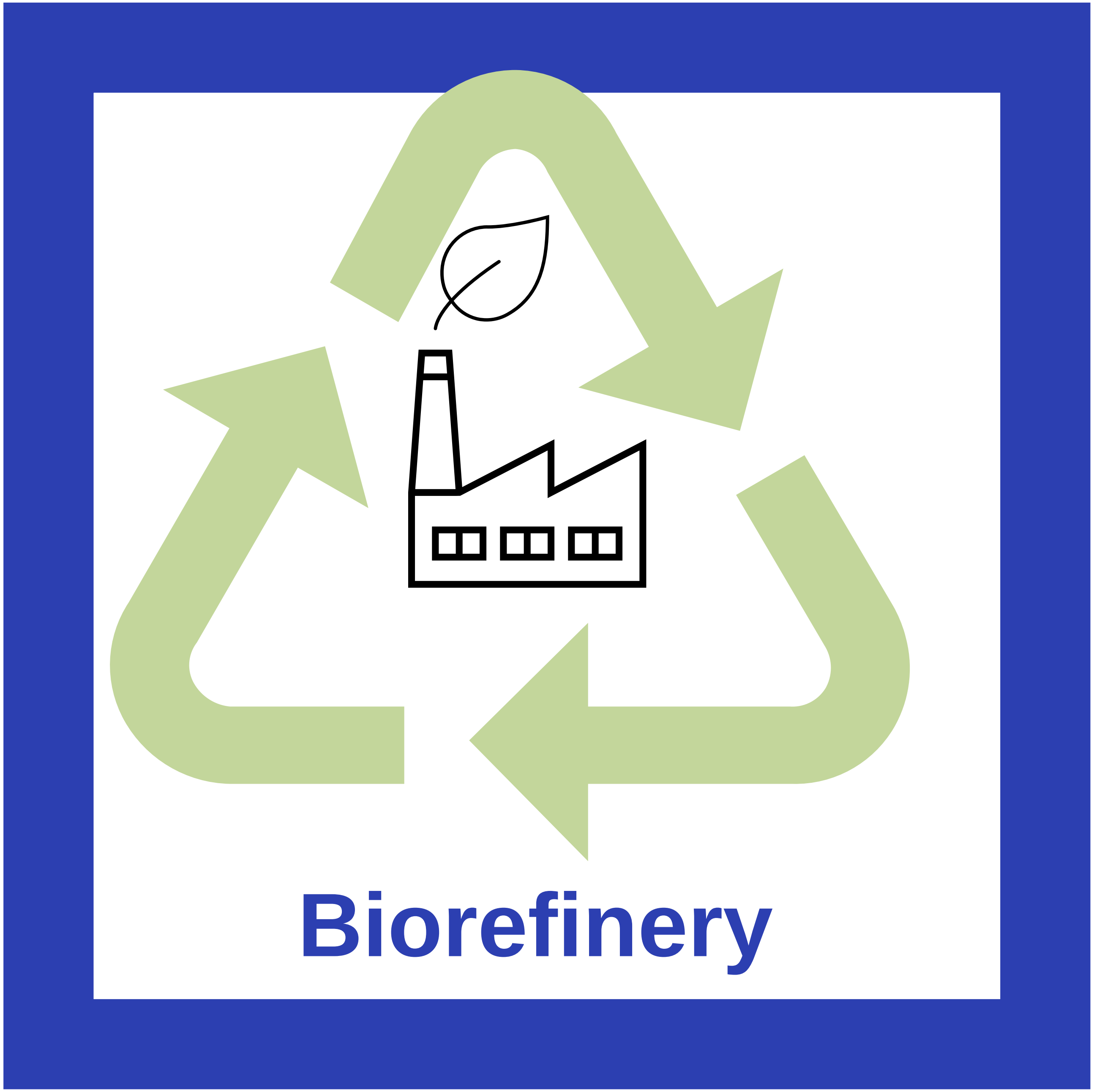
Ciências ULisboa

Faculdade
de Ciências
da Universidade
de Lisboa

Eng Energy & Environment


Biorefinery

Information

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

Wednesdays

16h-19h00

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
Technology Collaboration Programme

IEA Bioenergy Task 42
‘‘Biorefineries”

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

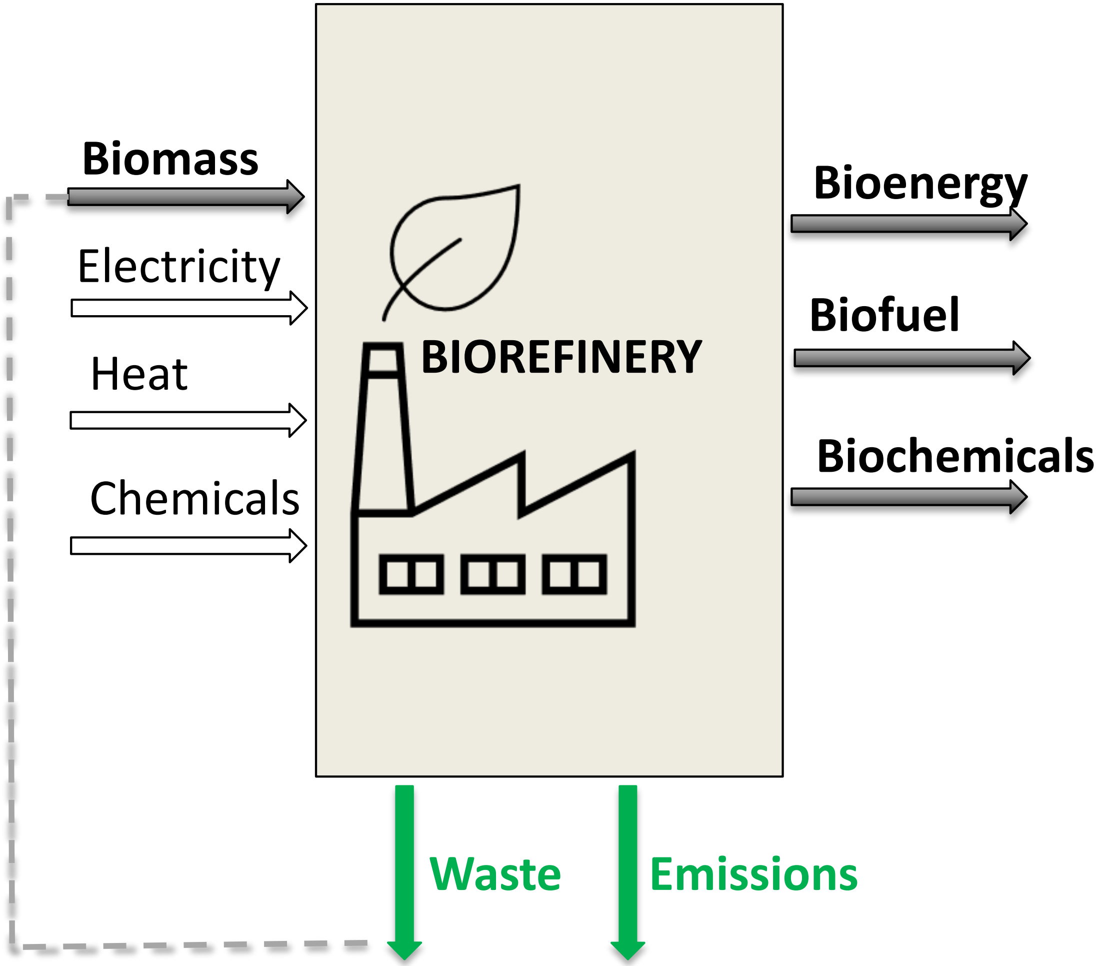
2007

Definition & examples

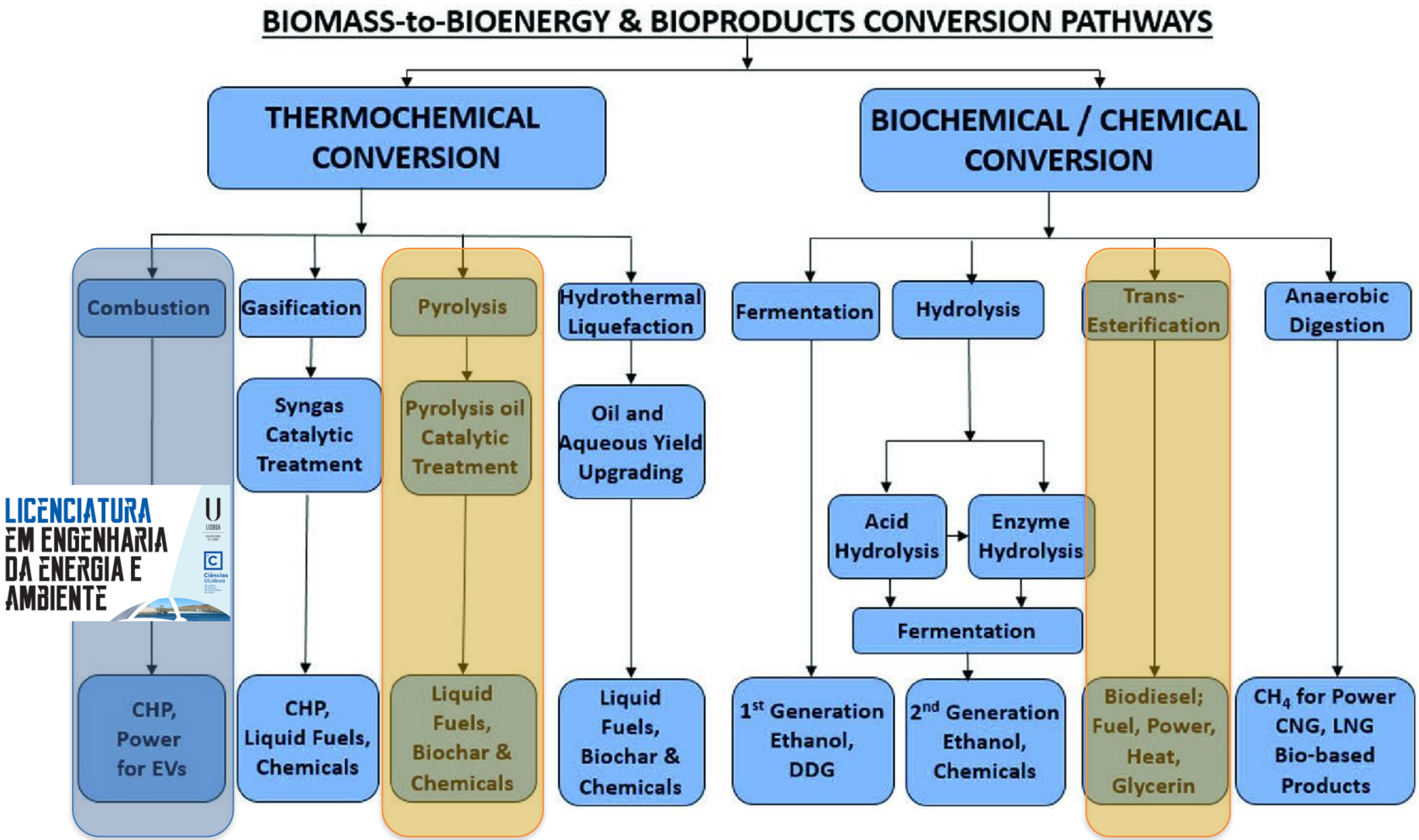
The biorefinery concept: Using biomass instead of oil for producing energy and chemicals, Energy Conversion and Management, Volume 51, Issue 7, 2010, Pages 1412-1421, ISSN 0196-8904, https://doi.org/10.1016/j.enconman.2010.01.015

Processes

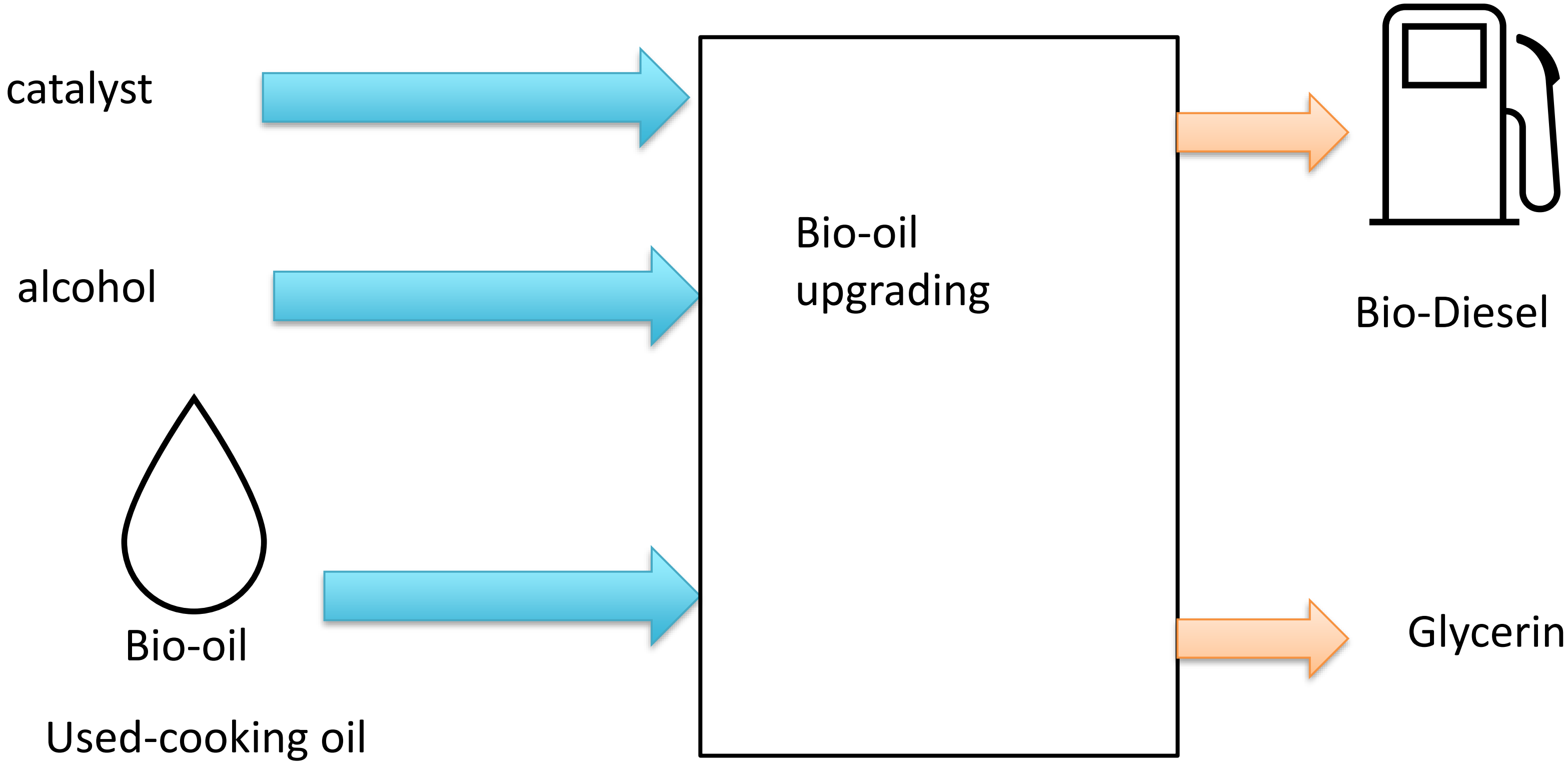
Collect and pre-treat: Decompose biomass in: Build products:



Processes – Conversion Technologies



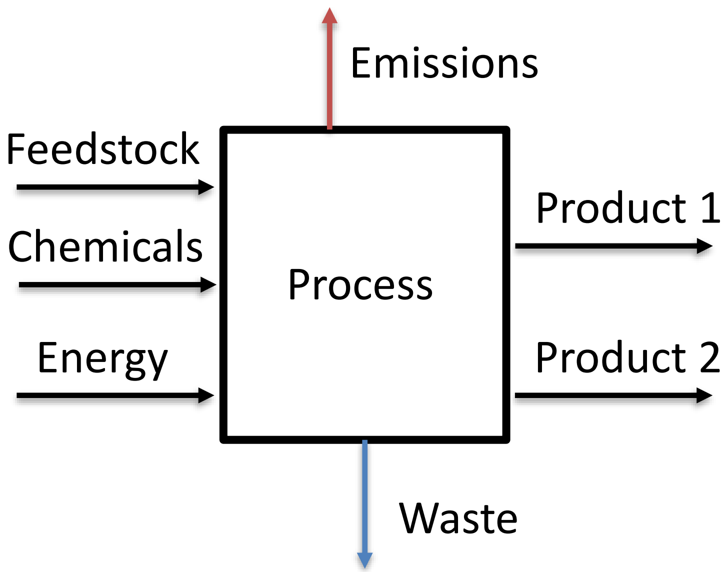
Processes – Esterification/Transesterification



https://www.youtube.com/watch?v=rrldwVGmmy4

Processes – Esterification & Transesterification

ALLOCATION – MASS BASIS

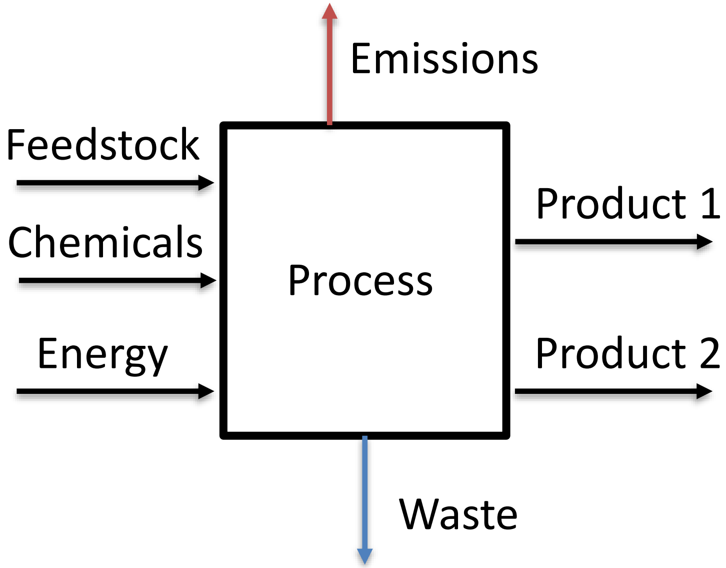


EP1= Emissions*massP1/(massP1+massP2)

EP2= Emissions*massP2/(massP1+massP2)

Processes – Esterification & Transesterification

ALLOCATION – ENERGY BASIS

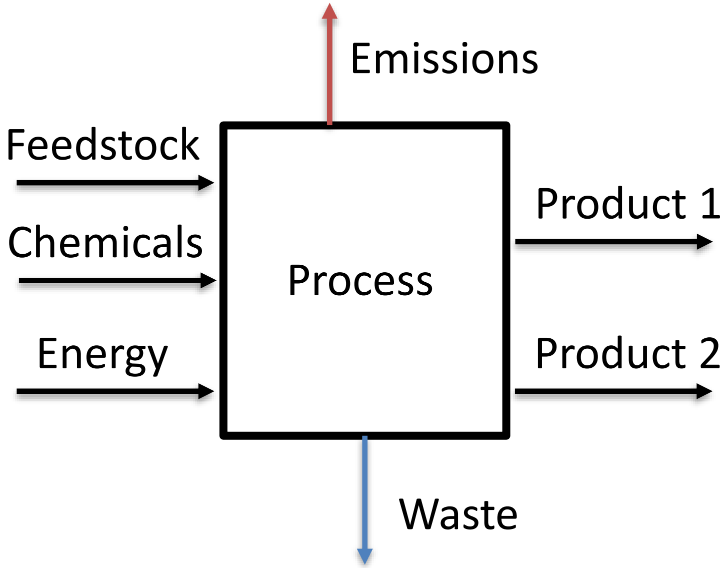


EP1= Emissions*energyP1/(energyP1+energyP2)

EP2= Emissions*energyP2/(energyP1+energyP2)

Energy content based on LHV = Lower Heating Value

ALLOCATION – ECONOMIC BASIS



EP1= Emissions*costP1/(costP1+costP2)

EP2= Emissions*costP2/(costP1+costP2)

ALLOCATION – ENERGY BASIS

Biodiesel several molecular formula possibilities

Fatty Acids, Molecular formula	Methyl Esters, Molecular formula	% age
$C_{16}H_{32}O_2$	$C_{17}H_{34}O_2$	24.5
$C_{18}H_{32}O_2$	$C_{19}H_{34}O_2$	14.3
$C_{18}H_{34}O_2$	$C_{19}H_{36}O_2$	37.5
$C_{18}H_{36}O_2$	$C_{19}H_{38}O_2$	22.5
$C_{20}H_{40}O_2$	$C_{21}H_{42}O_2$	1.5

Glycerin

$C_3H_8O_3$

Processes – Esterification/Transesterification

ALLOCATION – ENERGY BASIS

$C_3H_8O_3$ →

mC = 3*12/(3*12+8+3*16) = 0.39

mH = 8*1/(3*12+8+3*16)= 0.09

mO = 3*16/(3*12+8+3*16 = 0.52

LHV [MJ/kg] = 38.2 **mC** + 84.9 (**mH** − **mO**/8) − ΔHl, where ΔHl described latent heat. When the equation applied to gas, liquid and solid fuels, ΔHl should be 0, 0.5 and 0.62 kJ/g, respectively.

~ 16.5 MJ/kg

Modification of Dulong's formula to estimate heating value of gas, liquid and solid fuels, https://doi.org/10.1016/j.fuproc.2016.06.040. (https://www.sciencedirect.com/science/article/pii/S0378382016302995)

Processes – Esterification/Transesterification

ALLOCATION – ENERGY BASIS

FAME = 37.2 MJ/kg

Glycerin = 16.5 MJ/kg

$C_3H_8O_3$

2.5.3 Fuel properties

As a summary of the properties of the fuel used for the integration of the Well-To-Wheels pathways and the Tank-To-Wheels ones are detailed in the Table 8:

Table 8. Summary of fuel properties used for the Well-To-Wheels integration (Liquids)

Fuel	Density	RON / CN	LHV	Elemental composition of Carbon	CO_2 emission factor (Fuel combustion Note)	
	kg/m³	---	MJ/kg	%m	g/MJ	kg/kg
Gasoline 2016 (E0)	743	95	43.2	86.4	73.4	3.17
Gasoline 2016 (E5)	746	95	42.3	84.7	73.3	3.10
Gasoline E10	748	95	41.5	82.8	73.3	3.04
Gasoline High Octane. Case 1 (100 RON)	761	100	42.4	84.8	73.3	3.11
Gasoline High Octane. Case 2 (102 RON / E5eq)	759	102	42.4	84.8	73.3	3.11
Gasoline High Octane. Case 3 (102 RON/ E10eq)	759	102	41.6	83.3	73.4	3.05
Pyrolysis-based Naphtha	745	95	43.2	86.4	73.4	3.17
Ethanol	794	108	26.8	52.2	71.4	1.91
Methanol	793	132	19.9	37.5	68.9	1.37
MTBE	745	118	35.1	68.2	71.2	2.50
ETBE	750	119	36.3	70.6	71.3	2.59
Diesel (B0)	832	51	43.1	86.1	73.2	3.16
Pyrolysis-based Diesel	832	51	43.1	86.1	73.2	3.2
Diesel B7 market blend	836	53	42.7	85.4	73.4	3.13
FAME	890	56	37.2	77.3	76.2	2.83
ED95	820	n. a.	25.4	49.4	71.3	1.81
FT Diesel	780	70	44.0	85.0	70.8	3.12
HVO	780	70	44.0	85.0	70.8	3.12
OME	1067	84	19.2	43.5	83.3	1.60

Note) CO_2 emission factor refers to the emissions released during the total combustion (full oxidation) of the carbon contained in the fuel molecules (expressed per MJ (or kg) of a certain fuel burnt). Therefore, the factor is not linked to the production process but to the chemical composition, carbon content, of the fuel itself.

Estimation of CO_2 emissions from fuel combustion for a given fuel can be summarised as follows:

CO_2 emissions from fuel combustion = Fuel consumption * CO_2 Emission factor.

In the case of fuels from biogenic origin (biofuels), the emissions during combustion can be offset (net zero) as the carbon released during combustion is equal to the carbon captured by the plant/tree during its growing process). See Figure 8.

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.

Processes – Esterification/Transesterification

ALLOCATION – ECONOMIC BASIS

Year?? Which market?? Reference monetary unit…**Bitcoin**….US$…..€???

index mundi

https://www.indexmundi.com/commodities/

TRADING ECONOMICS

https://tradingeconomics.com/commodities

Marketplace
S&P Global

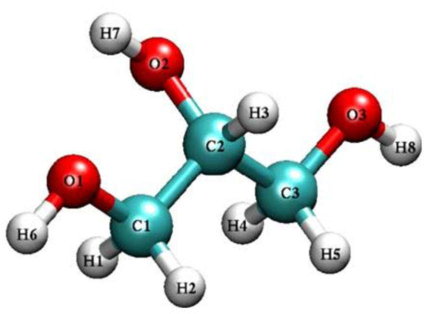
/ Datasets / Platts Market Data - Oil

S&P Global
Commodity Insights

Processes – Esterification/Transesterification

ALLOCATION – ECONOMIC BASIS

Year?? Which market?? Reference monetary unit…**Bitcoin**….US$…..€???



2002 450 US$/ton

2007 50 US$/ton

CRUDE GLYCEROL

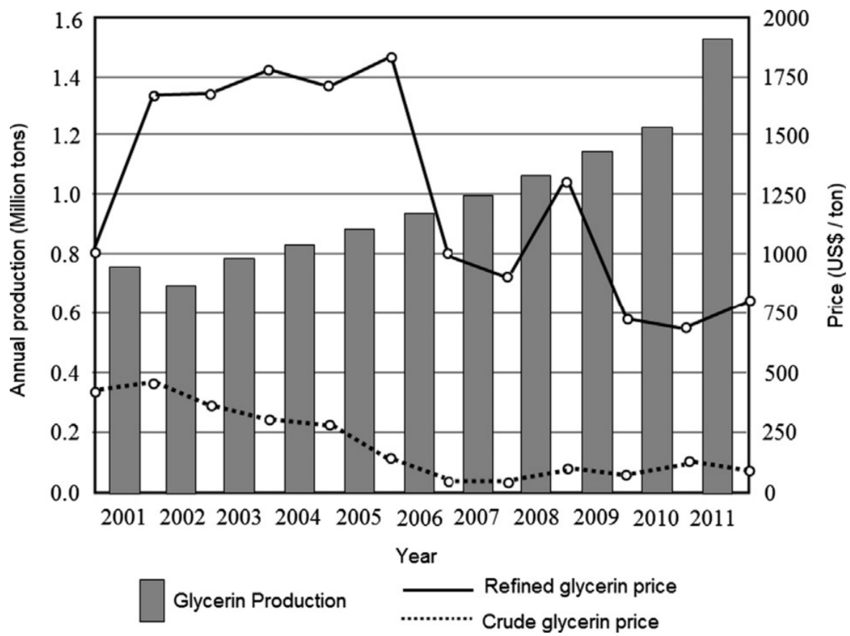


Fig. 3. Projection of global glycerol production and prices.

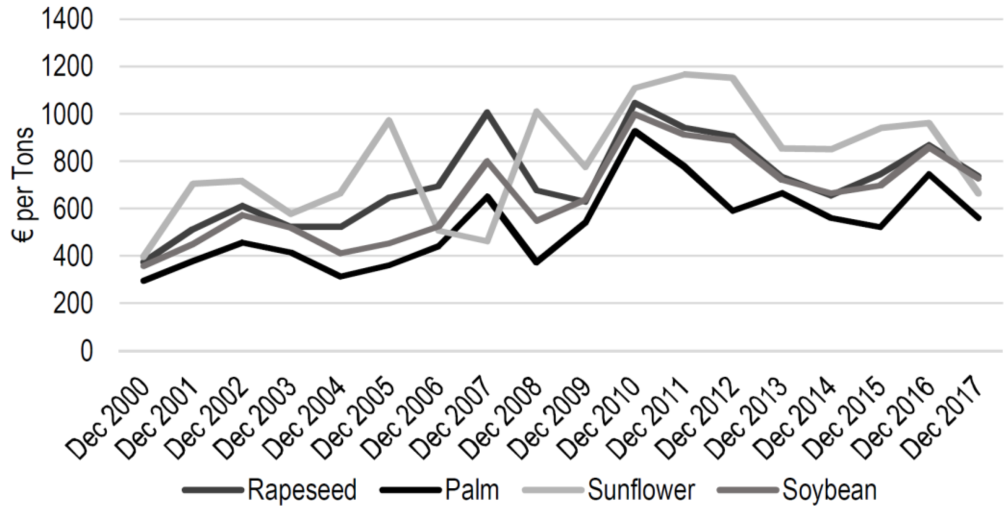
Quispe, C. A. G., Coronado, C. J. R., & Carvalho Jr., J. A. (2013). Glycerol: Production, consumption, prices, characterization and new trends in combustion. Renewable and Sustainable Energy Reviews, 27, 475–493. doi:10.1016/j.rser.2013.06.017

Processes – Esterification/Transesterification

ALLOCATION – ECONOMIC BASIS

Year?? Which market?? Reference monetary unit…**Bitcoin**….US$…..€???

REVISITING THE PALM OIL BOOM IN EUROPE AS A SOURCE OF RENEWABLE ENERGY: EVIDENCE FROM TIME SERIES ANALYSIS
Bentivoglio, Deborah; Bucci, Giorgia; Finco, Adele.
Calitatea, suppl. Quality-Access to Success: Acces la Success; Bucharest Vol. 19, Iss. S1, (Mar 2018): 59-66.



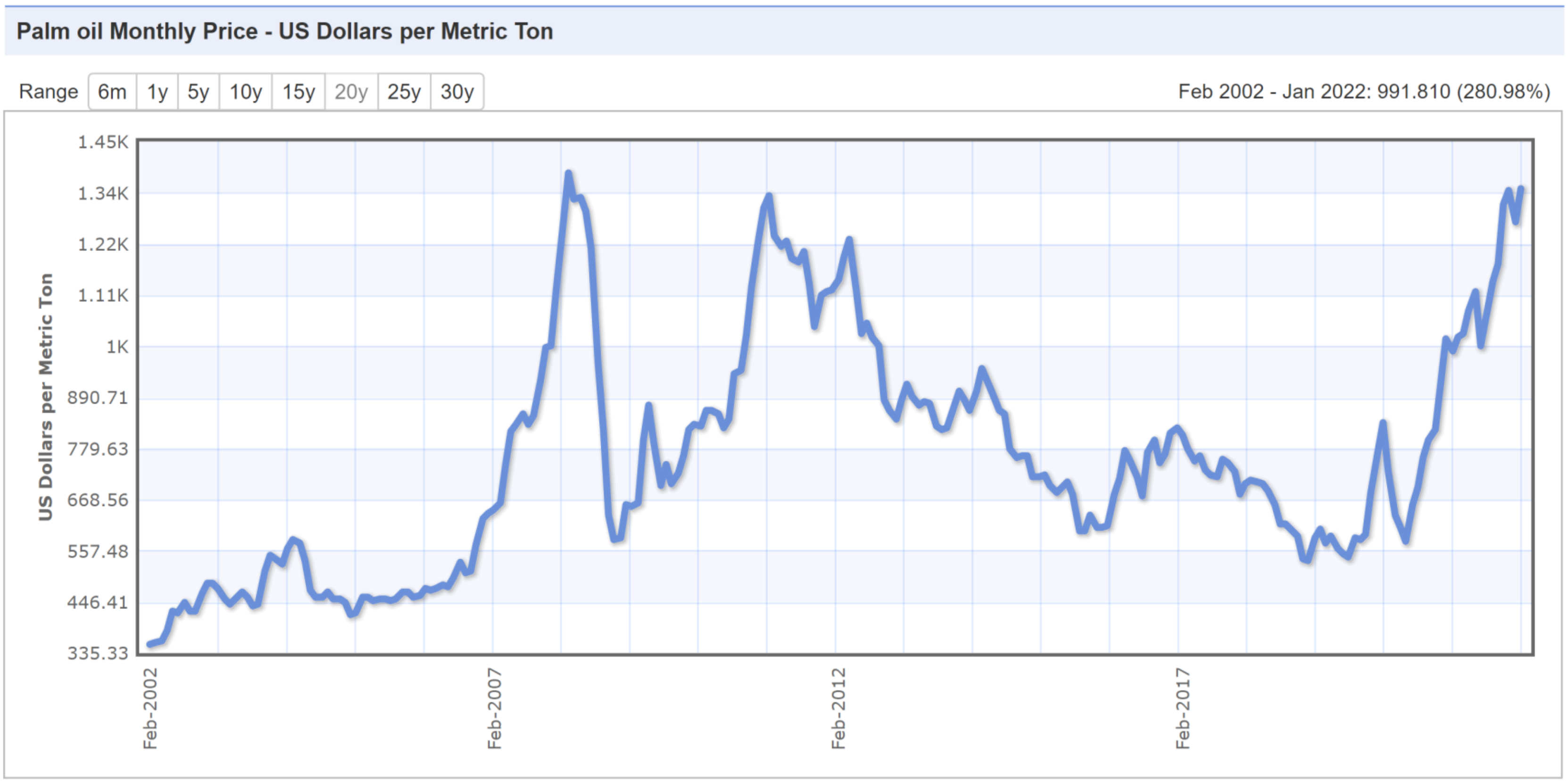
(Source: Index Mundi, 2017)

Figure 6. Vegetable oils prices from 2000 to 2017

Processes – Esterification/Transesterification

ALLOCATION – ECONOMIC BASIS

Year?? Which market?? Reference monetary unit…**Bitcoin**….US$…..€???



Description: Palm oil (Malaysia), 5% bulk, c.i.f. N. W. Europe

Processes – Esterification/Transesterification

ALLOCATION – ECONOMIC BASIS

BIODIESEL

2002 359 US$/ton

e.g 2002

2007 661 US$/ton

$$\frac{359\ US\$/ton * ton\ biodiesel}{359 \frac{US\$}{ton} * ton\ biodiesel + 450 \frac{US\$}{ton} * ton\ glycerol}$$

index mundi

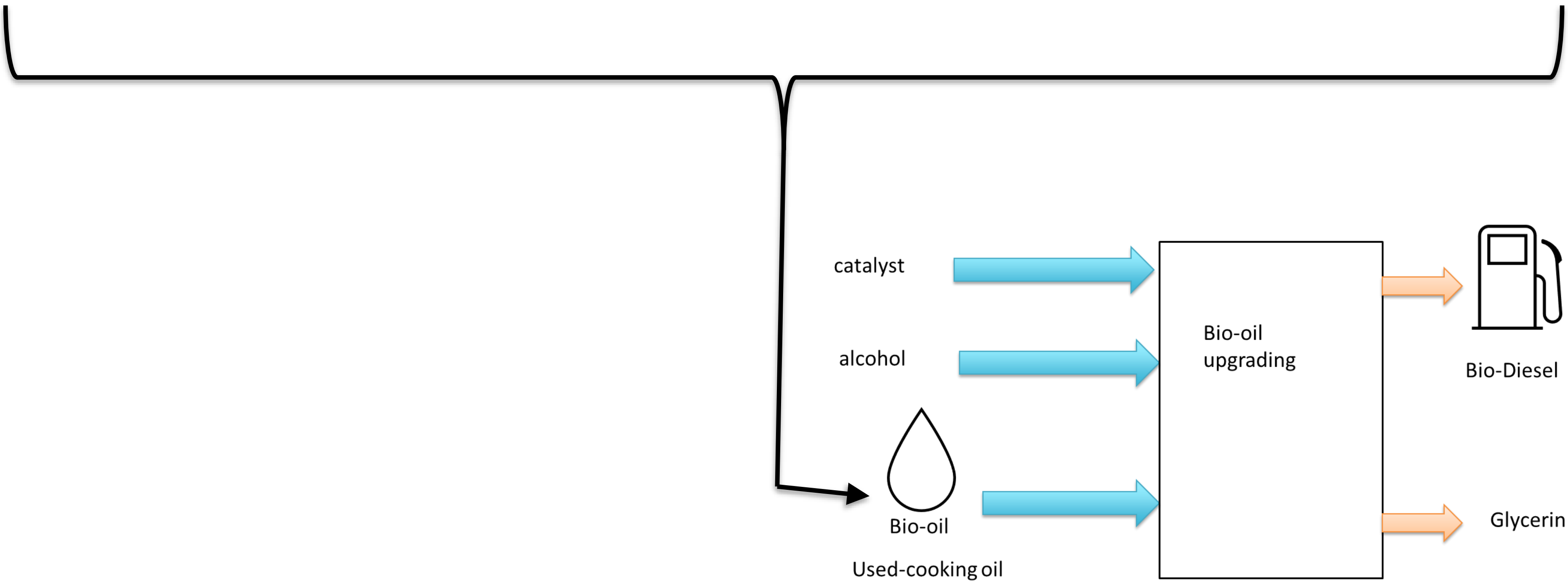
$$\frac{450\ US\$/ton * ton\ glycerol}{359 \frac{US\$}{ton} * ton\ biodiesel + 450 \frac{US\$}{ton} * ton\ glycerol}$$

Oil upgrading …continuation…..

Waste Vegetable Oils

Rendered beef tallow

Rendered poultry fat



Oil upgrading …continuation…..

INVENTORY #1

Table A.1
Inventory data for the production of rendered beef tallow (1015 kg).

Inputs		Outputs	
Materials		*Products*	
Cattle by-products	3.60 t	Rendered beef tallow	1015.36 kg
Energy		Meat and bone meal	820.95 kg
Thermal energy	7631.71 MJ	*Emissions to treatment*	
Electric energy	295.10 kWh	Cooking vapours	1765.80 kg
Transport by lorry			
To rendering plant	561.21 t km		

Oil upgrading …continuation…..

INVENTORY #2

Int J Life Cycle Assess (2017) 22:1837–1850
DOI 10.1007/s11367-017-1396-6

BEEF TALLOW BIODIESEL PRODUCTION

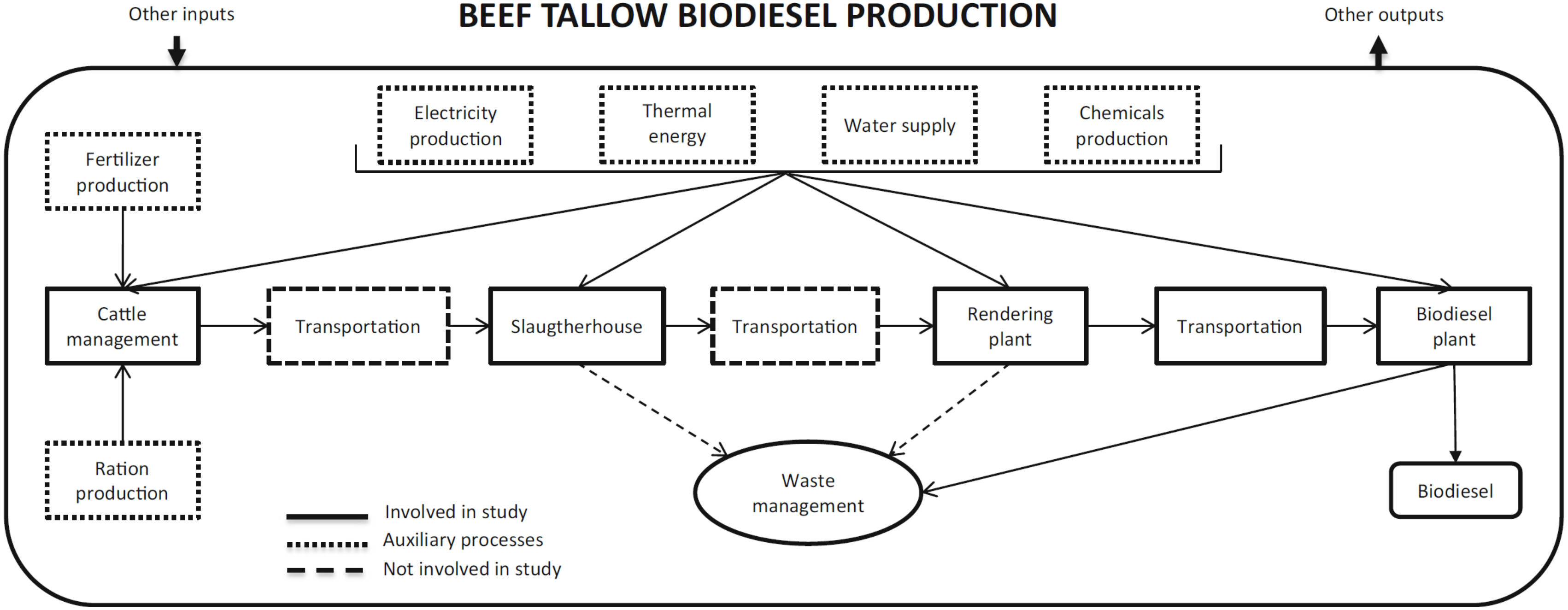


Fig. 1 General beef tallow biodiesel production flowchart

Oil upgrading …continuation…..

Int J Life Cycle Assess (2017) 22:1837–1850 DOI 10.1007/s11367-017-1396-6

INVENTORY #2

	Unit	Quantity	Origin	Source
Cattle management, slaughter, and rendering plant (tallow production)				
Inputs				
Agricultural implement	h	1.02×10^{-3}	Literature	Jacinto 2001*
Animal feed	kg	0.495	Literature	Corrêa et al. 2000*
Area	ha	5.64×10^{-4}	Estimated	–
Calcium phosphate	kg	1.9×10^{-2}	Literature	Ortolani 1999*
Carbon dioxide	kg	0.194	Estimated	–
Electricity	kWh	4.79×10^{-3}	Literature	Kägi and Nemecek 2007
Nitrogen/Potassium fertilizer	kg	6.76×10^{-3}	Literature	ANDA 2008*
Sodium chloride	kg	1.71×10^{-2}	Literature	Ortolani 1999*
Thermal energy	MJ	0.196	Literature	Kägi and Nemecek 2007
Triple superphosphate fertilizer	kg	6.76×10^{-3}	Literature	Cederberg et al. 2009*
Water	m^3	7.21×10^{-5}	Literature	Pacheco 2006*
Outputs				
Ammonia	kg	1.95×10^{-2}	Literature/calculated	Cadisch et al. 1994, Pacheco 2006*, Cederberg et al. 2009*
Beef tallow	kg	2.66×10^{-2}	–	–
Boneless meat	kg	0.147	Literature/calculated	Pacheco 2006*
Manure	kg	0.495	Estimated	–
Methane	kg	0.147	Literature/calculated	Brasil 2007*, Cederberg et al. 2009*
Nitrous oxide	kg	3.33×10^{-3}	Literature/calculated	Cederberg et al. 2009*
Oil and grease	kg	3.03×10^{-5}	Literature/calculated	Pacheco 2006*
Residues (entrails, leather and condemned parts)	kg	0.206	Literature/calculated	Pacheco 2006*
Water	m^3	7.21×10^{-5}	Literature	Pacheco 2006*

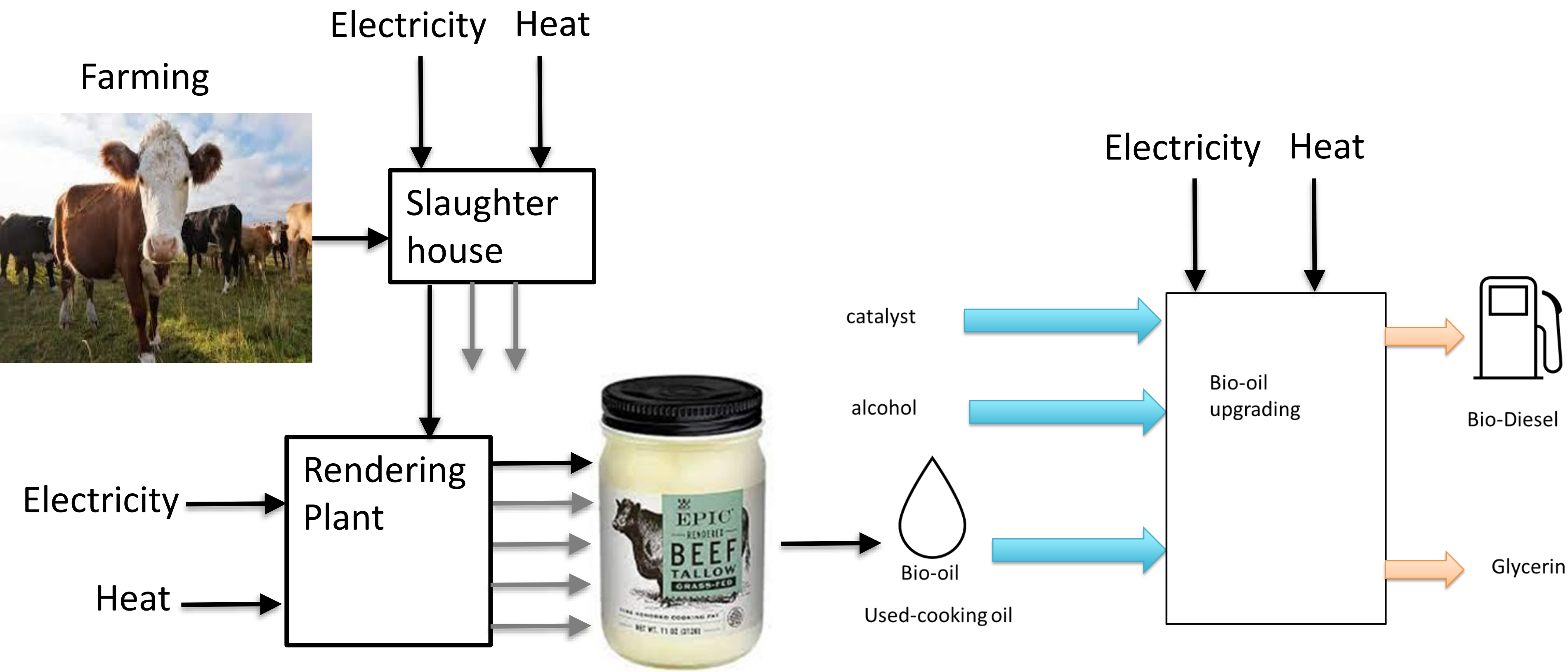
Oil upgrading …continuation…..

Table A.2
Inventory data for the production of rendered poultry fat (1013 kg).

Inputs		Outputs	
Materials		*Products*	
Poultry by-products	4.80 t	Rendered poultry fat	1013.00 kg
Energy		Poultry meal	911.00 kg
Thermal energy	7996.14 MJ	*Emissions to treatment*	
Electric energy	309.19 kWh	Cooking vapours	2877.00 kg
Transport by lorry			
To rendering plant	748.00 t km		

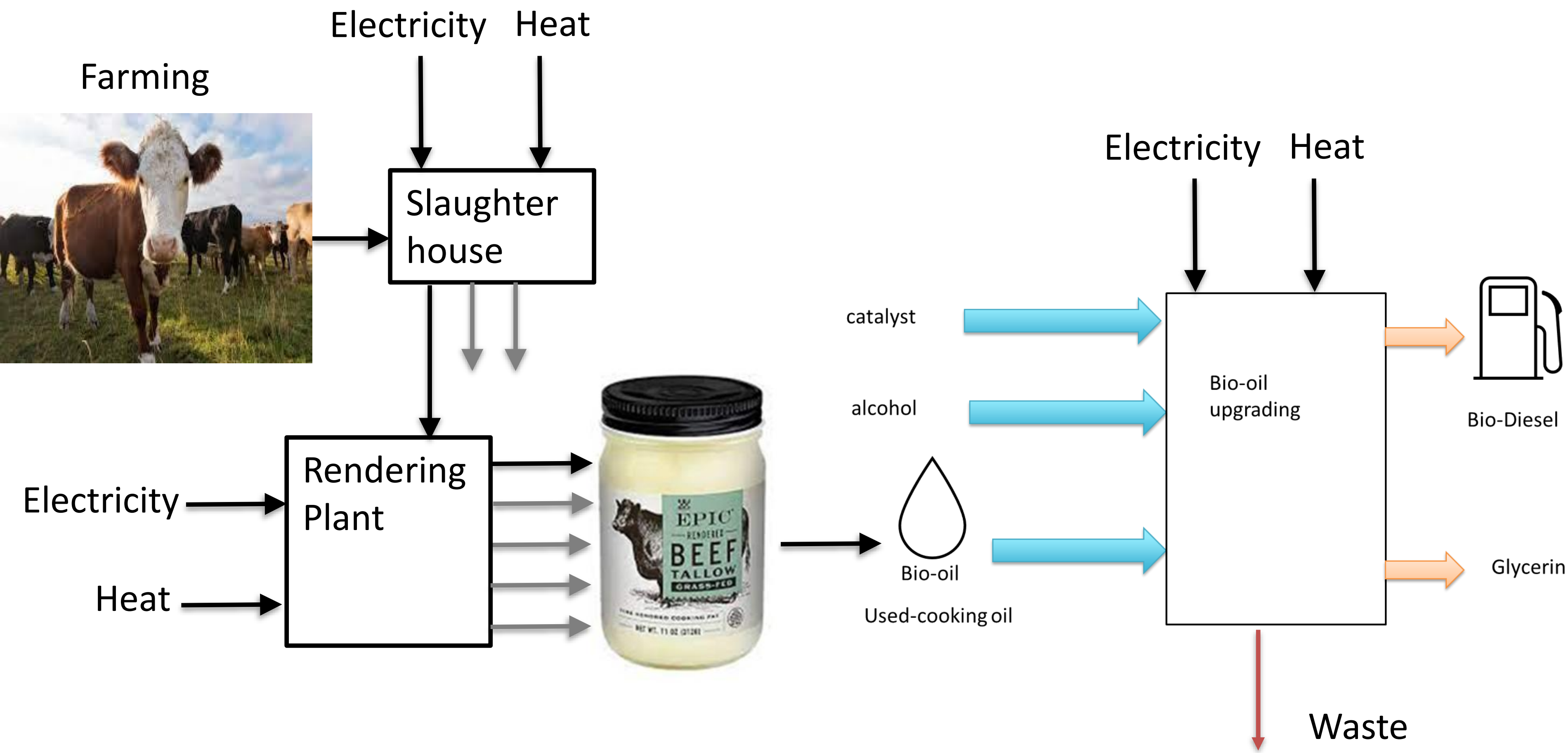
Oil upgrading ...continuation.....

Boundary enlargement....



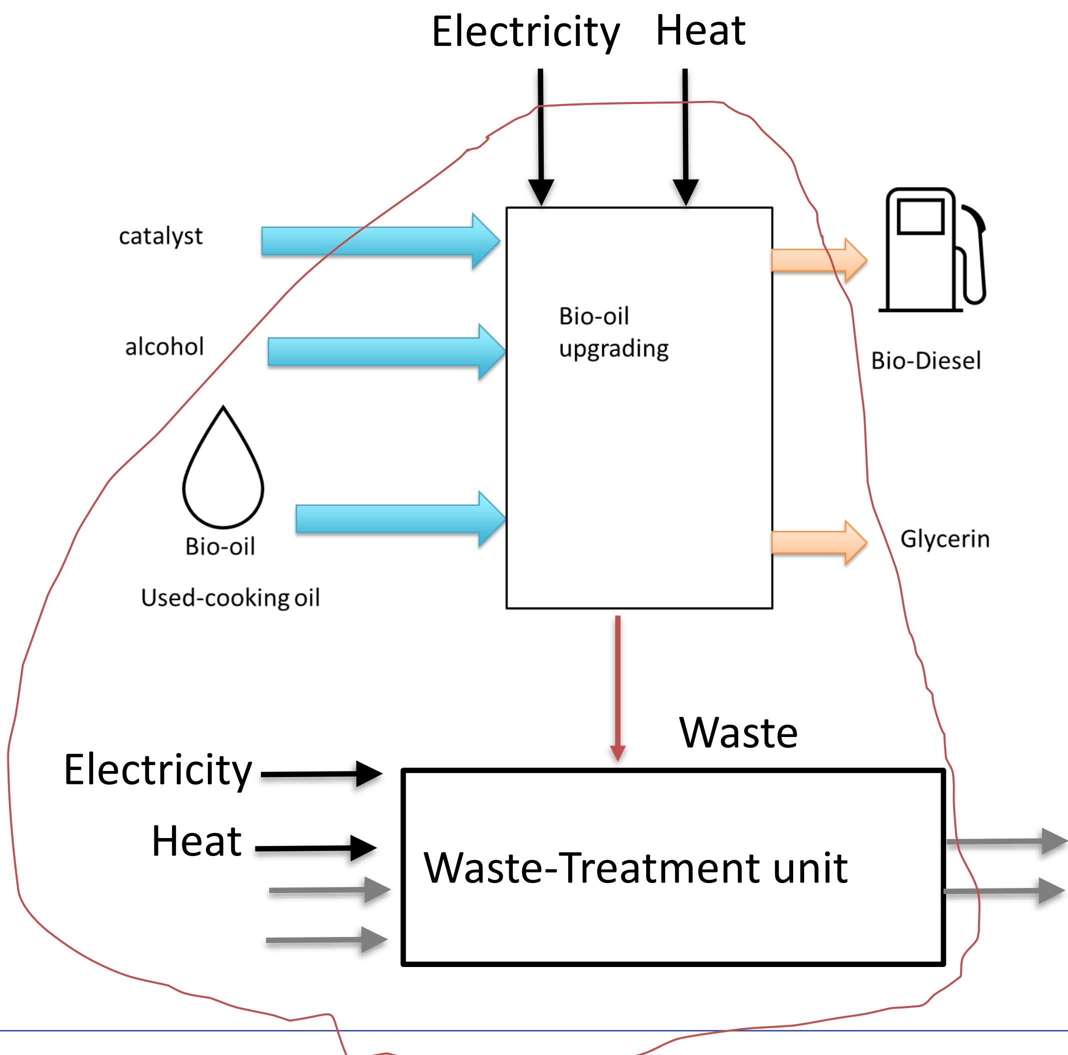
Oil upgrading …continuation…..

Boundary enlargement….



Oil upgrading ...continuation.....

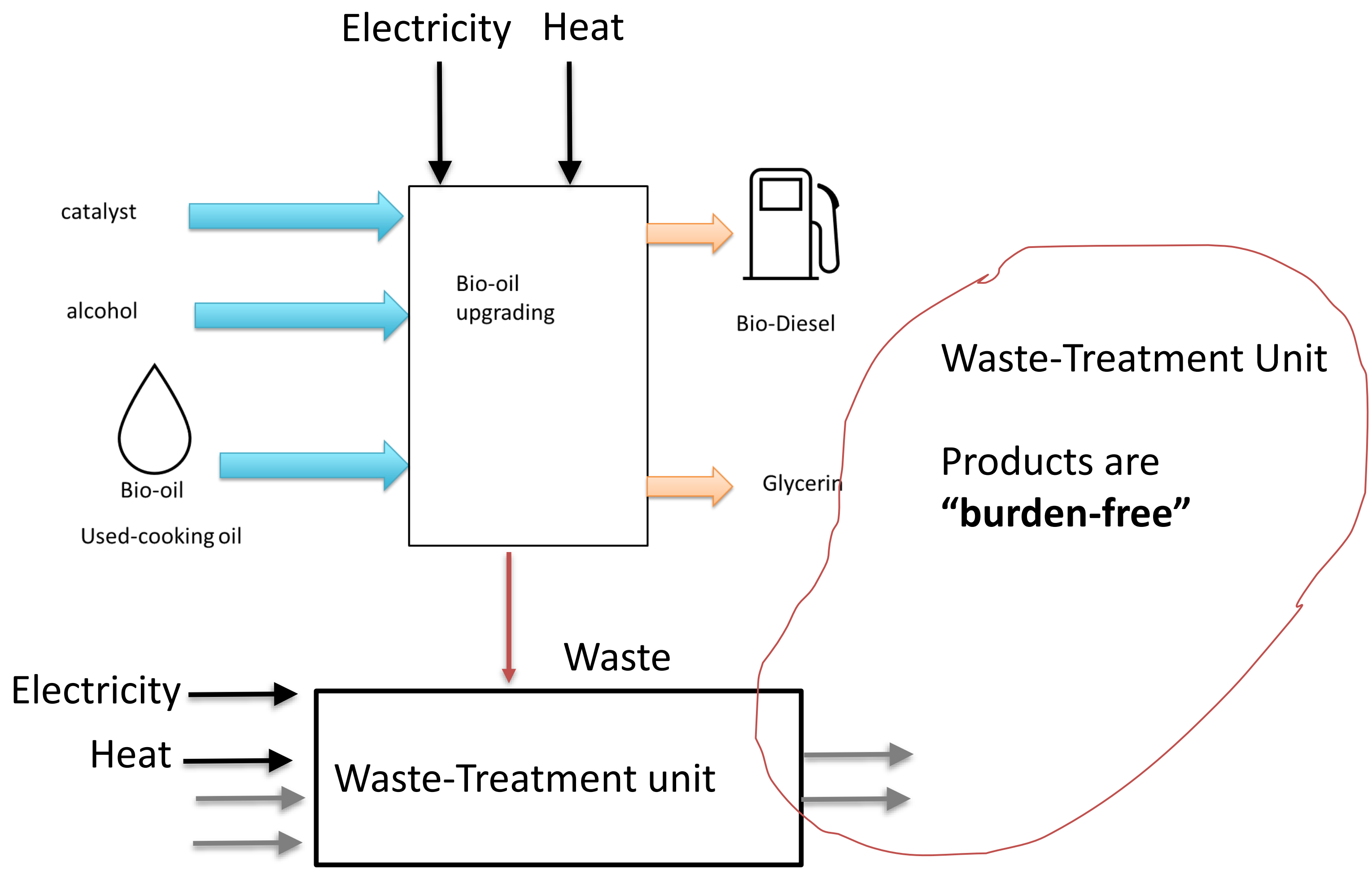
Boundary enlargement....



Bio-oil upgrading **responsible** for GHG emissions for the Waste-Treatment Unit

Oil upgrading ...continuation.....

Boundary enlargement....

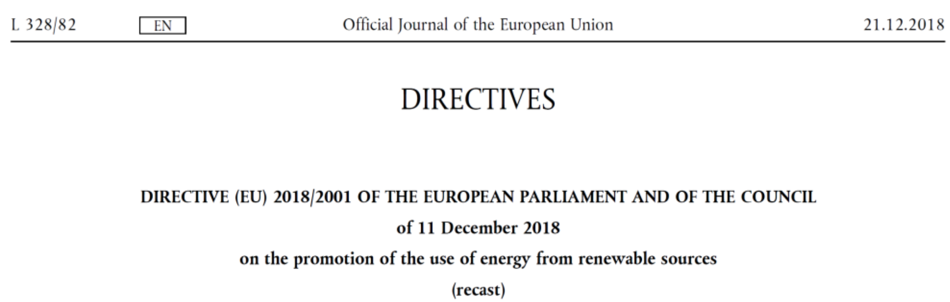


How to treat wastes IN TERMS OF CARBOON FOOTPRINT?????….

Waste Vegetable Oils

"Wastes and residues, including tree tops and branches, straw, husks, cobs and nut shells, and residues from processing, including crude glycerine (glycerine that is not refined) and bagasse, shall be considered to have **zero life-cycle greenhouse gas emissions** up to the process of collection of those materials irrespectively of whether they are processed to interim products before being transformed into the final product."

RED II


L 328/82 EN Official Journal of the European Union 21.12.2018

DIRECTIVES

DIRECTIVE (EU) 2018/2001 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL
of 11 December 2018
on the promotion of the use of energy from renewable sources
(recast)

Sustainability Criteria RED II

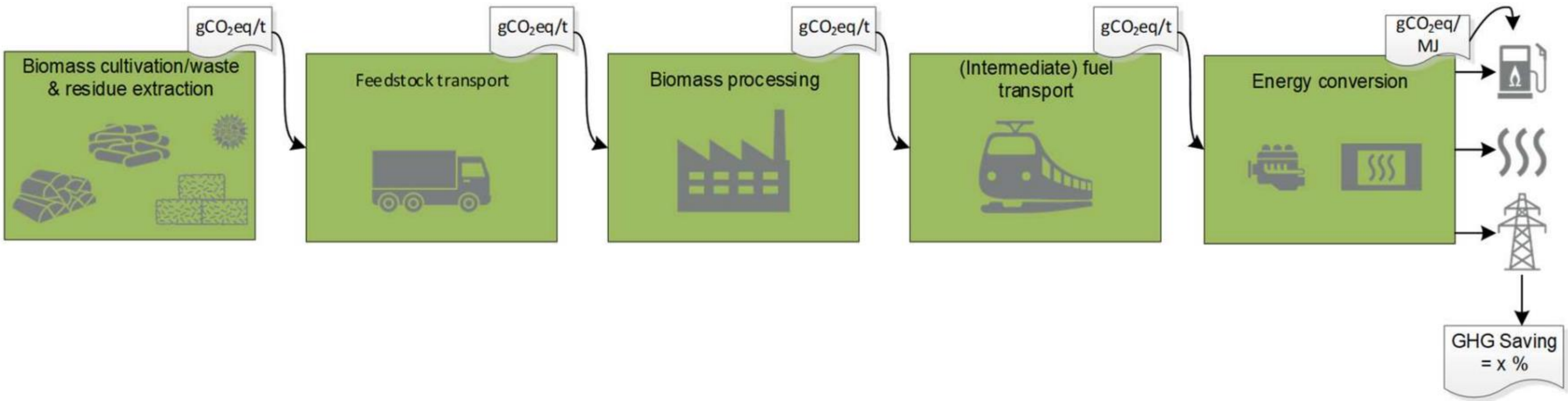


Figure 4: Exemplary bioenergy value chain with the flow of sustainability information by means of the GHG intensity.

RED II

potential for delivering **substantial greenhouse gas emissions savings compared to fossil fuels based on a life- cycle assessment of emissions**;

the fossil fuel comparator shall be 94 g CO_2eq/MJ for road vehicles

Sustainability Criteria RED II

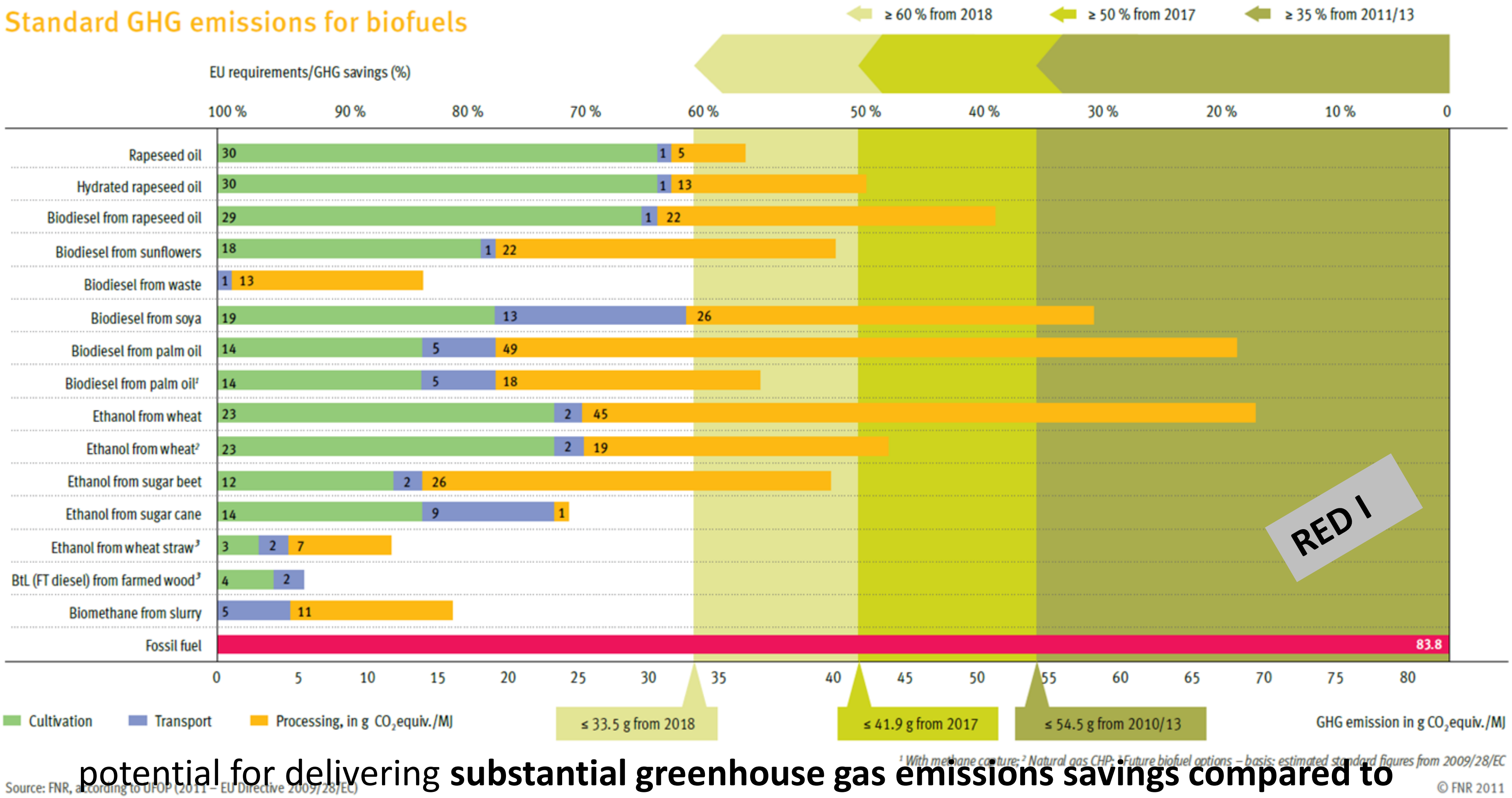
issions saving criteria	29(10)	The GHG emission savings from the use of biofuels, bioliquids and biomass fuels shall be: a) Consumption in the transport sector (biofuels, biogas/biomethane, bioliquids): - at least **50%** for installations in operation on or before 2015-10-05 - at least **60%** for installations starting operation between 2015-10-05 and 2020-12-31 - at least **65%** for installations starting operation from 2021-01-01

RED II

potential for delivering **substantial greenhouse gas emissions savings compared to fossil fuels based on a life- cycle assessment of emissions**;

the fossil fuel comparator EF(t) shall be 94 g CO2eq/MJ.

Sustainability Criteria RED II



potential for delivering **substantial greenhouse gas emissions savings compared to fossil fuels based on a life- cycle assessment of emissions**;

the fossil fuel comparator EF(t) shall be 83.8 g CO2eq/MJ no LUC

Oil upgrading …continuation…..

Land intensive – food competing

1st generation (1G)

e.g. palm oil
Rapeseed
Sunflower
Soybean

Wastes/ Lignocellulose

Not land intensive

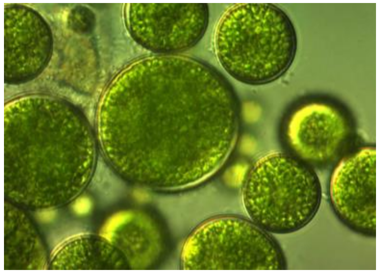
2nd gen. (2G)

e.g. tallow
Rendered fat
Industrial, household and agriculture wastes

Algae/marine

Not land intensive

3rd gen. (3G)



e.g. autotrophic, heterotrophic microalgae

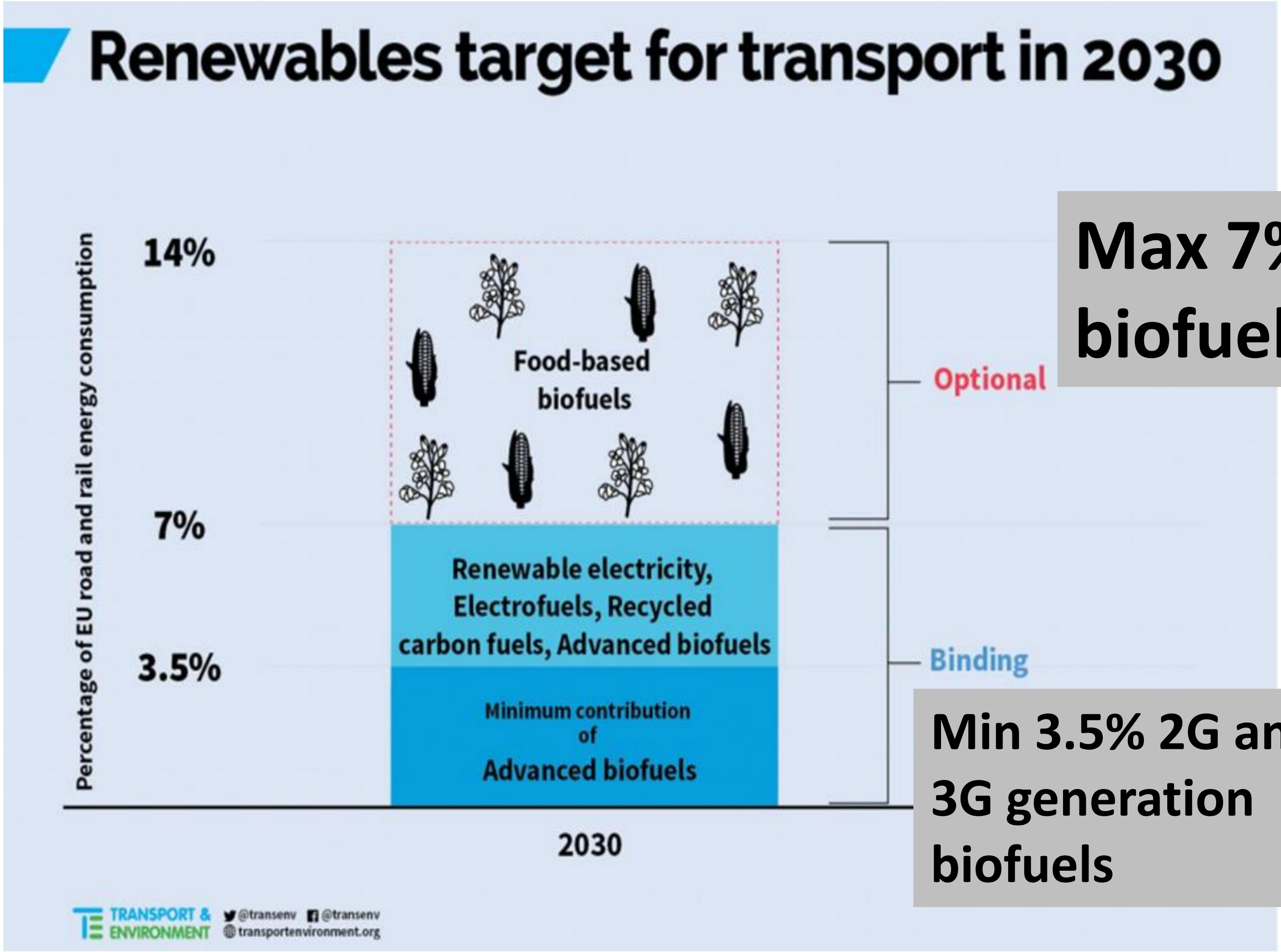
Genetic modified biomass

Not land intensive

4rd gen (4G)

e.g. genetic enhanced microalgae for oil production

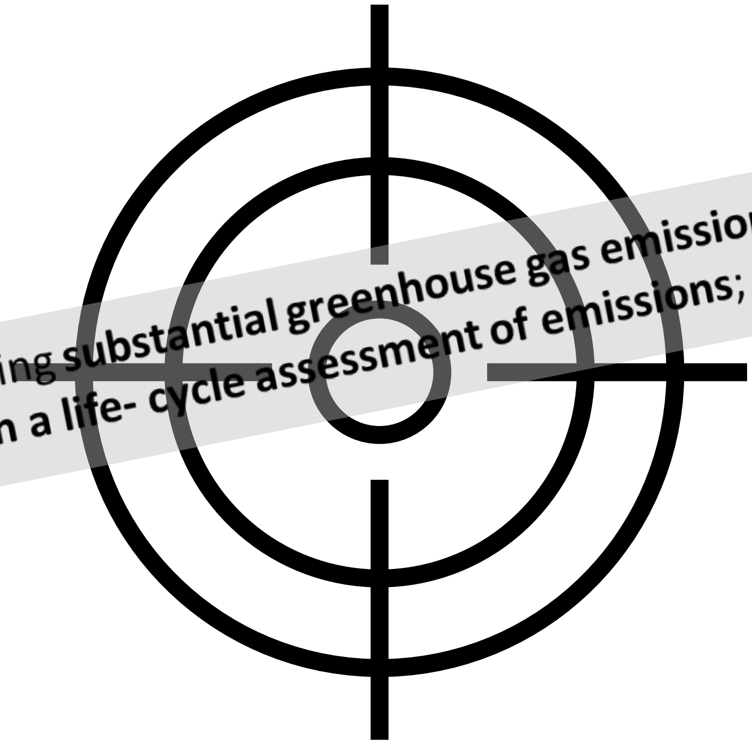
Oil upgrading ...continuation.....



Max 7% 1G biofuels

Min 3.5% 2G and 3G generation biofuels

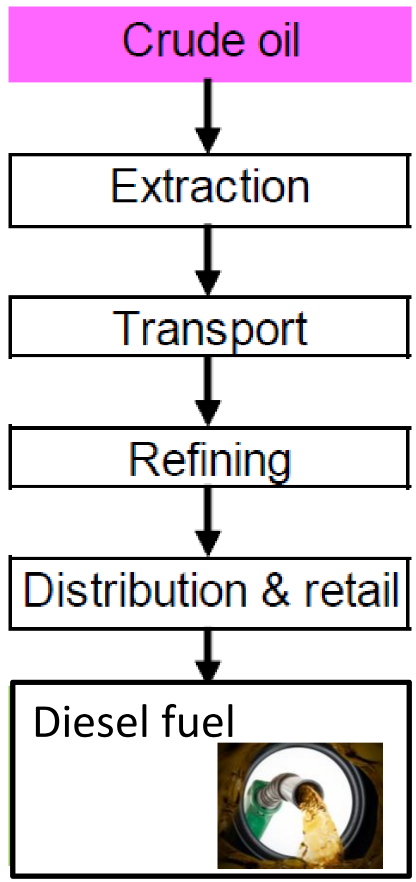
Oil upgrading …continuation…..



potential for delivering **substantial greenhouse gas emissions savings compared to fossil fuels based on a life- cycle assessment of emissions;**

Fossil Fuel Comparator of Biodiesel?

Fossil Fuel Comparator of Biodiesel?



Refinery scheme

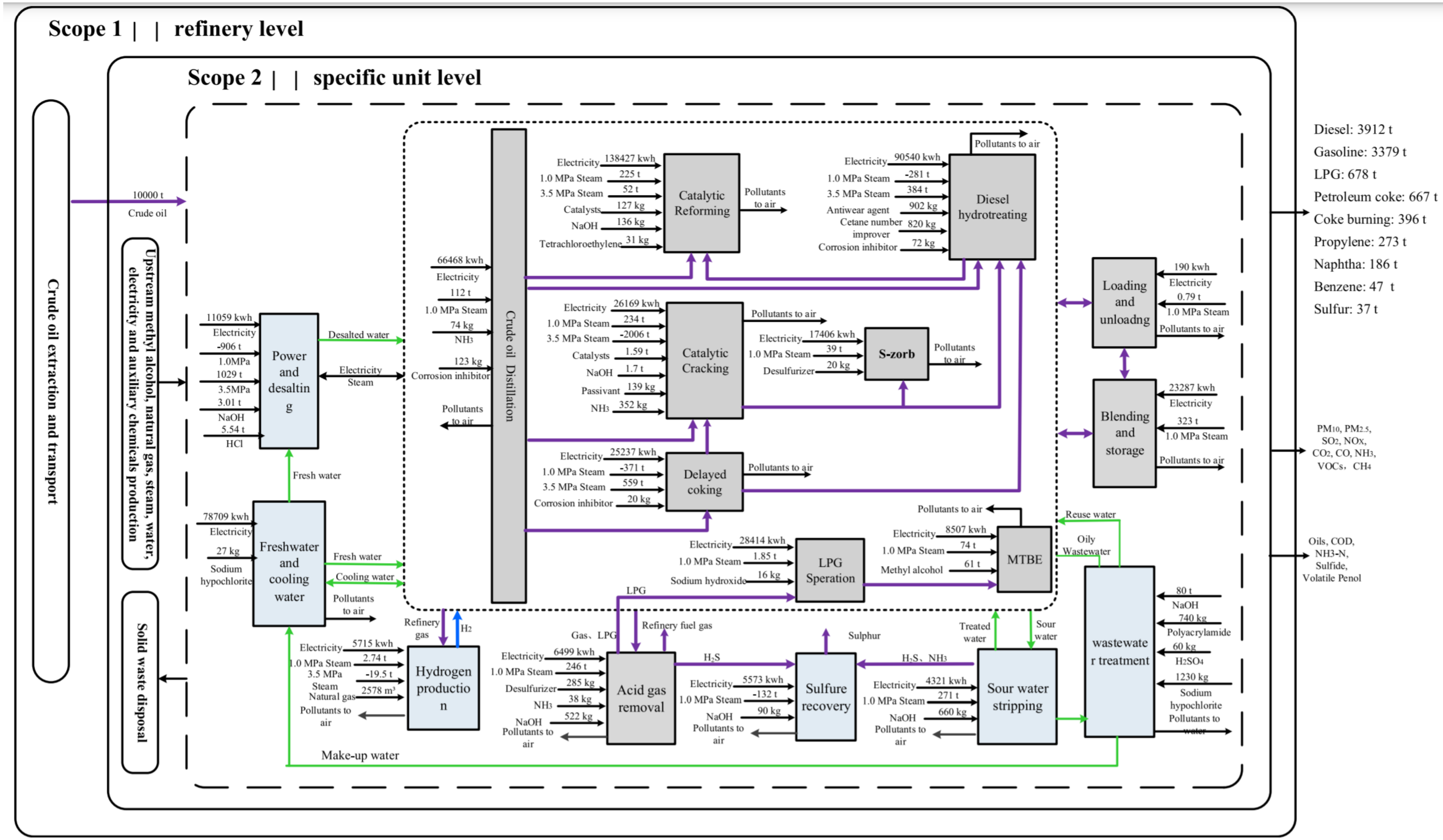


Fig. 1. System boundary of petroleum products production.

Refinery inventory

10000 tons of crude oil

- Diesel: 3912 t
- Gasoline: 3379 t
- LPG: 678 t
- Petroleum coke: 667 t
- Coke burning: 396 t
- Propylene: 273 t
- Naphtha: 186 t
- Benzene: 47 t
- Sulfur: 37 t

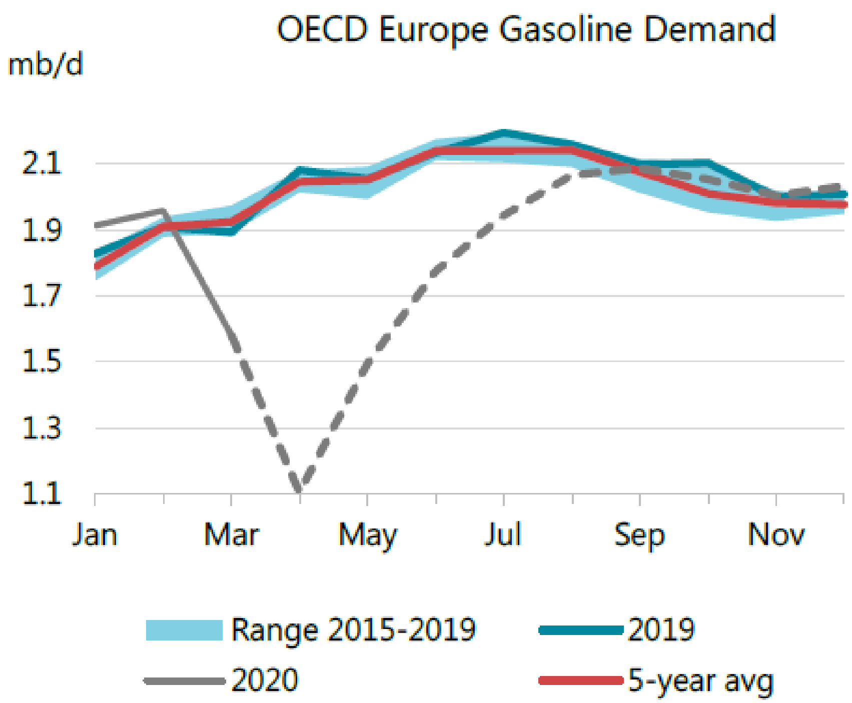
154.17 ton steam

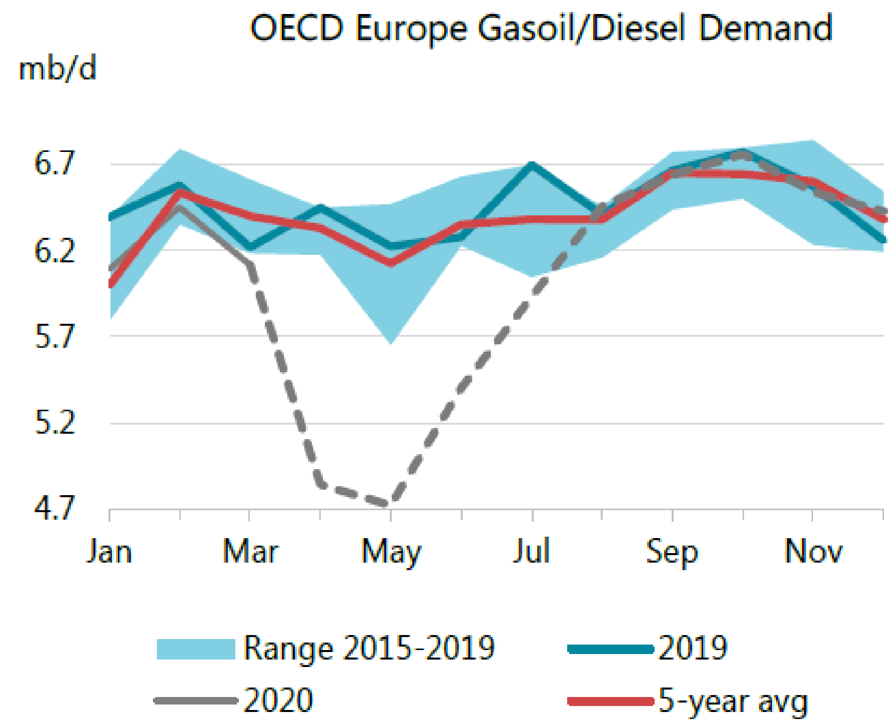
Table 1
Life cycle inventory of the whole refinery (values were presented per function unit).

Category	Substance	Unit	Amount
Material	Crude oil	t	10000
	Methyl alcohol	t	44.41
	Natural gas	t	1.86
	Water	t	7427.28
	NaOH	t	6.43
	HCl	t	5.92
	Catalyst	t	5.32
	Sodium hypochlorite	t	1.23
	Polyacrylamide	t	0.74
	Liquid ammonia	t	0.46
	Corrosion inhibitor	t	0.22
	Others	t	2.20
Energy	Electricity	kwh	565007.51
	Steam	t	−154.17
Emissions to air	$PM_{2.5}$	t	0.16
	PM_{10}	t	0.17
	SO_2	t	0.71
	NO_X	t	1.54
	VOCs	t	3.21
	CO	t	7.22
	CO_2	t	453.21
	NH_3	kg	4.32
	nickel	kg	31.18
Emissions to water	Wastewater	t	2961.00
	Oils	kg	1.63
	COD	kg	118
	Total phosphorus	kg	9.34
	Total nitrogen	kg	20.91
	sulfide	kg	0.08
	Cyanide	kg	0.06
	Nickel	kg	0.30
	Arsenic	kg	0.01
	Methylbenzene	kg	0.17
	Ethylbenzene	kg	0.08
	Xylene	kg	0.54
	Benzene	kg	0.18
Solid waste	Dead catalysts	t	5.94
	Refinery sludge	t	2.56

Refinery inventory

Europe demand of crude oil





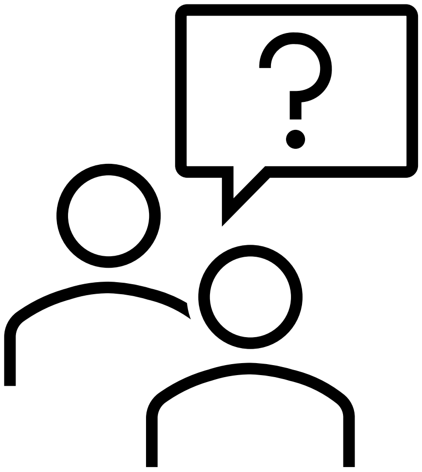
Source: IEA Monthly Oil Market Rerport

Challenge #3

a) **Consider the origin of the biomass from oil upgrading processes of challenge #2. Enlarge the boundary of your analysis and compute new values of biodiesel and glycerin carbon footprint for beef tallow and poultry fat.**

b) **Consider Energy allocation. Compute diesel fossil fuel comparator carbon footprint from the refinery inventory provided.**

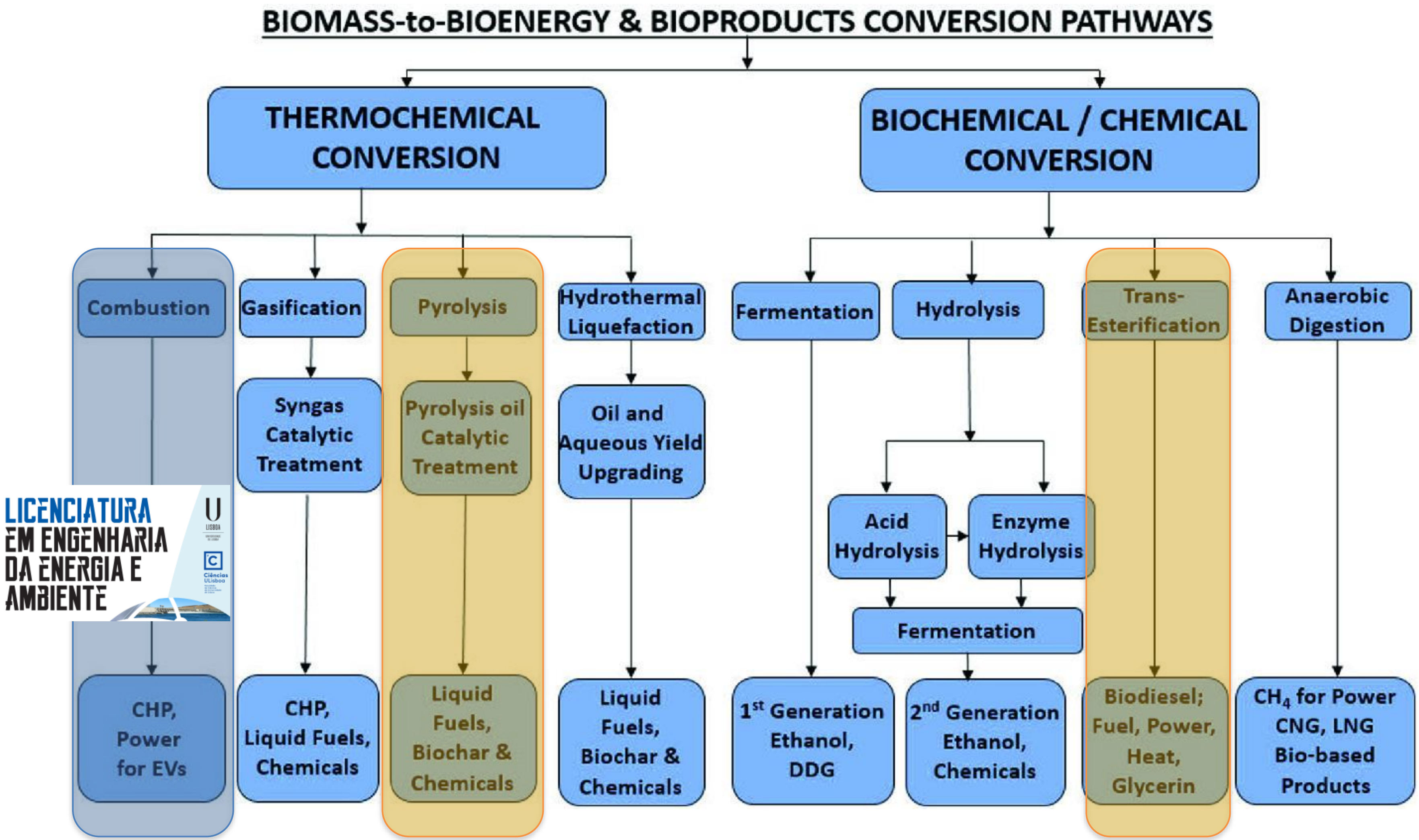
c) **Compare biodiesel with diesel fossil carbon footprint and estimate the GHG savings, absolute and relative of using, in Europe 6mb/d for a year. Justify the boundary used.**



Deadline: 20 April

Delivery: pdf by e-mail camsilva@fc.ul.pt

Processes – Conversion Technologies



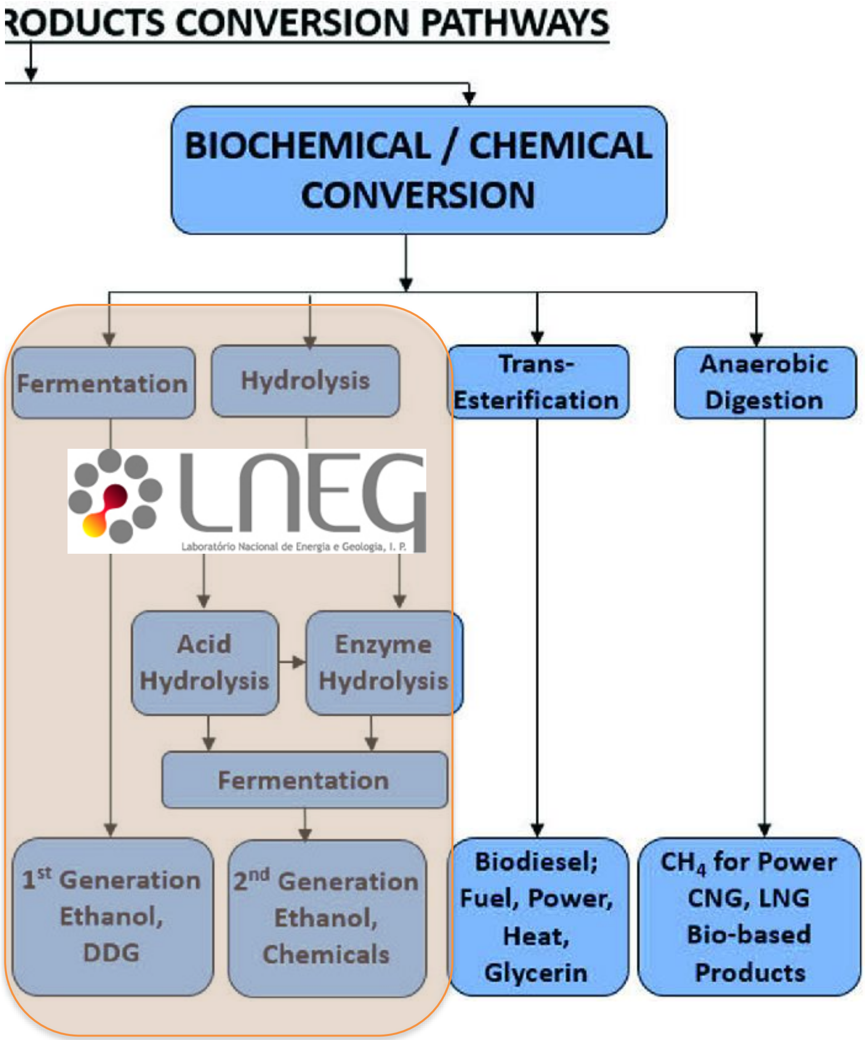
Processes – Biochemical conversion

Day 6 April: Biorrefinarias com processos de fermentação.

Easter holydays 13 - 19 April

Day 20 April: Visita de estudo projeto GREENFUEL edificio F LNEG.

Day 27 April: Exercises and Challenge biochemical pathway



Thanks

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