K		
Press. bar	Temp. °C	Sat. Liquid $v_f \times 10^3$	Sat. Vapor v_g	Sat. Liquid u_f	Sat. Vapor u_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	Sat. Vapor s_g	Press. bar
0.04	28.96	1.0040	34.800	121.45	2415.2	121.46	2432.9	2554.4	0.4226	8.4746	0.04
0.06	36.16	1.0064	23.739	151.53	2425.0	151.53	2415.9	2567.4	0.5210	8.3304	0.06
0.08	41.51	1.0084	18.103	173.87	2432.2	173.88	2403.1	2577.0	0.5926	8.2287	0.08
0.10	45.81	1.0102	14.674	191.82	2437.9	191.83	2392.8	2584.7	0.6493	8.1502	0.10
0.20	60.06	1.0172	7.649	251.38	2456.7	251.40	2358.3	2609.7	0.8320	7.9085	0.20
0.30	69.10	1.0223	5.229	289.20	2468.4	289.23	2336.1	2625.3	0.9439	7.7686	0.30
0.40	75.87	1.0265	3.993	317.53	2477.0	317.58	2319.2	2636.8	1.0259	7.6700	0.40
0.50	81.33	1.0300	3.240	340.44	2483.9	340.49	2305.4	2645.9	1.0910	7.5939	0.50
0.60	85.94	1.0331	2.732	359.79	2489.6	359.86	2293.6	2653.5	1.1453	7.5320	0.60
0.70	89.95	1.0360	2.365	376.63	2494.5	376.70	2283.3	2660.0	1.1919	7.4797	0.70
0.80	93.50	1.0380	2.087	391.58	2498.8	391.66	2274.1	2665.8	1.2329	7.4346	0.80
0.90	96.71	1.0410	1.869	405.06	2502.6	405.15	2265.7	2670.9	1.2695	7.3949	0.90
1.00	99.63	1.0432	1.694	417.36	2506.1	417.46	2258.0	2675.5	1.3026	7.3594	1.00
1.50	111.4	1.0528	1.159	466.94	2519.7	467.11	2226.5	2693.6	1.4336	7.2233	1.50
2.00	120.2	1.0605	0.8857	504.49	2529.5	504.70	2201.9	2706.7	1.5301	7.1271	2.00

TABLE A-3 Properties of Saturated Water (Liquid–Vapor): Pressure Table

		Specific Volume m^3/kg		Internal Energy kJ/kg		Enthalpy kJ/kg			Entropy kJ/kg · K		
Press. bar	Temp. °C	Sat. Liquid $v_f \times 10^3$	Sat. Vapor v_g	Sat. Liquid u_f	Sat. Vapor u_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	Sat. Vapor s_g	Press. bar
3.50	138.9	1.0786	0.5243	583.95	2546.9	584.33	2148.1	2732.4	1.7275	6.9405	3.50
4.00	143.6	1.0836	0.4625	604.31	2553.6	604.74	2133.8	2738.6	1.7766	6.8959	4.00
4.50	147.9	1.0882	0.4140	622.25	2557.6	623.25	2120.7	2743.9	1.8207	6.8565	4.50
5.00	151.9	1.0926	0.3749	639.68	2561.2	640.23	2108.5	2748.7	1.8607	6.8212	5.00
6.00	158.9	1.1006	0.3157	669.90	2567.4	670.56	2086.3	2756.8	1.9312	6.7600	6.00
7.00	165.0	1.1080	0.2729	696.44	2572.5	697.22	2066.3	2763.5	1.9922	6.7080	7.00
8.00	170.4	1.1148	0.2404	720.22	2576.8	721.11	2048.0	2769.1	2.0462	6.6628	8.00
9.00	175.4	1.1212	0.2150	741.83	2580.5	742.83	2031.1	2773.9	2.0946	6.6226	9.00
10.0	179.9	1.1273	0.1944	761.68	2583.6	762.81	2015.3	2778.1	2.1387	6.5863	10.0
15.0	198.3	1.1539	0.1318	843.16	2594.5	844.84	1947.3	2792.2	2.3150	6.4448	15.0
20.0	212.4	1.1767	0.09963	906.44	2600.3	908.79	1890.7	2799.5	2.4474	6.3409	20.0
25.0	224.0	1.1973	0.07998	959.11	2603.1	962.11	1841.0	2803.1	2.5547	6.2575	25.0
30.0	233.9	1.2165	0.06668	1004.8	2604.1	1008.4	1795.7	2804.2	2.6457	6.1869	30.0
35.0	242.6	1.2347	0.05707	1045.4	2603.7	1049.8	1753.7	2803.4	2.7253	6.1253	35.0
40.0	250.4	1.2522	0.04978	1082.3	2602.3	1087.3	1714.1	2801.4	2.7964	6.0701	40.0
45.0	257.5	1.2692	0.04406	1116.2	2600.1	1121.9	1676.4	2798.3	2.8610	6.0199	45.0
50.0	264.0	1.2859	0.03944	1147.8	2597.1	1154.2	1640.1	2794.3	2.9202	5.9734	50.0
60.0	275.6	1.3187	0.03244	1205.4	2589.7	1213.4	1571.0	2784.3	3.0267	5.8892	60.0
70.0	285.9	1.3513	0.02737	1257.6	2580.5	1267.0	1505.1	2772.1	3.1211	5.8133	70.0
80.0	295.1	1.3842	0.02352	1305.6	2569.8	1316.6	1441.3	2758.0	3.2068	5.7432	80.0
90.0	303.4	1.4178	0.02048	1350.5	2557.8	1363.3	1378.9	2742.1	3.2858	5.6772	90.0
100.	311.1	1.4524	0.01803	1393.0	2544.4	1407.6	1317.1	2724.7	3.3596	5.6141	100.
110.	318.2	1.4886	0.01599	1433.7	2529.8	1450.1	1255.5	2705.6	3.4295	5.5527	110.

Thermochemical processes

Tab.

TABLE A-4 *(Continued)*

T °C	v m³/kg	u kJ/kg	h kJ/kg	s kJ/kg · K	v m³/kg	u kJ/kg	h kJ/kg	s kJ/kg · K
	p = 160 bar = 16.0 MPa (T_{sat} = 347.44°C)				p = 180 bar = 18.0 MPa (T_{sat} = 357.06°C)			
Sat.	0.00931	2431.7	2580.6	5.2455	0.00749	2374.3	2509.1	5.1044
360	0.01105	2539.0	2715.8	5.4614	0.00809	2418.9	2564.5	5.1922
400	0.01426	2719.4	2947.6	5.8175	0.01190	2672.8	2887.0	5.6887
440	0.01652	2839.4	3103.7	6.0429	0.01414	2808.2	3062.8	5.9428
480	0.01842	2939.7	3234.4	6.2215	0.01596	2915.9	3203.2	6.1345
520	0.02013	3031.1	3353.3	6.3752	0.01757	3011.8	3378.0	6.2960
560	0.02172	3117.8	3465.4	6.5132	0.01904	3101.7	3444.4	6.4392
600	0.02323	3201.8	3573.5	6.6399	0.02042	3188.0	3555.6	6.5696
640	0.02467	3284.2	3678.9	6.7580	0.02174	3272.3	3663.6	6.6905
700	0.02674	3406.0	3833.9	6.9224	0.02362	3396.3	3821.5	6.8580
740	0.02808	3486.7	3935.9	7.0251	0.02483	3478.0	3925.0	6.9623

T °C	v m³/kg	u kJ/kg	h kJ/kg	s kJ/kg · K	v m³/kg	u kJ/kg	h kJ/kg	s kJ/kg · K
	p = 200 bar = 20.0 MPa (T_{sat} = 365.81°C)				p = 240 bar = 24.0 MPa			
Sat.	0.00583	2293.0	2409.7	4.9269				
400	0.00994	2619.3	2818.1	5.5540	0.00673	2477.8	2639.4	5.2393
440	0.01222	2774.9	3019.4	5.8450	0.00929	2700.6	2923.4	5.6506
480	0.01399	2891.2	3170.8	6.0518	0.01100	2838.3	3102.3	5.8950
520	0.01551	2992.0	3302.2	6.2218	0.01241	2950.5	3248.5	6.0842
560	0.01689	3085.2	3423.0	6.3705	0.01366	3051.1	3379.0	6.2448
600	0.01818	3174.0	3537.6	6.5048	0.01481	3145.2	3500.7	6.3875
640	0.01940	3260.2	3648.1	6.6286	0.01588	3235.5	3616.7	6.5174
700	0.02113	3386.4	3809.0	6.7993	0.01739	3366.4	3783.8	6.6947
740	0.02224	3469.3	3914.1	6.9052	0.01835	3451.7	3892.1	6.8038
800	0.02385	3592.7	4069.7	7.0544	0.01974	3578.0	4051.6	6.9567

Thermochemical processes

STEAM (T=Temperature, P = Pressure) Energy Content

Specific Enthalpy = kJ/kg

From tables, for example, SUPERHEATED VAPOUR

@99.63 °C, 1 atm, 2675.5 kJ/kg (**2.68 MJ/kg**)

@750 °C, 200 atm, 3940 kJ/kg (**3.94 MJ/kg**)

Thermochemical processes

T (K)	$\bar{c}_p$ [kJ/(kmol K)]	$\left(\bar{h}^o(T)-\bar{h}_f^o(298)\right)$ (kJ/kmol)	$\bar{h}_f^o(T)$ (kJ/kmol)	$\bar{s}^o(T)$ [kJ/(kmol K)]	$\bar{g}_f^o(T)$ (kJ/kmol)
200	32,255	–3227	–240 838	175,602	–232 779
298	33,448	0	–241 845	188,715	–228 608
300	33,468	62	–241 865	188,922	–228 526
400	34,437	3458	–242 858	198,686	–223 929
500	35,337	6947	–243 822	206,467	–219 085
600	36,288	10 528	–244 753	212,992	–214 049
700	37,364	14 209	–245 638	218,665	–208 861
800	38,587	18 005	–246 461	223,733	–203 550
900	39,930	21 930	–247 209	228,354	–198 141
1000	41,315	25 993	–247 879	232,633	–192 652
1100	42 638	30 191	–248 475	236,634	–187 100
1200	43,874	34 518	–249 005	240,397	–181 497
1300	45,027	38 963	–249 477	243,955	–175 852
1400	46,102	43 520	–249 895	247,332	–170 172
1500	47,103	48 181	–250 267	250,547	–164 464
1600	48,035	52 939	–250 597	253,617	–158 733
1700	48,901	57 786	–250 890	256,556	–152 983
1800	49,705	62 717	–251 151	259,374	–147 216
1900	50,451	67 725	–251 384	262,081	–141 435
2000	51,143	72 805	–251 594	264,687	–135 643
2100	51,784	77 952	–251 783	267,198	–129 841
2200	52,378	83 160	–251 955	269,621	–124 030
2300	52,927	88 426	–252 113	271,961	–118 211
2400	53,435	93 744	–252 261	274,225	–112 386
2500	53,905	99 112	–252 399	276,416	–106 555
2600	54,340	104 524	–252 532	278,539	–100 719

Tabela A2.7

Água (H_2O). *(Valores determinados a partir das expressões do Apêndice 2.) (continua)*

Processes – Esterification & Transesterification

Table 9. Summary of fuel properties used for the Well-To-Wheels integration (Gases)

Fuel	Density	RON / CN	LHV	Elemental composition of Carbon	CO_2 emission factor (Fuel combustion)	
	kg/ m³i.N.*	---	MJ/kg	%m	g/MJ	kg/kg
DME (liquefied via pressurisation at 288.15 K)	670	55	28.4	52.2	67.3	1.91
LPG (liquefied via pressurisation at 288.15 K)	550	**	46.0	82.4	65.7	3.02
CNG (EU mix piped NG)	0.780	**	46.6	70.8	56.1	2.60
CNG (2016 Mix)	0.782	**	46.6	71.3	56.2	2.62
CNG (2030 Mix average)	0.782	**	46.8	71.7	56.2	2.63
H-CNG (2016)	0.775	**	48.0	73.5	56.2	2.69
H-CNG (2030)	0.775	**	48.0	73.5	56.2	2.70
CNG (Russian NG quality)	0.727	**	49.2	73.9	55.1	2.71
CNG (upgraded biogas)	0.752	**	46.1	71.3	56.7	2.61
LNG (EU mix. 2016/2030)	0.798	**	49.1	75.6	56.4	2.77
LNG (Upgraded biogas 2016/2030)	0.716	**	50.0	74.9	54.9	2.74
Shale gas	0.727	**	49.2	73.9	55.1	2.71
Hydrogen (CGH2 & cCGH2)	0.090***	#	120.0	0.0	0.0	0.00
Liquid Hydrogen			120.0	0.0	0.0	0.00

Notes:
*) All values are related to standard conditions according to DIN 1343 (0.1013 MPa; 273.15 K) & ISO 2533 (288.15 K);
**) can vary significantly;
***) 0.084 kg/m³ @ 288.15 K (as indicated in the TTW report). The pressure of the CGH2 at the refueling station amounts to 88 MPa. CGH2 is stored in the vehicle at a pressure of maximum 70 MPa at 15°C.
The pressure of the CNG in the stationary CNG storage at the refueling station amounts to 25 MPa. CNG is stored at a pressure of maximum 20 MPa in the vehicle at 15°C.

Additional components:

- AdBlue CO_2 emission factor: 0.24 kg/kg

Prussi, M., Yugo, M., Padella, M., Edwards, R., Lonza, L and De Prada, L., JEC Well-to-Tank report v5: Annexes, Hamje, H., editor, EUR 30269 EN, Publications Office of the European Union, Luxembourg, 2020, ISBN 978-92-76-21707-7, doi:10.2760/06704, JRC119036.

Thermochemical processes

Steam production by Natural Gas combustion

Natural Gas
(EU mix piped NG)

LHV = 46 MJ/kg

56.1 gCO_2/MJ

How much natural gas to produce 100 kg hot water?

Heat exchanger efficiency = 85%

Thermochemical processes

Steam production by Natural Gas combustion

How much natural gas to produce 100 kg hot water?

Natural Gas
(EU mix piped NG)

LHV = 46 MJ/kg

56.1 gCO_2/MJ

$$mNG*LHV = \frac{mcp\Delta T}{\eta}$$

$$mNG = \frac{mcp\Delta T}{LHV*0.85}$$

$$mNG = \frac{100kg*4.18\frac{kJ}{kgK}*50K}{46000\frac{kJ}{kg}*0.85} = 0.69kg$$

CO_2 = 56.1*0.69*46*10^-3 = 1.79 kg

Heat exchanger efficiency = 85%

Steam production by Natural Gas combustion

How much emissions to produce **100 kg** water?

$$mNG*LHV= \frac{mcp\Delta T}{\eta}$$

$$mNG= \frac{mcp\Delta T}{LHV*0.85}$$

$$mNG= \frac{100kg*4.18\frac{kJ}{kgK}*50K}{46000\frac{kJ}{kg}*0.85}= 0.69kg$$

CO_2 = 56.1*0.69*46*10^-3 = 1.79 kg

Thermochemical processes

Steam production by Natural Gas combustion

How much emissions to produce **100 kg** steam ? @750 °C, 200 atm, 3940 kJ/kg (**3.94 MJ/kg**)

$$mNG*LHV= \frac{\frac{MJ}{kg}*kg}{\eta}$$

$$mNG= \frac{3.94*100}{56.1*0.85}$$

$$CO_2 = \frac{3.94*100}{0.85} *46*10^{-3} = 21.3 \text{ kg}$$

Emission Factor (EF)

$EF_{\text{vapor produced natural gas}}$ = 21.3/100 = 0.213 kg CO2/kg = 0.05 kg CO2/MJ

IPCC CO_2eq

Table 1. CO_2 equivalency factors

Gas	AR5 w/o feedback	AR5 w/ feedback	AR6 w/ feedback
CO_2	1	1	1
CH_4 (fossil)	28	34	29.8
CH_4 (biogenic)	28	34	27.2
N_2O	265	298	273
C_2H_6	0.4	0.4	0.4
CO[1]	2	2	2
H_2[1]	5.8	5.8	5.8

1 Values from IPCC AR5

Challenge #2

Consider the SMR from the class example. How much hydrogen in pure form do you get, for 700 ºC, 850 ºC and 1000 ºC? If you burn the off-gas to provide heat, how would change the CO_2eq emissions coming out of the system, per kg H_2; the water consumption, per kg H_2, and the CH_4 consumption, per kg H_2?, and if you burn off-gas to heat and electricity? justify with calculations.

Extract Portuguese data regarding natural gas that is consumed in crude oil Refinery. Assuming it is converted to hydrogen, by SMR, how much hydrogen is used for thermal cracking and desulphurization in Portugal per year? Potential heat recovery and electricity production?

https://www.dgeg.gov.pt/pt/estatistica/energia/gas-natural/consumos/

Challenge #2

Deliver excel by 19 April

E-mail: camsilva@ciencias.ulisboa.pt

Thanks

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