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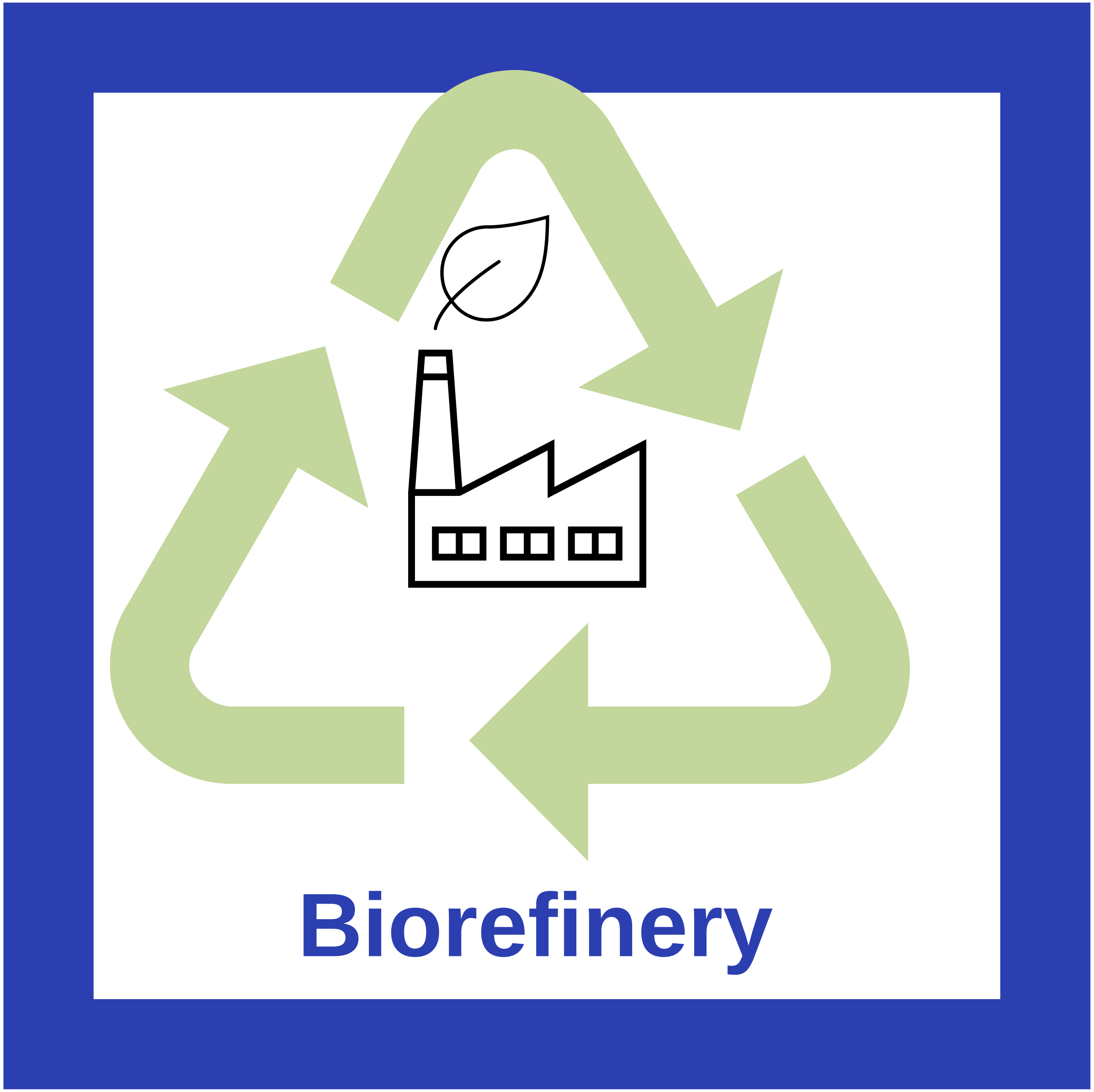
Eng Energy & Environment


Biorefinery

Information

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

Wednesdays

16h-19h30

Room: 8.2.13

Information

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

5 challenges!

Oral evaluation: discussing the challenges

07-06-2022

27-06-2022

20-07-2022

Definition & examples

IEA Bioenergy Task 42
‘‘Biorefineries”

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

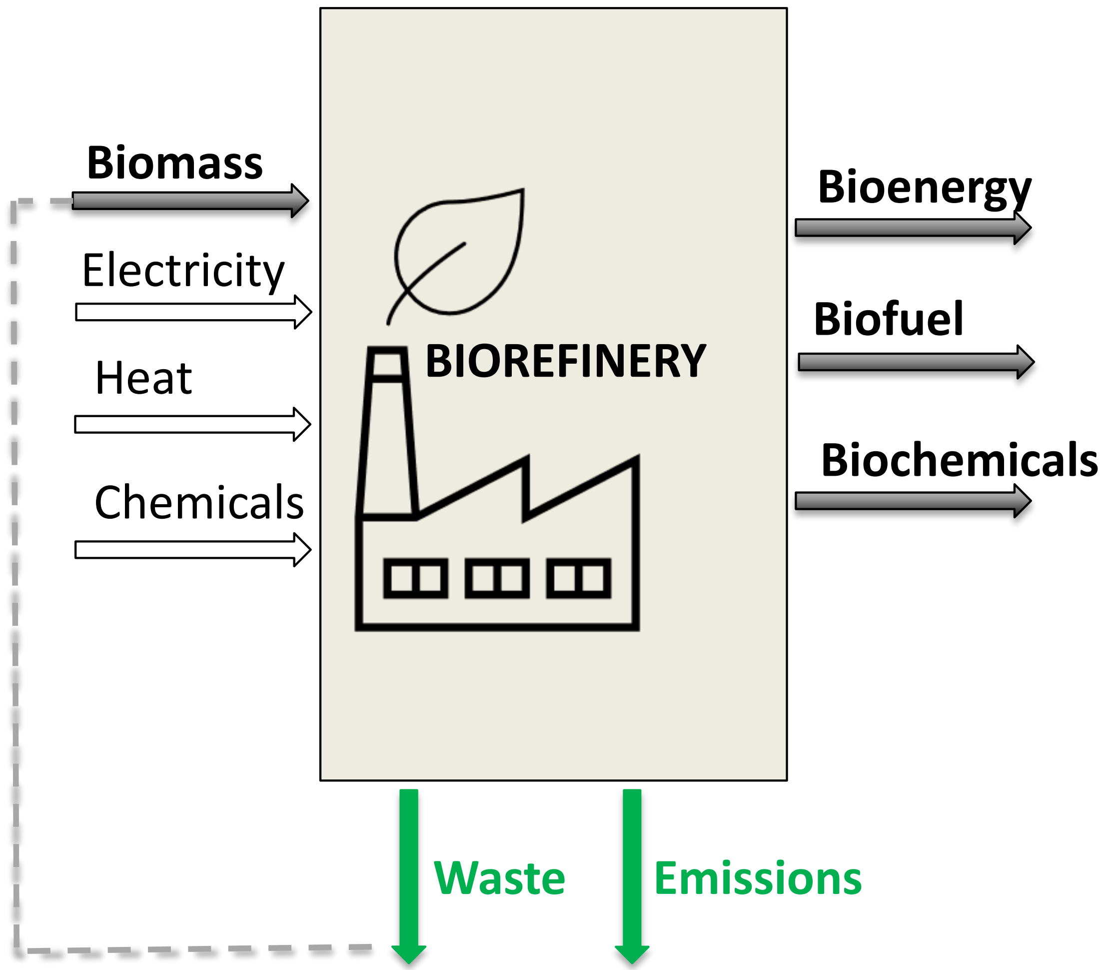
2007

Definition & examples

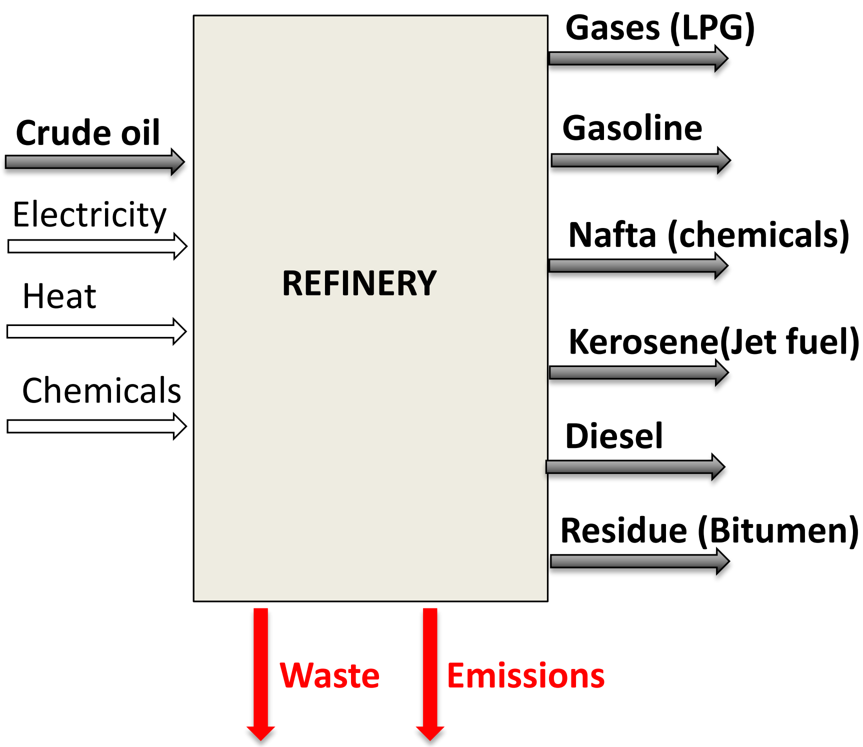
The biorefinery concept: Using biomass instead of oil for producing energy and chemicals, Energy Conversion and Management, Volume 51, Issue 7, 2010, Pages 1412-1421, ISSN 0196-8904, https://doi.org/10.1016/j.enconman.2010.01.015

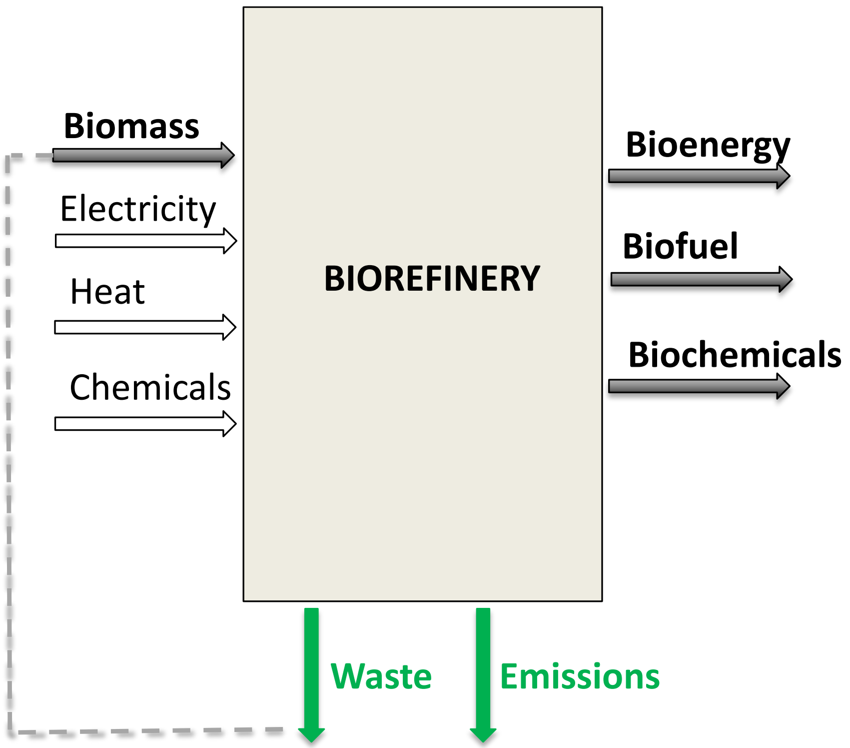
Processes

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



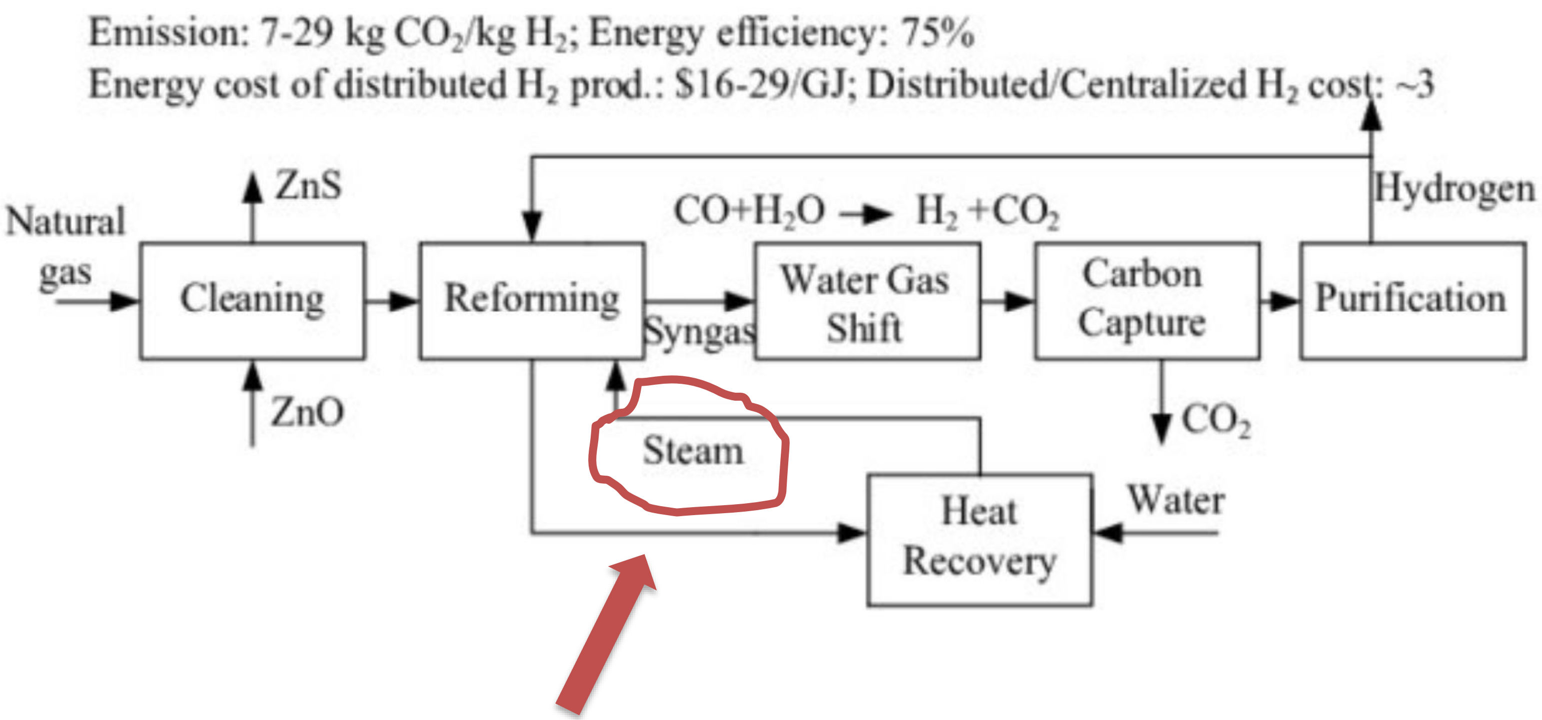
Definition & examples





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

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

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

205.9 kJ/mol

STEAM 750 °C

Endothermal

$$C_2H_6 + 2\ H_2O \leftrightarrows 2\ CO + 5\ H_2$$

374.3 kJ/mol

Hydrogen Production by Natural Gas

Water gas-shift

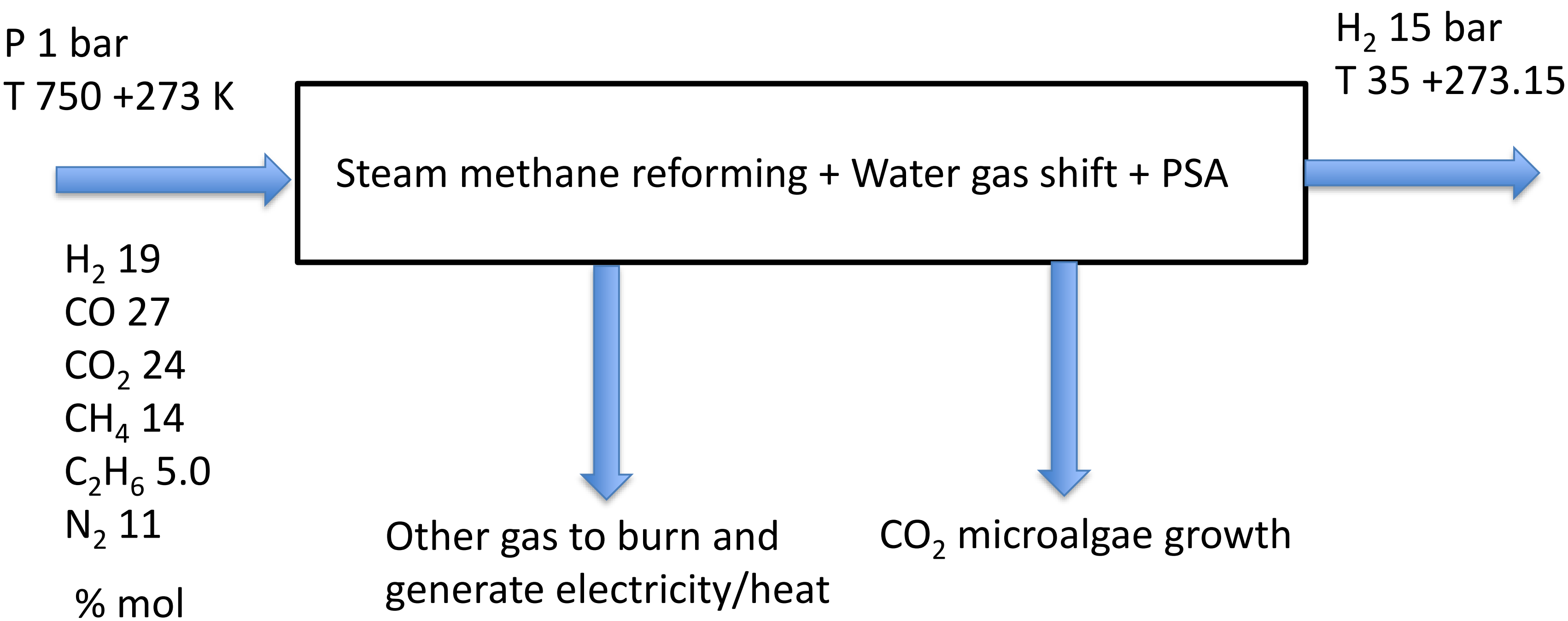
$CO + H_2O \leftrightarrow CO_2 + H_2$

-41 kJ/mol

Exothermal

Thermochemical processes

Hydrogen Production by Steam reforming



Thermochemical processes

H_2

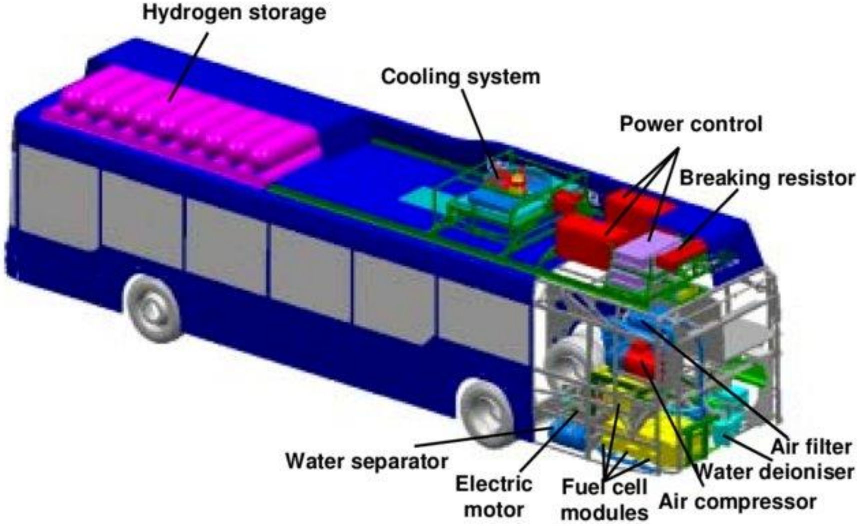
P 15 bar

T 35 +273 K

880 bar

H_2

750 bar



Thermochemical processes

880 bar

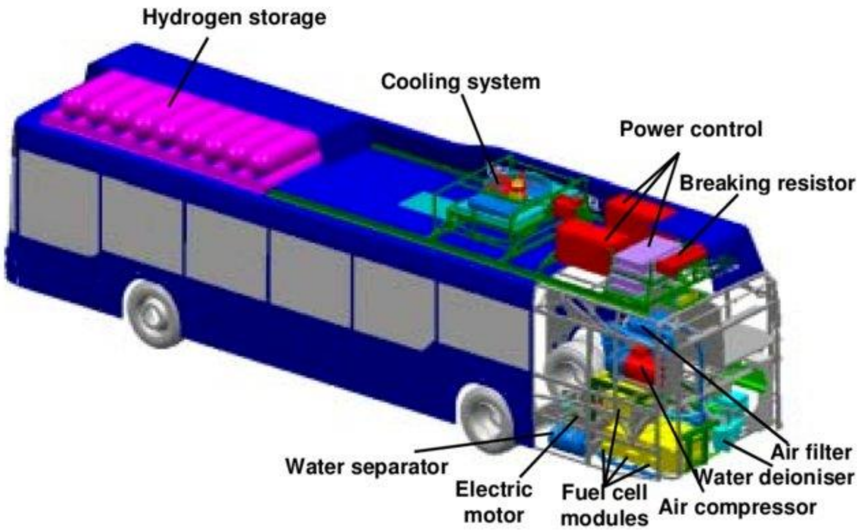
H_2

P 15 bar

T 35 +273 K

H_2

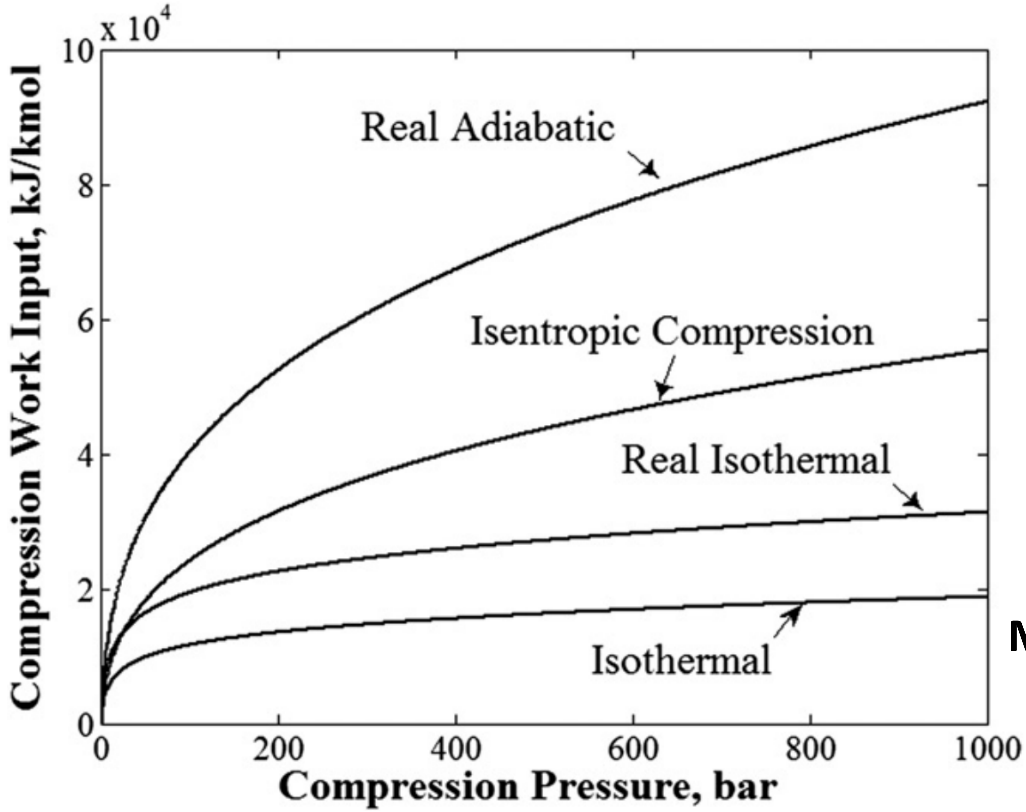
750 bar



8 bar

20% hydrogen/natural gas blend

Thermochemical processes



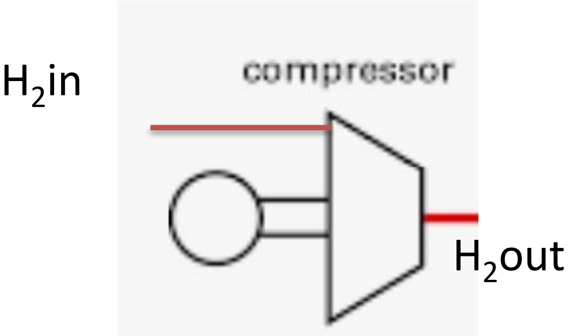
MINIMUM ENERGY TO COMPRESS

Fig. 1 – Compression work input for different compression processes [based on data in Ref. 8].

https://doi.org/10.1016/j.ijhydene.2011.12.047

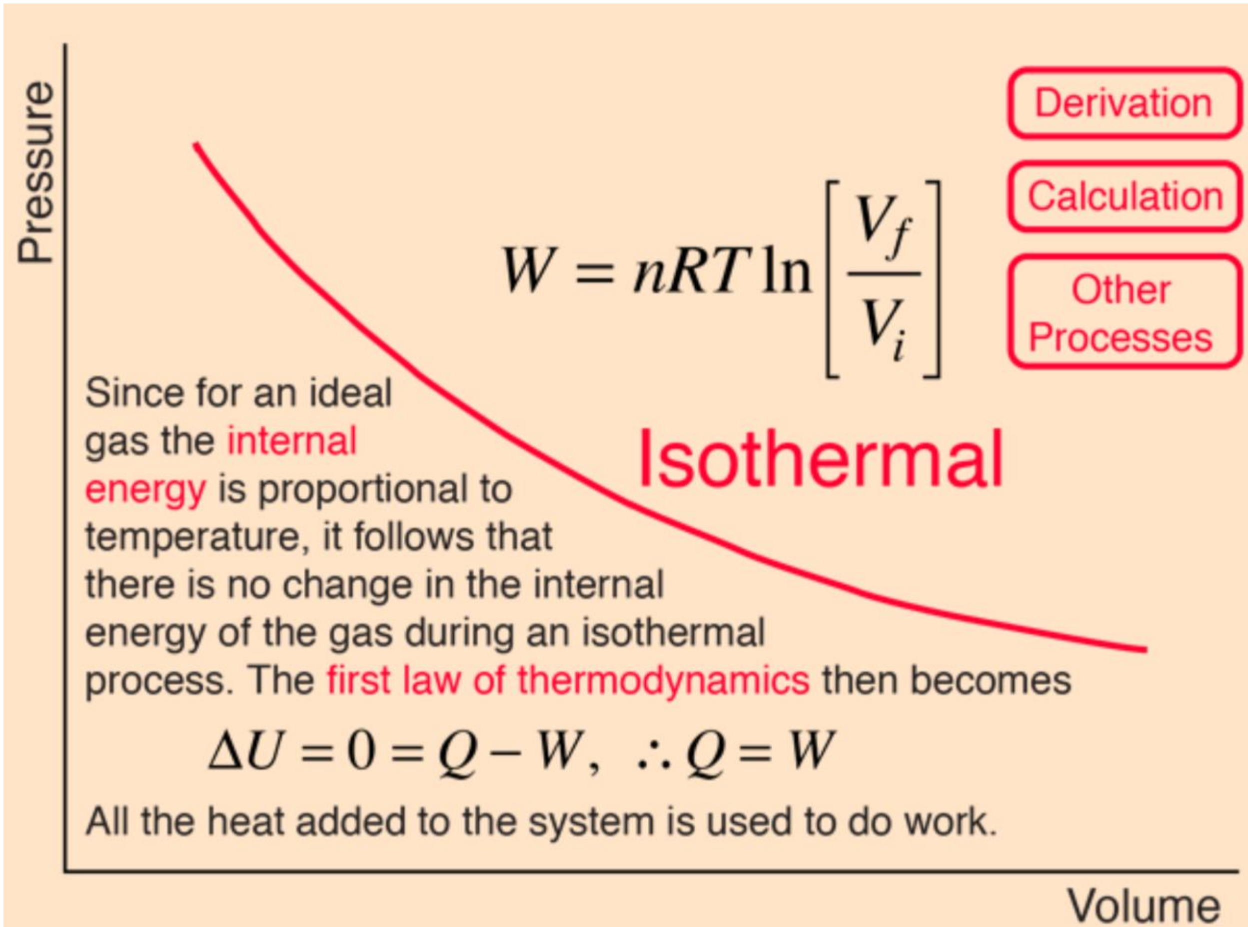
Isothermal compression = MINIMUM ENERGY TO COMPRESS

$$\begin{cases} W = \int p dV \\ pV = nRT \end{cases} \Leftrightarrow W = nRT\ln(Vf/Vi)$$



https://www.hydrogen.energy.gov/pdfs/9013_energy_requirements_for_hydrogen_gas_compression.pdf

Thermochemical processes



Thermochemical processes

START

H_2 15 bar
T 35 +273.15

END

H_2 750 bar
T 35 +273.15

nRTln(Vf/Vi) = m/M*RTln(Vf/Vi)= 5011 kJ

Vf/Vi = pi/pf = 15/750 = 0.02

⇒ 5 MJ/kg = 4% of LHV (120 MJ/kg)

η = 50% (non-isentropic and motor efficiency)

⇒ 9.6 /3.5 kWh/kg = 2.75 kWh/kgH_2

https://www.hydrogen.energy.gov/pdfs/9013_energy_requirements_for_hydrogen_gas_compression.pdf
DOE Technology Validation Project data for compression from on-site H2 production is 1.7 to 6.4 kWh/kgH2

Thermochemical processes

START

H_2 15 bar
T 35 +273.15

END

H_2 1 bar
T -253 +273.15

https://www.hydrogen.energy.gov/pdfs/9013_energy_requirements_for_hydrogen_gas_compression.pdf

8-12 kWh/kg LH2

Thermochemical processes

Fossil Fuel Comparator for Biodiesel

Table 1. Summary. Refinery allocation results based on extended literature review[4]

	Consequential "Marginal" (gCO_{2eq}/MJ)			**Attributional "Average" ($g\ CO_{2eq}/MJ$)**			
	JEC [1] (Concawe)		JRC paper (2017)	Aramco paper [4]		JRC paper[2]	Sphera (2020)
	JEC v4 [1]	**JEC v5 [3]**	JRC [2]	Standard mass allocation	Customized allocation [4]*	EN (2)	Mass & Energy
Gasoline	7	**5.5**	5.8	10.2	7.6	5.7 - 5.8	9.6
Diesel	8.6	**7.2**	7.2	5.4	6.8	5.8 -	3.4

Thermochemical processes

Fossil Fuel Comparator for Biodiesel

JEC WTW study Version 5

WTT pathway — Back to menu

Code	**TOFA3**	*Description*				
Final fuel	**Biodiesel**	Tallow oil to biodiesel Glycerine to internal biogas				
Transportation to market	Carcass transportation	0.01	0.4	0.42	0.00	0.00
Transformation near market	Tallow production	0.08	4.6	4.28	0.27	0.01
	Tallow transport	0.00	0.3	0.34	0.00	0.00
	Biodiesel production	0.17	7.4	6.90	0.48	0.00
Conditioning & distribution	Distribution	0.01	0.8	0.76	0.00	0.00
	Dispensing at retail site	0.01	0.4	0.37	0.00	0.00
Total WTT		**0.28**	**13.8**			
Min		*0.27*	*13.7*			
Max		*0.28*	*14.0*			
of which Fossil		0.22				
of which Nuclear		0.02				
Combustion CO_2 emissions			76.2			
of which Renewable (shown as negative)			-76.2			
Total non-renewable emissions including combustion			**13.8**			
% GHG savings relative to diesel (pathway COD1)			**85%**			

Readiness level:

Technology TRL	Commercial CRL
9	6

"Tallow oil to biodiesel and Glycerine to internal biogas"

Development stage 0-9

RED II directive

Disaggregated default values for processing: 'e_p' as defined in Part C of this Annex

Biofuel and bioliquid production pathway	Greenhouse gas emissions – typical value ($g\ CO_2eq/MJ$)	Greenhouse gas emissions – default value ($g\ CO_2eq/MJ$)
rape seed biodiesel	11,7	16,3
sunflower biodiesel	11,8	16,5
soybean biodiesel	12,1	16,9
palm oil biodiesel (open effluent pond)	30,4	42,6
palm oil biodiesel (process with methane capture at oil mill)	13,2	18,5
waste cooking oil biodiesel	9,3	13,0
animal fats from rendering biodiesel ([*2])	13,6	19,1

([*2])
Note: applies only to biofuels produced from animal by-products classified as category 1 and 2 material in accordance with Regulation (EC) No 1069/2009, for which emissions related to hygenisation as part of the rendering are not considered.

Thermochemical processes

Fossil Fuel Comparator for Biodiesel RED II directive

For biofuels, for the purposes of the calculation referred to in point 3, the fossil fuel comparator EF(t) shall be 94 g CO2eq/MJ.

As fronteiras recomendadas para avaliação de uma cadeia de produção são:

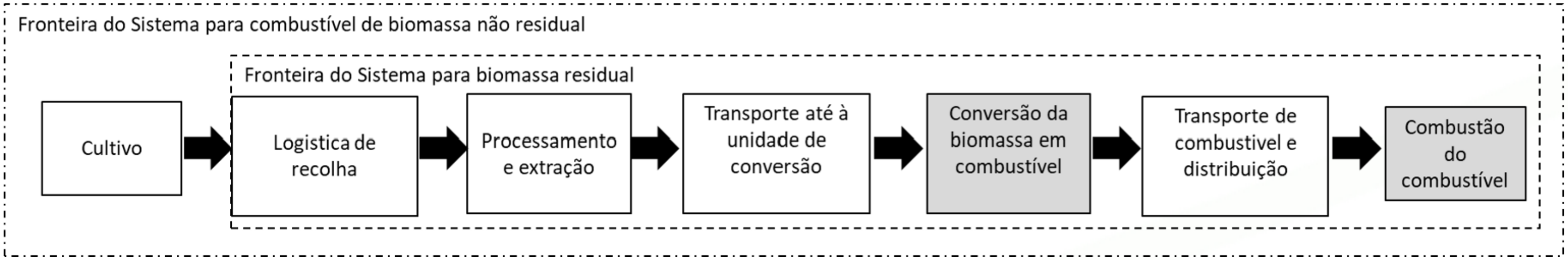


Figura 1 | Fronteiras recomendadas pela RED II para a avaliação de emissões de GEE

Emissions of the fuel in use, eu, shall be taken to be zero for biofuels and bioliquids. Emissions of non-CO_2 greenhouse gases (N_2O and CH_4) of the fuel in use shall be included in the eu factor for bioliquids

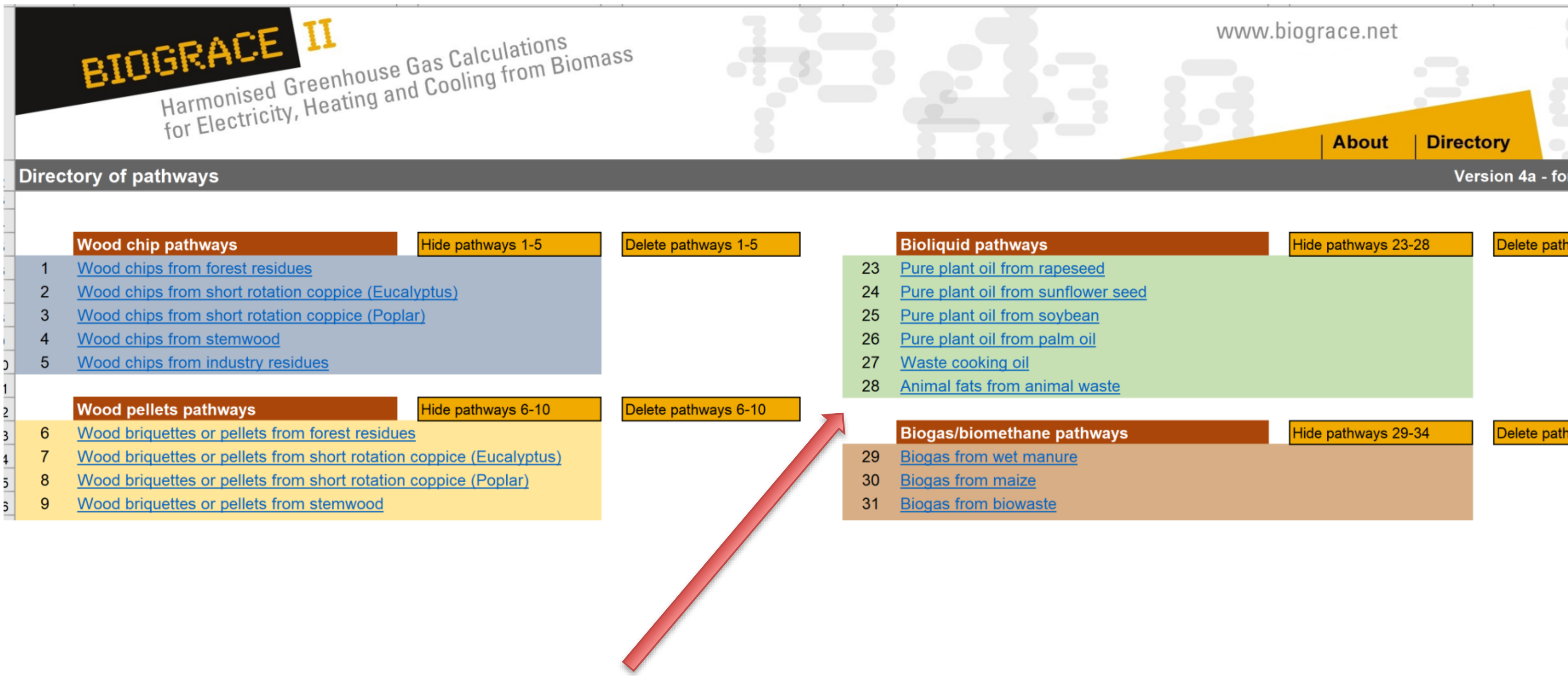
Fossil Fuel Comparator for Biodiesel

For biofuels, for the purposes of the calculation referred to in point 3, the fossil fuel comparator EF(t) shall be 94 g CO2eq/MJ.

Disaggregated default values for transport and distribution: 'e_{td}' as defined in Part C of this Annex

Biofuel and bioliquid production pathway	Greenhouse gas emissions – typical value ($g\ CO_2eq/MJ$)	Greenhouse gas emissions – default value ($g\ CO_2eq/MJ$)
rape seed biodiesel	1,8	1,8
sunflower biodiesel	2,1	2,1
soybean biodiesel	8,9	8,9
palm oil biodiesel (open effluent pond)	6,9	6,9
palm oil biodiesel (process with methane capture at oil mill)	6,9	6,9
waste cooking oil biodiesel	1,9	1,9
animal fats from rendering biodiesel ([*4])	1,7	1,7

Thermochemical processes



Processes – Esterification&Transesterification

https://doi.org/10.1016/j.renene.2011.07.016

Inputs

Feedstock

Chemicals

Energy

	Biodiesel production from:				
	Waste vegetable oils	Rendered beef tallow	Rendered poultry fat	Dried sewage sludges	
Inputs					
Materials					
Lipid feedstock	1205.12	1015.36	1013.00	10,000.00	kg
Methanol	112.67	113.32	99.00	670.18	kg
Sulphuric acid	0.15	–	–	76.35	kg
Calcium oxide	0.10	–	–	–	kg
Water	56.08	71.32	32.00	0.88	kg
Sodium hydroxide	9.80	4.00	5.00	–	kg
Sodium methoxide	–	11.00	12.00	–	kg
Phosphoric acid	7.95	–	–	–	kg
Hydrogen chloride	–	6.00	7.00	–	kg
Hexane	–	–	–	76.28	kg
Energy					
Thermal energy (rendering)	1628.93	–	–	–	MJ
Electric energy (rendering)	133.12	–	–	–	kWh
Thermal energy (esterification)	222.30	175.94	90.04	–	MJ
Electric energy (esterification)	31.43	28.93	10.08	–	kWh
Thermal energy (transesterification)	1650.84	1733.48	1886.96	2542.95	MJ
Electric energy (transesterification)	20.34	30.36	28.98	28.47	kWh

Thermochemical processes

WATER	Process Water Other Water deion.	0.80 kg CO_2eq/m^3
HCL	Hydrogen Cloride	1.06 kg CO_2eq/ kg
NaOH	Sodium hydroxide	0.53 kg CO_2eq/ kg

Thermochemical processes

BIOGRACE II
Harmonised Greenhouse Gas Calculations for Electricity, Heating and Cooling from Biomass
www.biograce.net
About | Directory

Directory of pathways — Version 4a - for

	Wood chip pathways	Hide pathways 1-5	Delete pathways 1-5
1	Wood chips from forest residues		
2	Wood chips from short rotation coppice (Eucalyptus)		
3	Wood chips from short rotation coppice (Poplar)		
4	Wood chips from stemwood		
5	Wood chips from industry residues		

	Wood pellets pathways	Hide pathways 6-10	Delete pathways 6-10
6	Wood briquettes or pellets from forest residues		
7	Wood briquettes or pellets from short rotation coppice (Eucalyptus)		
8	Wood briquettes or pellets from short rotation coppice (Poplar)		
9	Wood briquettes or pellets from stemwood		

	Bioliquid pathways	Hide pathways 23-28	Delete pathw
23	Pure plant oil from rapeseed		
24	Pure plant oil from sunflower seed		
25	Pure plant oil from soybean		
26	Pure plant oil from palm oil		
27	Waste cooking oil		
28	Animal fats from animal waste		

	Biogas/biomethane pathways	Hide pathways 29-34	Delete pathw
29	Biogas from wet manure		
30	Biogas from maize		
31	Biogas from biowaste		

Thermochemical processes

BIOGRACE II
Harmonised Greenhouse Gas Calculations for Electricity, Heating and Cooling from Biomass

www.biograce.net

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Standard Calculation Values

1	2	3	4	5	6	7	8	9	10	11	12	
Parameter:	GWP	GHG emission coefficient								Density	LHV MJ/kg	Fuel efficien
unit:	$gCO_{2,eq}$ / g	gCO_2/kg	gCH_4/kg	gN_2O/kg	$gCO_{2\text{-}eq}$/kg	gCO_2/MJ	gCH_4/MJ	gN_2O/MJ	$gCO_{2\text{-}eq}$/MJ	kg/m^3	(at 0% water)	MJ/t.k
Forestry residues											19.0	
Glycerol											16.0	
Industry residues (wood)											19.0	
Manure											12.0	
Maize (grain only)											17.3	
Maize whole crop											16.9	
Meat and bone meal											18.0	
Palm kernel meal										570	18.5	
Palm kernel oil											37.0	
Poplar (SRC)											19.0	
Rapeseed											27.0	
Rapeseed oil cake											18.4	
Rye											17.1	

Thermochemical processes

Production of FAME from Waste vegetable or animal oil (UCO) (steam from natural gas boiler) — **Version 4d for Compliance**

Overview Results

All results in g $CO_{2,eq}$ / MJ $_{FAME}$	Non- allocated results	Allocation factor	Allocated results	Total	Actual/ Default	Default values RED Annex V.D
Cultivation e_{ec}				0.0	A	0
Collection of waste vegetabl	0.00	94.5%	0.00			0.00
Processing e_p				20.0	A	13
Refining of vegetable oil	1.08	94.5%	1.02			12.80
Esterification	20.10	94.5%	18.99			
Transport e_{td}				1.3	A	1
Transport of waste vegetabl	0.00	94.5%	0.00			0.00
Transport of refined oil	0.00	94.5%	0.00			0.00
Transport of FAME to depot	0.47	100.0%	0.47			0.83
Transport to filling station	0.80	100.0%	0.80			0.44
e_{ccr} + e_{ccs}	0.0	100.0%	0.0	0.0		0
Totals	**22.4**			**21.3**		**14**

Allocation factors
Esterification
94.5% to FAME
4.1% to Refined glycerol
1.4% to Bio-oil

Emission reduction
Fossil fuel reference (diesel)
83.8 g $CO_{2,eq}$/MJ
GHG emission reduction
75%

Calculations in this Excel sheet......

- [x] **strictly follow the methodology as given in Directives 2009/28/EC and 2009/30/EC**
- [ ] ***~~follow JEC calculations by using GWP values 25 for CH4 and 298 for N2O~~***

As explained in "About" under "Inconsistent use of GWP's"

When using this GHG calculation tool, **the BioGrace calculation rules must be respected.**
The rules are included in the zip file in which you downloaded this tool. The rules are also available at www.BioGrace.net

Calculation per phase

Track changes: ON

Collection of waste vegetable or animal oil

Yield		
Raw waste vegetable / animal o	1	MJ
Moisture content	0.0%	

Quantity of product

1.000 MJ / $MJ_{Raw\ waste\ oil,\ input}$
37.1 MJ / $kg_{Raw\ waste\ oil,\ input}$
0.029 $kg_{Raw\ waste\ oil,\ input}$/$MJ_{FAME}$

Calculated emissions

Emissions per MJ FAME	g CO_2	g CH_4	g N_2O	g $CO_{2,eq}$
Total	**0.00**	**0.00**	**0.00**	**0.00**

Info

per kg waste veg. / animal oil
g $CO_{2,eq}$
0.00

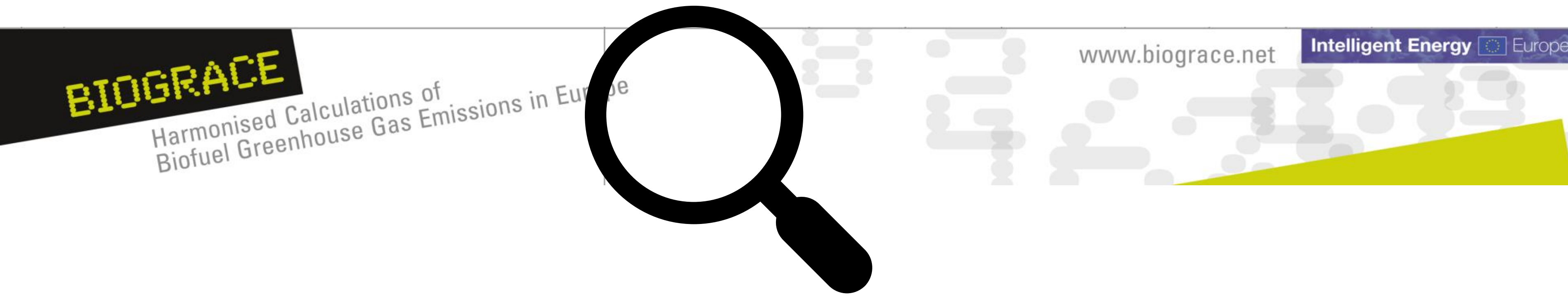
Thermochemical processes

Version 4 - Public		
	1	2
STANDARD VALUES parameter:		**GWP**
unit:		$gCO_{2,eq}$ / g
Global Warming Potentials (GWP's)		
CO_2		1
CH_4		23
N_2O		296

Thermochemical processes

Greenhouse Gas	100 Year Time Period			20 Year Time Period		
	AR4 2007	AR5 2014	AR6 2021	AR4 2007	AR5 2014	AR6 2021
CO_2	1	1	1	1	1	1
CH_4 fossil origin	25	28	29.8	72	84	82.5
CH_4 non fossil origin			27.2			80.8
N_2O	298	265	273	289	264	273

Thermochemical processes



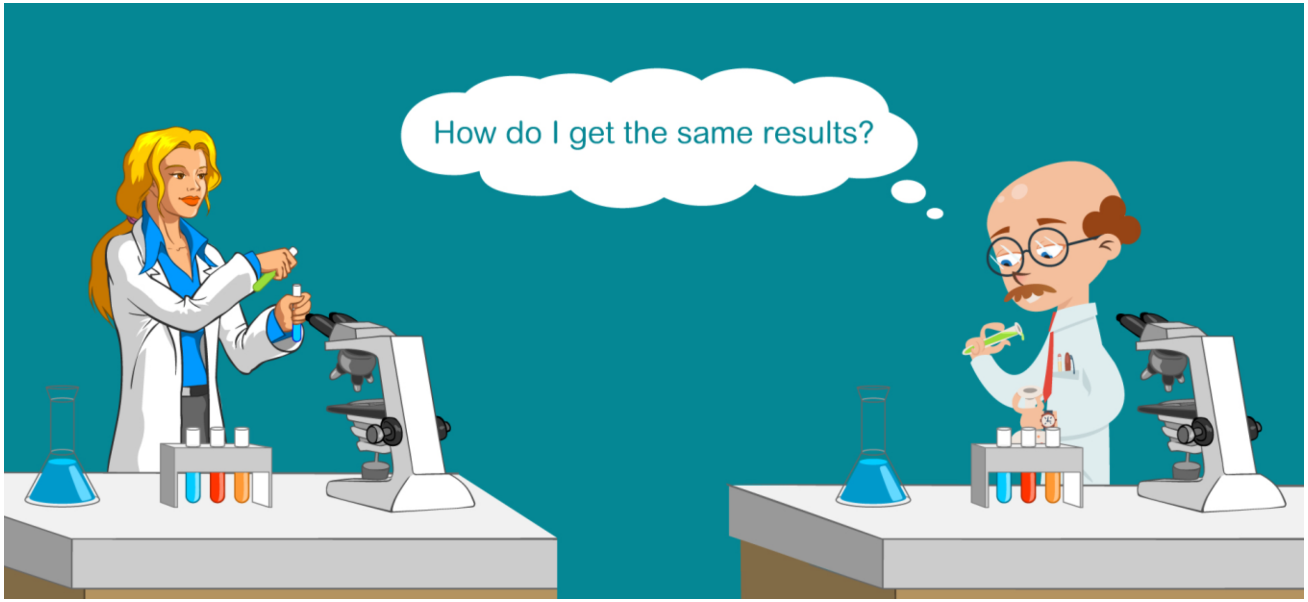
Rendering + Esterification/Transesterification

Thermochemical processes

- ✓ USED EMISSION FACTORS
- ✓ IPCC ASSESSEMENT REPORT???
- ✓ ALLOCATION FACTORS

TRANSPARENCY

REPRODUTIBILITY



Thanks

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