Sustainability Assessment of Biorefinery Systems

Conference: Biorefining from raw material to high value products
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Copernicus Institute of Sustainable development

Biorefinery

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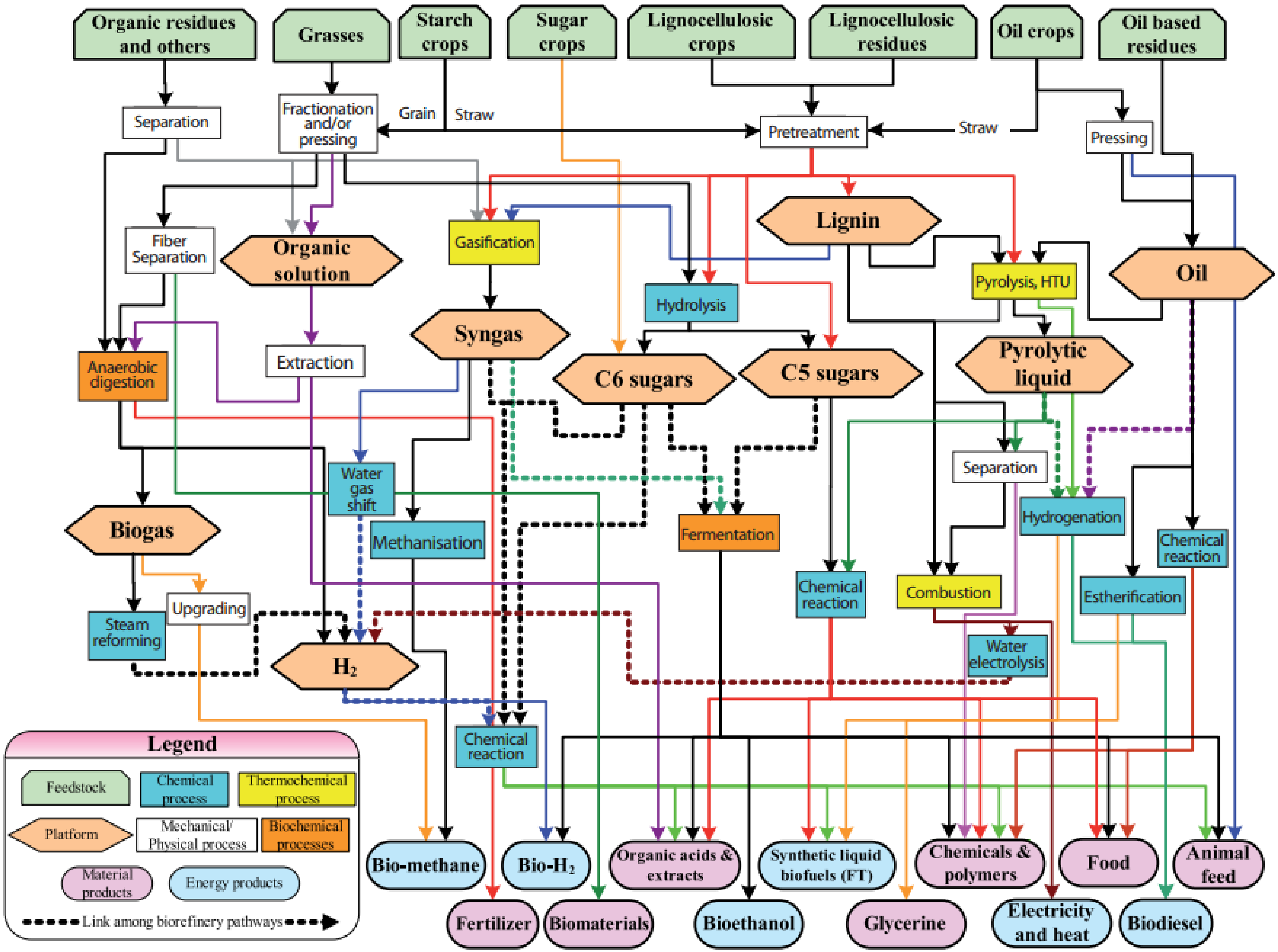
Definition (one among many others):

– A biorefinery is a facility (or a network of facilities) that integrates biomass conversion technologies to produce fuels, chemicals, polymers, pharmaceuticals, food and/or feed.

Biomass[1,2]	Conversion Technologies	Products
cellulose: 10-95% (av.: 43%) hemicellulose: 5-65% (av.: 20%) lignin: 5-40% (av.: 27%)	Thermochemical: gasification, pyrolysis, combustion, liquefaction, Chemical: hydrolysis, esterification, WGS Biochemical: fermentative, enzymatic	platform chem. building blocks secondary chem. intermediates consumer prod. heat/electricity

1. Menon, & Rao. Progress in Energy and Combustion Science 38 (2012) 522-550 ; 2. Cherubini & Strømman, Biofuels, Ch.1. Principles of biorefining,



Adapted from 2. Cherubini & Strømman, Biofuels, Ch.1. Principles of biorefining,

Biorefinery Systems

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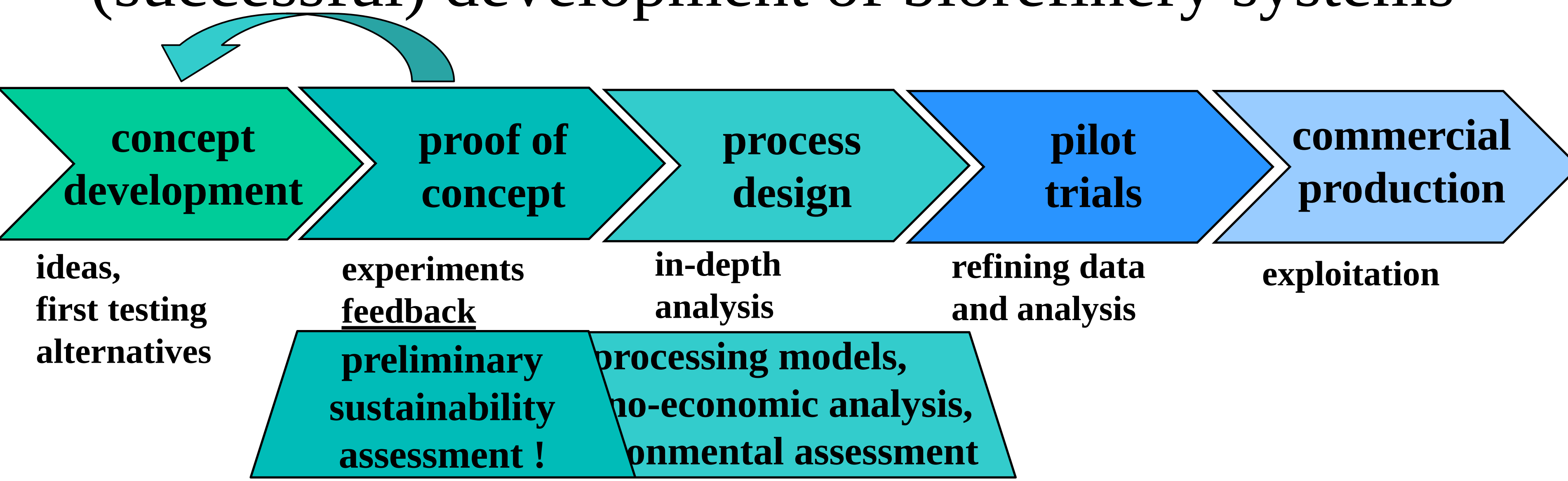
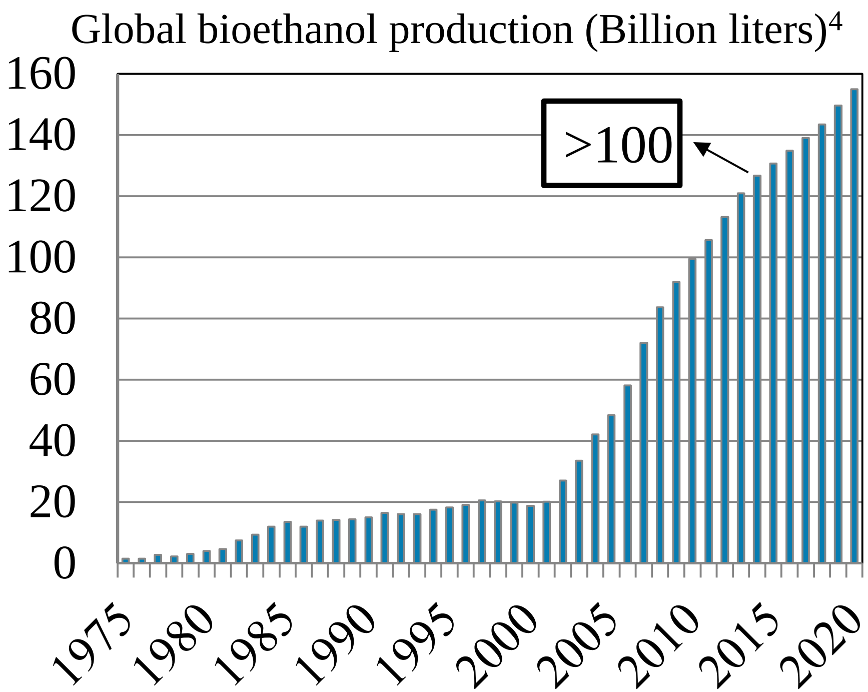
- There is a wide variety of raw materials, conversion routes, technologies and end products/configurations.
  - What are the best raw materials, conversion routes, technologies for an specific product (configuration)?

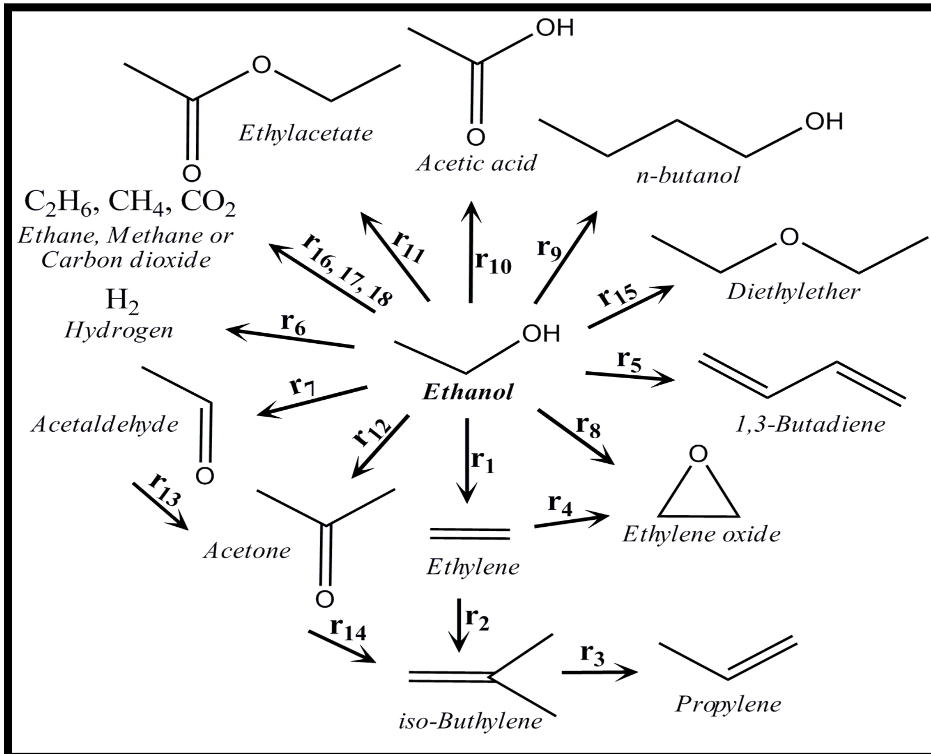
- (successful) development of biorefinery systems



Early Stage Analysis

- case study: derivatives of bioethanol[3]



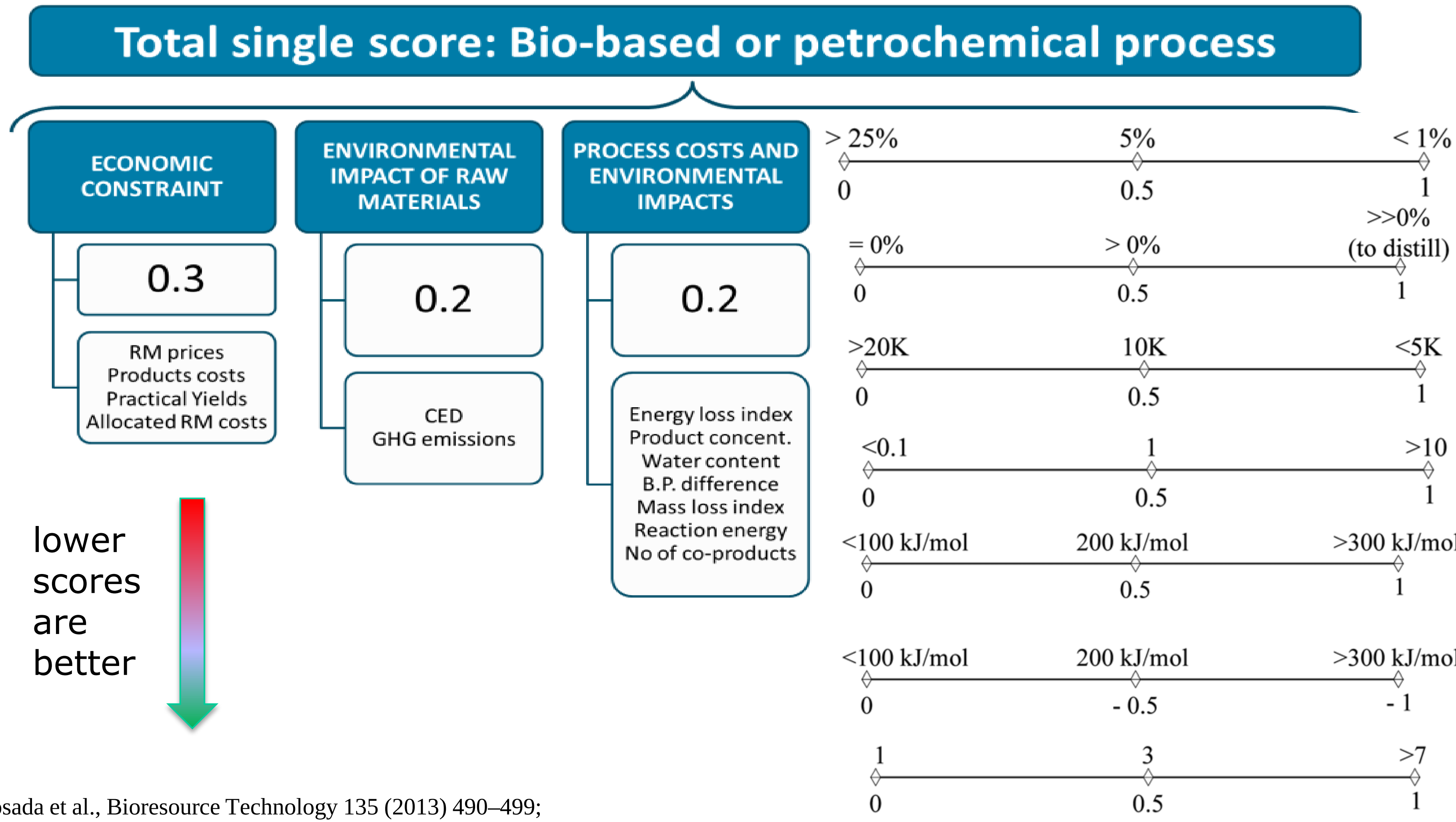


Goals:
- Identify those bioethanol derivatives that offer largest benefits in sustainability terms.
- Explore whether the applied methodology is applicable to screen the conversion steps that are particularly attractive for future biorefinery systems.

3. Posada et al., Bioresource Technology 135 (2013) 490–499.; 4. OECD-FAO, Agricultural Outlook 2011-2020. <http://stats.oecd.org/Index.aspx>

Early Stage Analysis

- <u>case study</u>: derivatives of bioethanol[3,4,5]



3. Posada et al., Bioresource Technology 135 (2013) 490–499;
4. Patel et al.., Energy Environ. Sci., 2012, 5 (9), 8430–8444 ;
5. Sugityama et al., AIChE Journal. 54 (2008) 1037-1053

Early Stage Analysis

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- case study: derivatives of bioethanol[3,4,5]

Total single score: Bio-based or petrochemical process

ECONOMIC CONSTRAINT
0.3

RM prices
Products costs
Practical Yields
Allocated RM costs

ENVIRONMENTAL IMPACT OF RAW MATERIALS
0.2

CED
GHG emissions

PROCESS COSTS AND ENVIRONMENTAL IMPACTS
0.2

Energy loss index
Product concent.
Water content
B.P. difference
Mass loss index
Reaction energy
No of co-products

ENVIRONMENTAL-HEALTH-SAFETY INDEX
0.2

Environmental:
- Persistency
- Air hazard
- Water hazard
- Solid waste

Health
- Irritation
- Chronic toxicity

Safety
- Mobility
- Fire/Explosion
- Reactivity
- Acute toxicity

RISKS ASPECTS
0.1

Global feedstock availability
Local feedstock potential
Market size
Infrastructure compatibility
Inherent benefits

lower scores are better

3. Posada et al., Bioresource Technology 135 (2013) 490–499;
4. Patel et al.., Energy Environ. Sci., 2012, 5 (9), 8430–8444 ;
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- case study: derivatives of bioethanol[3,4,5].

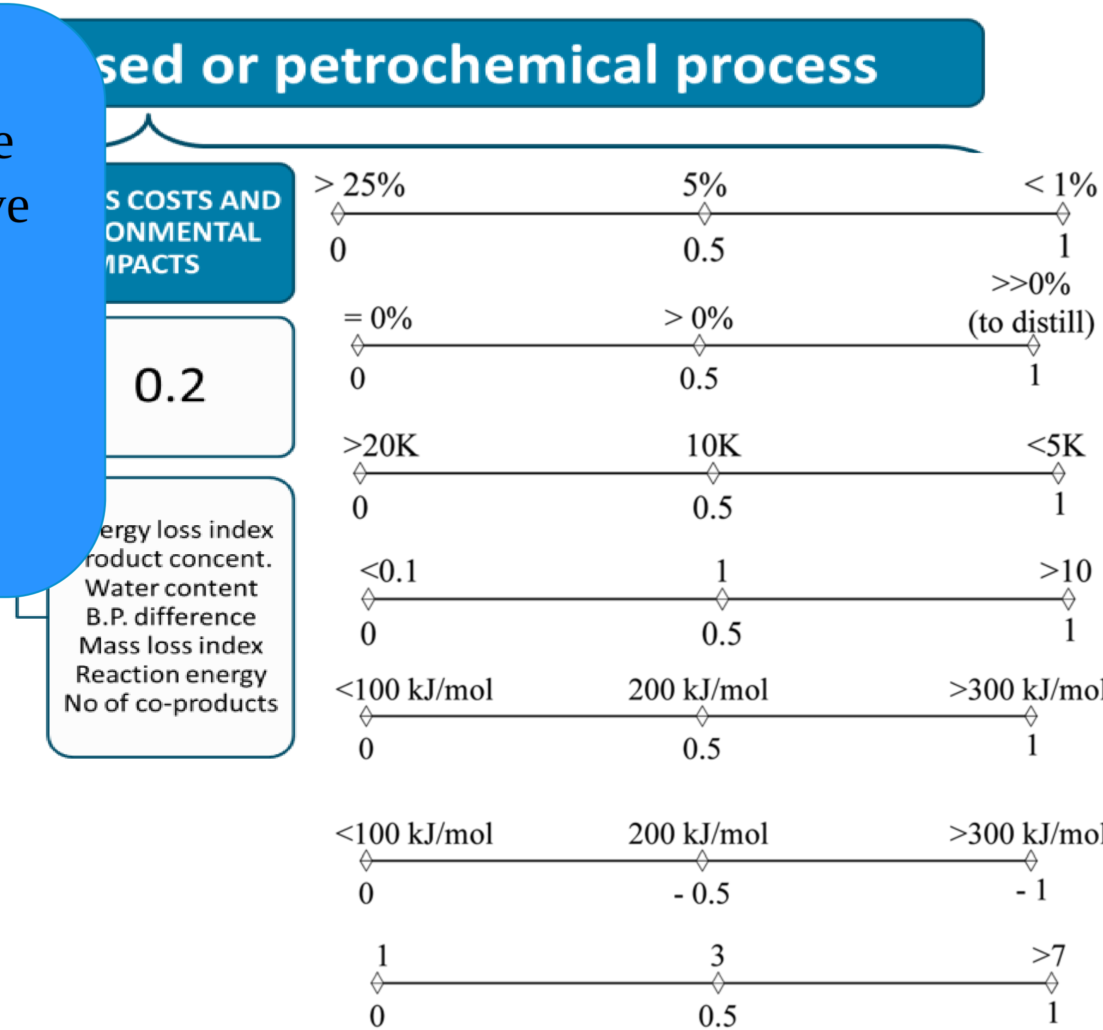
Normalization!

- Scores for the new process are normalized against the respective scores for the comparable conventional process

-Scores are normalized to 1

-Weighting

-Single score indicator



lower scores are better

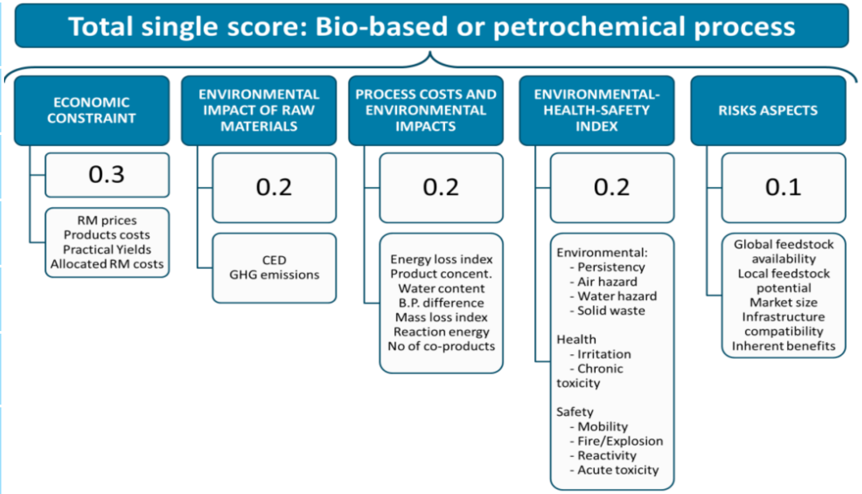
3. Posada et al., Bioresource Technology 135 (2013) 490–499;
4. Pater et al.., Energy Environ. Sci., 2012, 5 (9), 8430–8444 ;
5. Sugityama et al., AIChE Journal. 54 (2008) 1037-1053

Early Stage Analysis

- <u>case study</u>: derivatives of bioethanol.

Product	Mass & (molar) Yields*	Temp (^{O}C)	Involved Reactions*	Conventional process	Main uses	Commercial price (€/tonn)**
Ethylene	0.60 (0.99)	450	$\gamma_1, \gamma_7, \gamma_{15}, \gamma_{16}$	Steam Cracking of naphtha	Raw material	1230
Propylene	0.32 (0.35)	550	$\gamma_1, \gamma_2, \gamma_3$	Steam cracking of naphtha	Raw material	1245
1,3-butadiene	0.51 (0.44)	350	$\gamma_7, \gamma_{13}, \gamma_{14}$	Steam cracking of naphtha	Raw material	2050
iso-Butylene	0.34 (0.28)	450	$\gamma_1, \gamma_5, \gamma_7$	Steam cracking of naphtha	Raw material	581
Hydrogen	0.21 (4.79)	450	$\gamma_6, \gamma_{17}, \gamma_{18}$	Methane steam reforming	Chemical agent	1940
Acetaldehyde	0.75 (0.78)	230	γ_7, γ_{18}	Oxidation of ethylene	Raw material	826
Ethylene oxide	0.92 (0.96)	325	$\gamma_1, \gamma_4,$	Oxidation of ethylene	Raw material	1375
n-Butanol	0.21 (0.13)	400	$\gamma_1, \gamma_5, \gamma_7, \gamma_9,$	Propylene hydroformilation	Raw material and solvent	1025
Acetic acid	1.25 (0.96)	150	γ_{10}, γ_{18}	Methanol carbonylation	Raw material and solvent	850
Ethyl acetate	0.63 (0.33)	260	$\gamma_7, \gamma_{11},$	Esterif. of acetic acid with ethanol	Solvent and coating agent	1120
Acetone	0.57 (0.46)	400	γ_1, γ_{12}	Cumene oxidation (Hock process)	Raw material and solvent	1024
Diethyl ether	0.59 (0.37)	350	$\gamma_1, \gamma_{15},$	Direct hydration of ethylene	Solvent	1925

* see Figure 1., ** for 2008-2011.



functional unit: 1 kg of ethanol-derivative

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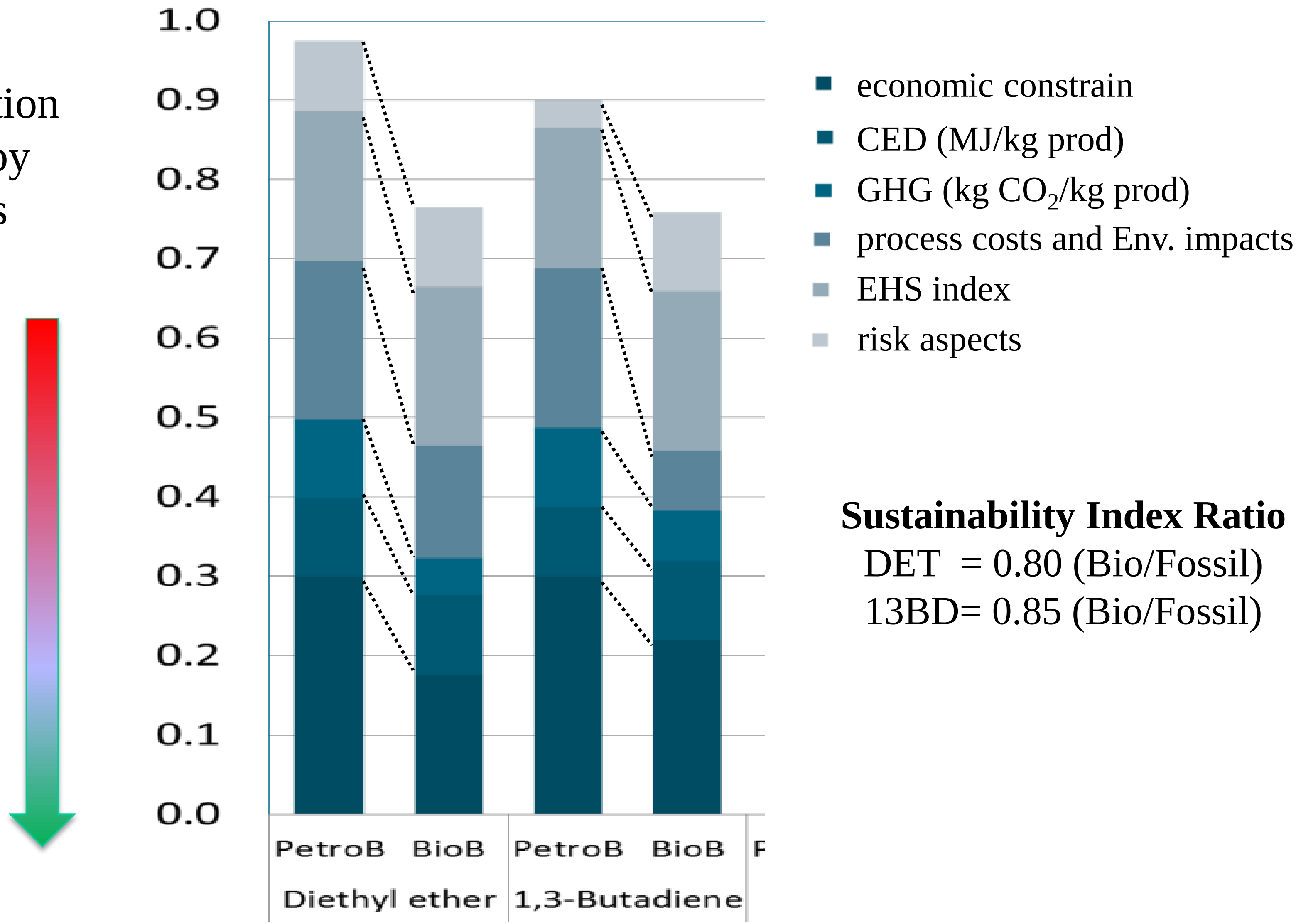
- case study: derivatives of bioethanol.

Contribution analysis by indicators

lower scores are better



Sustainability Index Ratio

DET = 0.80 (Bio/Fossil)

13BD= 0.85 (Bio/Fossil)

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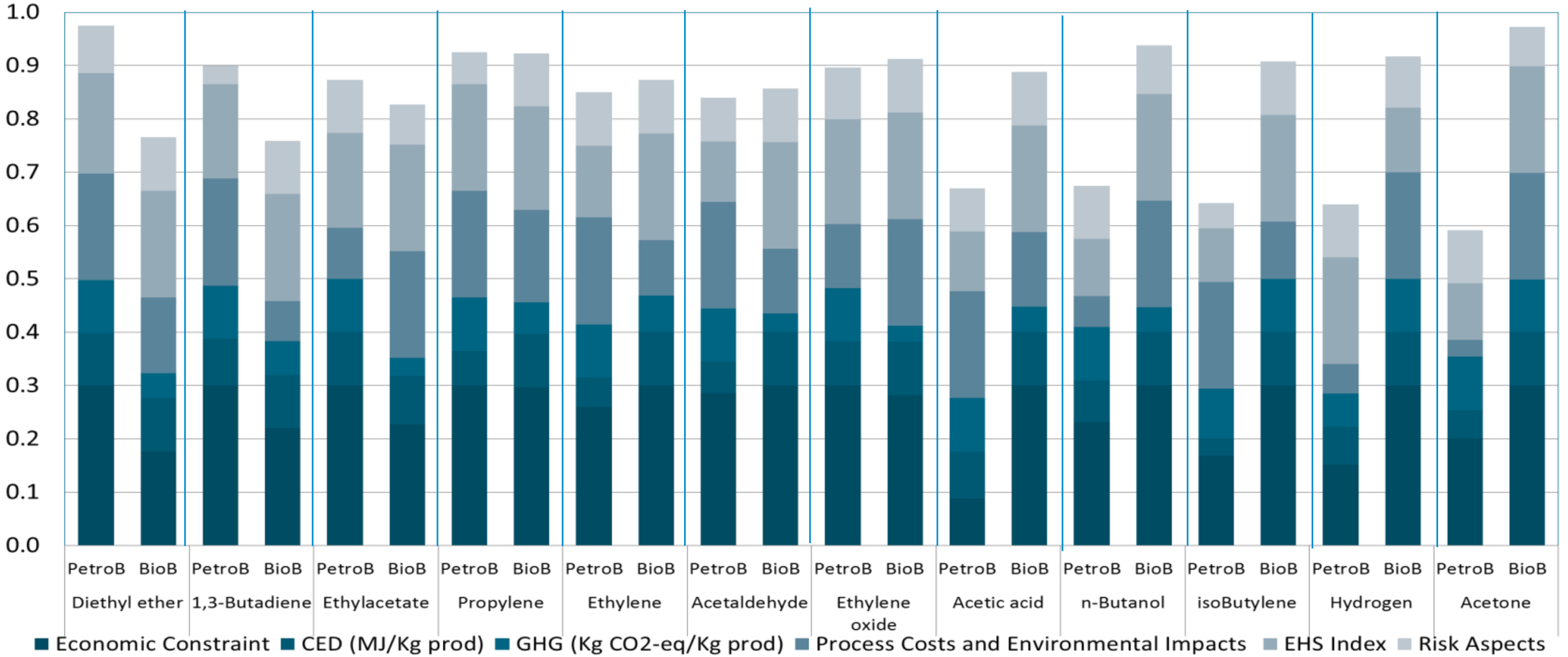
  results



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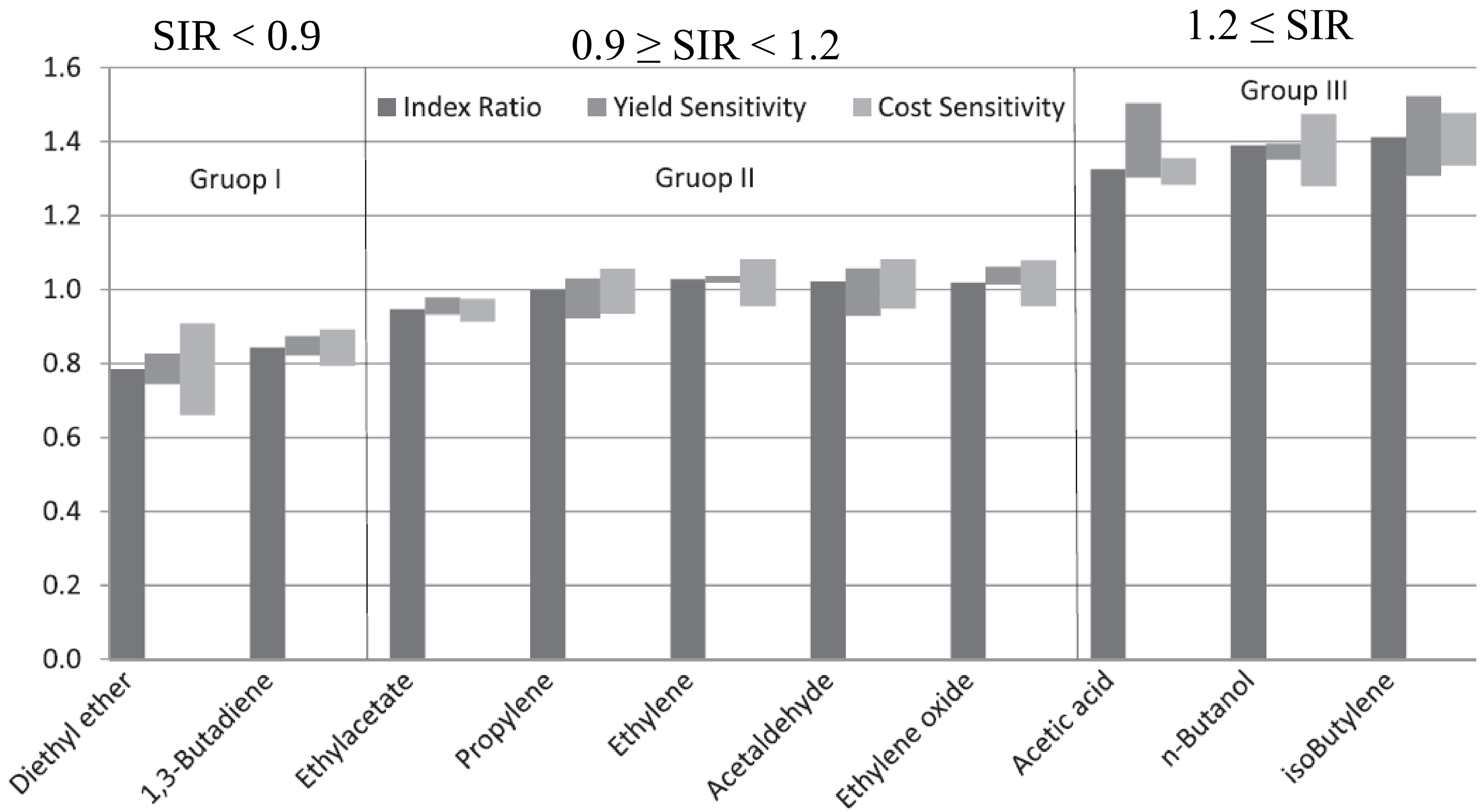
- case study: derivatives of bioethanol.

Single Index Ratio (Biobased/Petrochem)

sensitivity analysis on yields (theo. & -20%) and costs (±20%)



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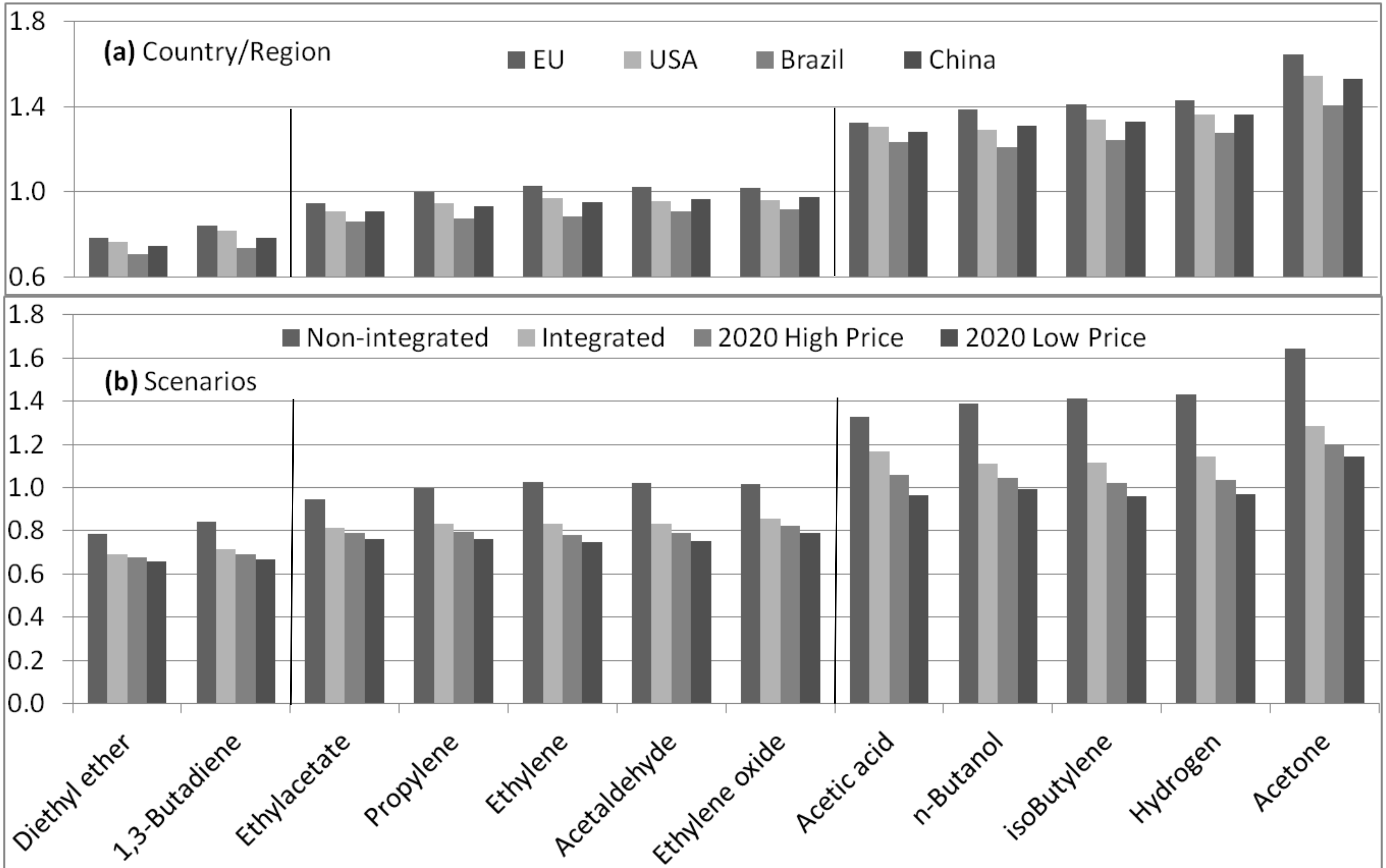
<u>scenarios</u> analysis on: location, BR integration, timeframe (2020)



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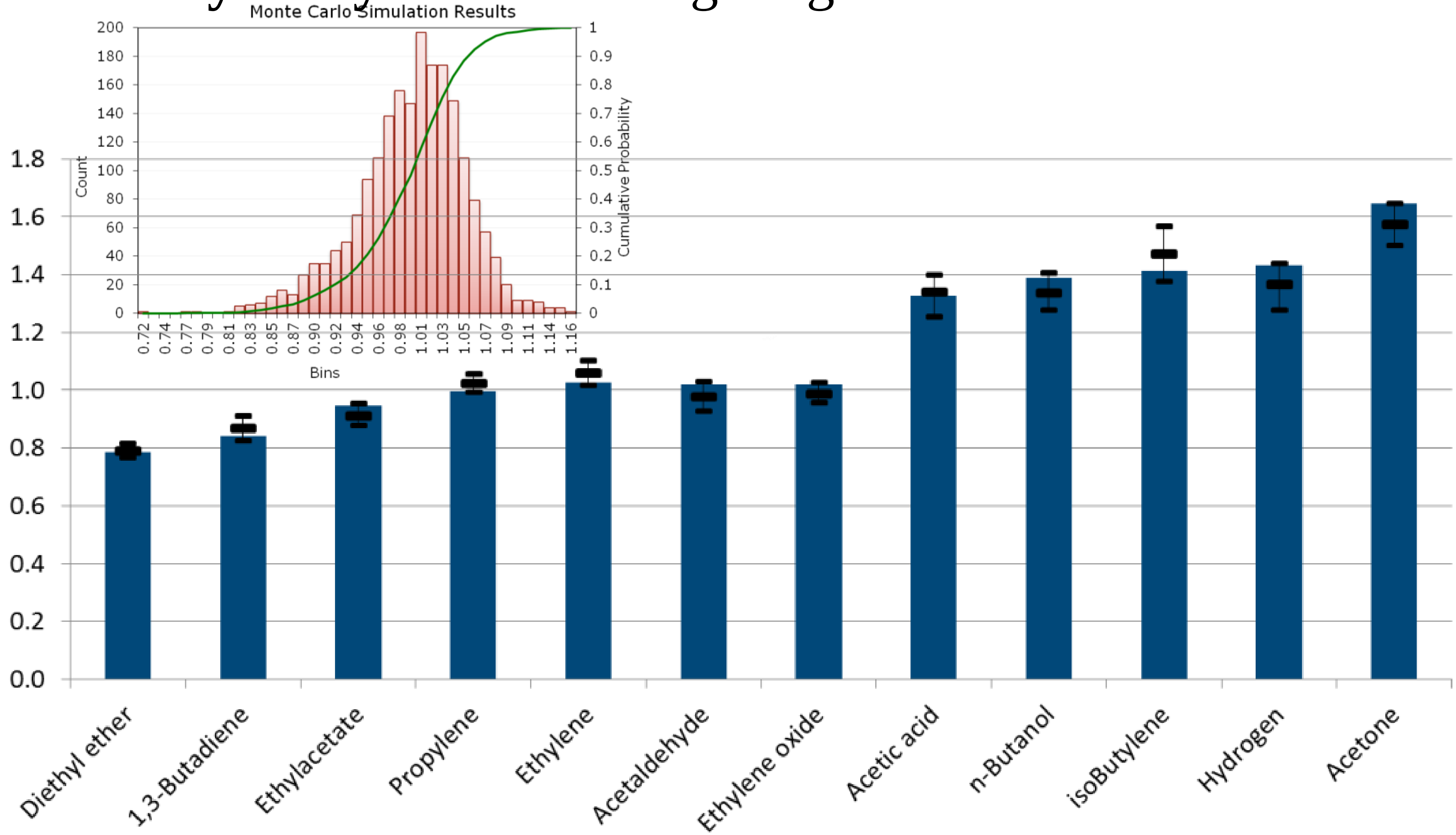
- <u>case study</u>: derivatives of bioethanol.

Single Index Ratio (Biobased/Petrochem)

uncertainty analysis on the weighting factors



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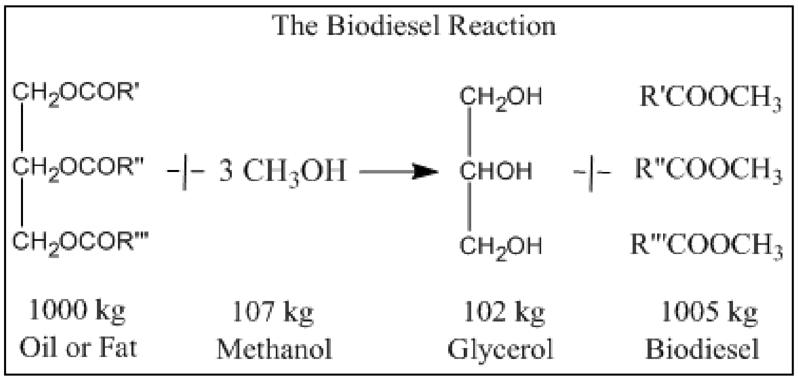
- case study: derivatives of bioethanol.

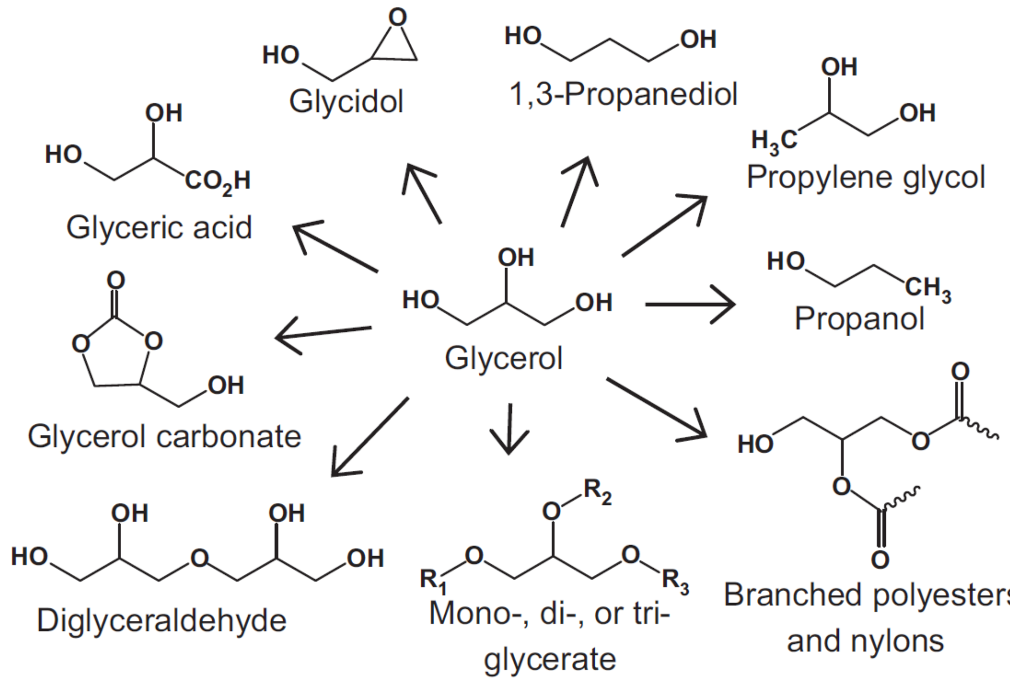
Type of BR	Country /Region	Diethyl ether	1,3-bu tadiene	Ethyl acetate	Propyl ene	Ethyl ene	Acetal dehyde	Ethylene oxide	Acetic acid	n-Buta nol	isoButyl ene	Aceto ne	Hydro gen
Non-int. BR	EU	G-I	G-I	G-II	G-II	G-II	G-II	G-II	G-III	G-III	G-III	G-III	G-III
	USA	G-I	G-I	G-I	G-I	G-I	G-II	G-II	G-III	G-III	G-III	G-III	G-III
	Brazil	G-I	G-I	G-I	G-I	G-I	G-I	G-I	G-III	G-III	G-III	G-III	G-III
	China	G-I	G-I	G-I	G-I	G-I	G-II	G-II	G-III	G-III	G-III	G-III	G-III
Int. BR	EU	G-I	G-I	G-I	G-I	G-I	G-I	G-I	G-III	G-III	G-III	G-III	G-III
	USA	G-I	G-I	G-I	G-I	G-I	G-I	G-I	G-III	G-III	G-III	G-III	G-III
	Brazil	G-I	G-I	G-I	G-I	G-I	G-I	G-I	G-II	G-II	G-II	G-III	G-III
	China	G-I	G-I	G-I	G-I	G-I	G-I	G-I	G-III	G-III	G-III	G-III	G-III

Considered indicators	Diethyl ether	1,3-buta-diene	Acetal-dehyde	Ethyl-ene	Ethyl acetate	Propyl-ene	Ethylene oxide	Acetic acid	n-Buta-nol	isobutyl-ene	Hydro-gen	Ace-tone
All (1 to 5)	G-I	G-I	G-II	G-II	G-II	G-II	G-II	G-III	G-III	G-III	G-III	G-III
(EC, EI & PCEI)	G-I	G-I	G-I	G-II	G-II	G-II	G-II	G-III	G-III	G-III	G-III	G-III
(EC & PCEI)	G-I	G-I	G-I	G-I	G-II	G-II	G-III	G-III	G-III	G-III	G-III	G-III
(EI & PCEI)	G-I	G-I	G-I	G-I	G-II	G-II	G-II	G-II	G-III	G-III	G-III	G-III

Techno-economic Analysis

- case study: derivatives of glycerol





Production has increased by **400%**.

Sale price has decreased by **10 fold**

High functionality and occurrence in nature allow it to be transformed by a chemical route or by a fermentative way.

Techno-economic Analysis

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- case study: derivatives of glycerol

Aim: process design, simulation and economic assessment of new technological schemes

Full Process Characterization (detailed technical data):

-actual conversion and selectivity
-process units
-process temperature
-process pressure
-productivity (scale)
-energy requirements

a process design strategy based on knowledge

- **Considers both heuristic rules and researcher's experience.**
- **Economic and environmental advantages and disadvantages are also considered.**

process simulation using Aspen Plus

- **material balances**
- **energy balances**

economic assessment using Aspen Icarus

- **capital costs**
- **operation costs**
- **production costs**

Techno-economic Analysis

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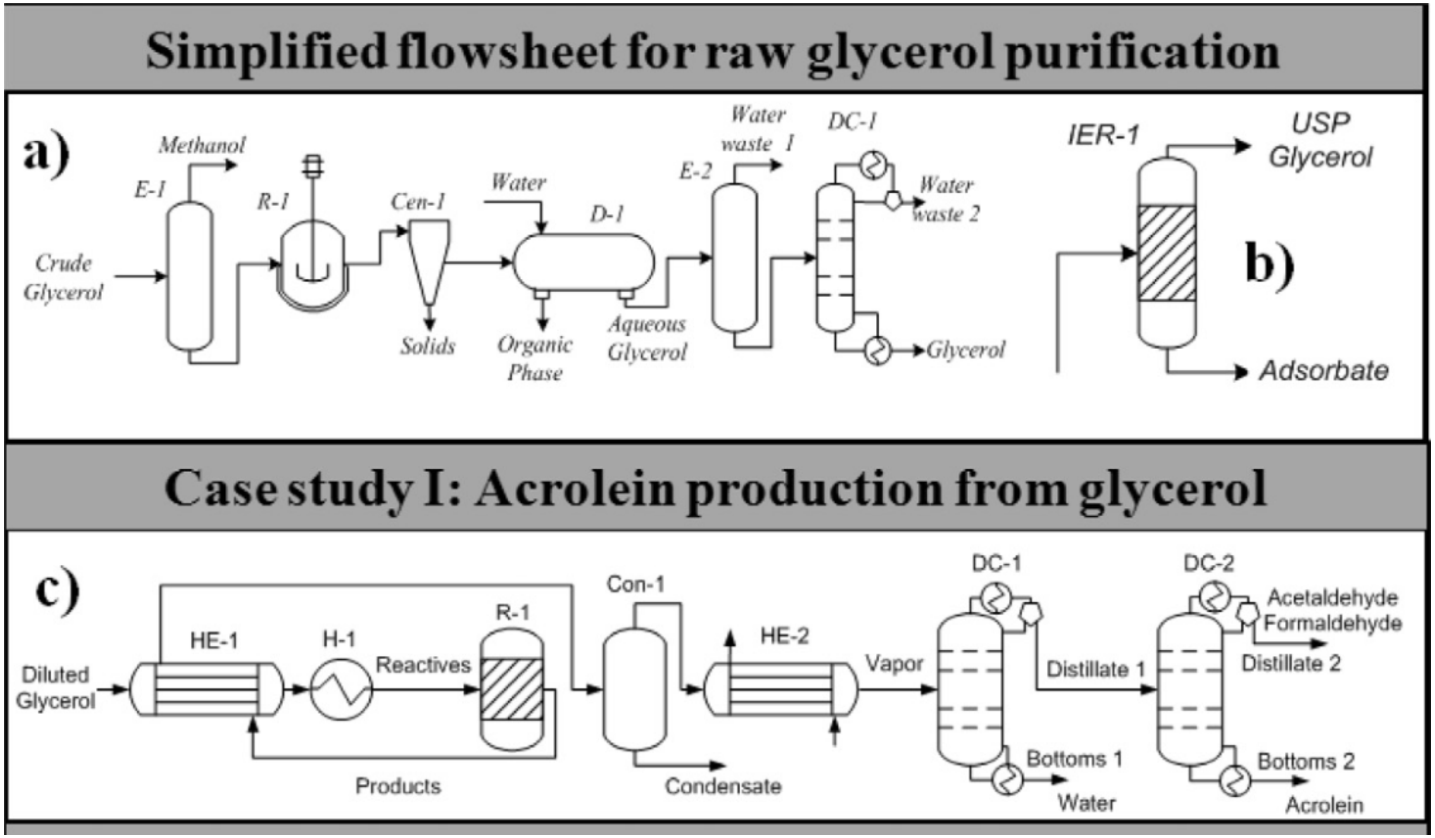
- case study: derivatives of glycerol



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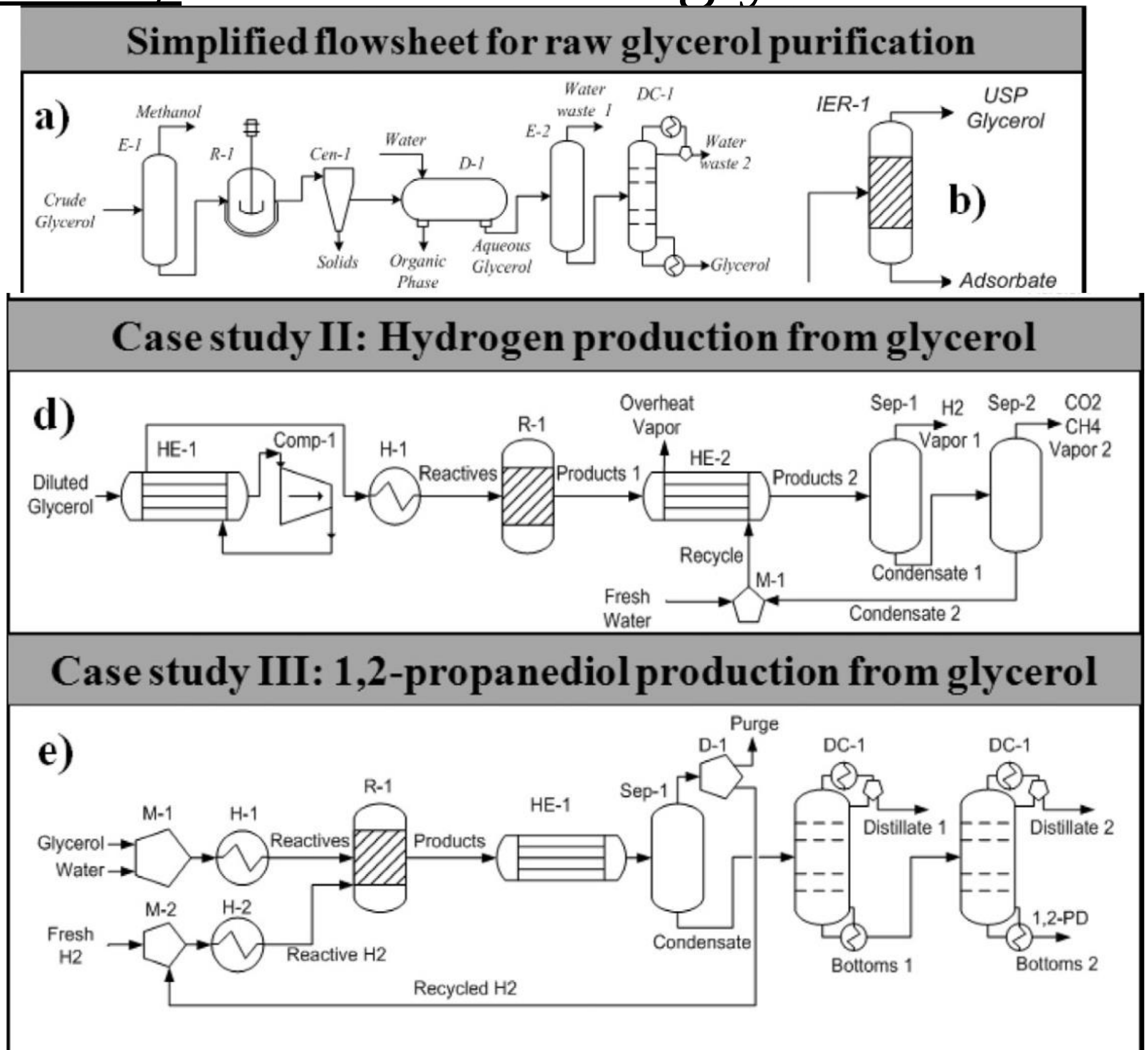
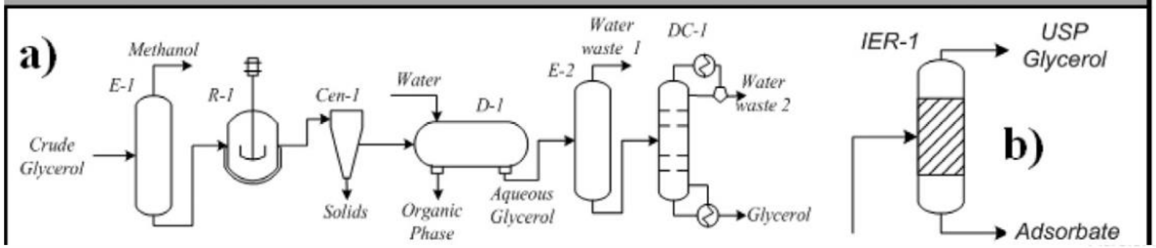
- case study: derivatives of glycerol



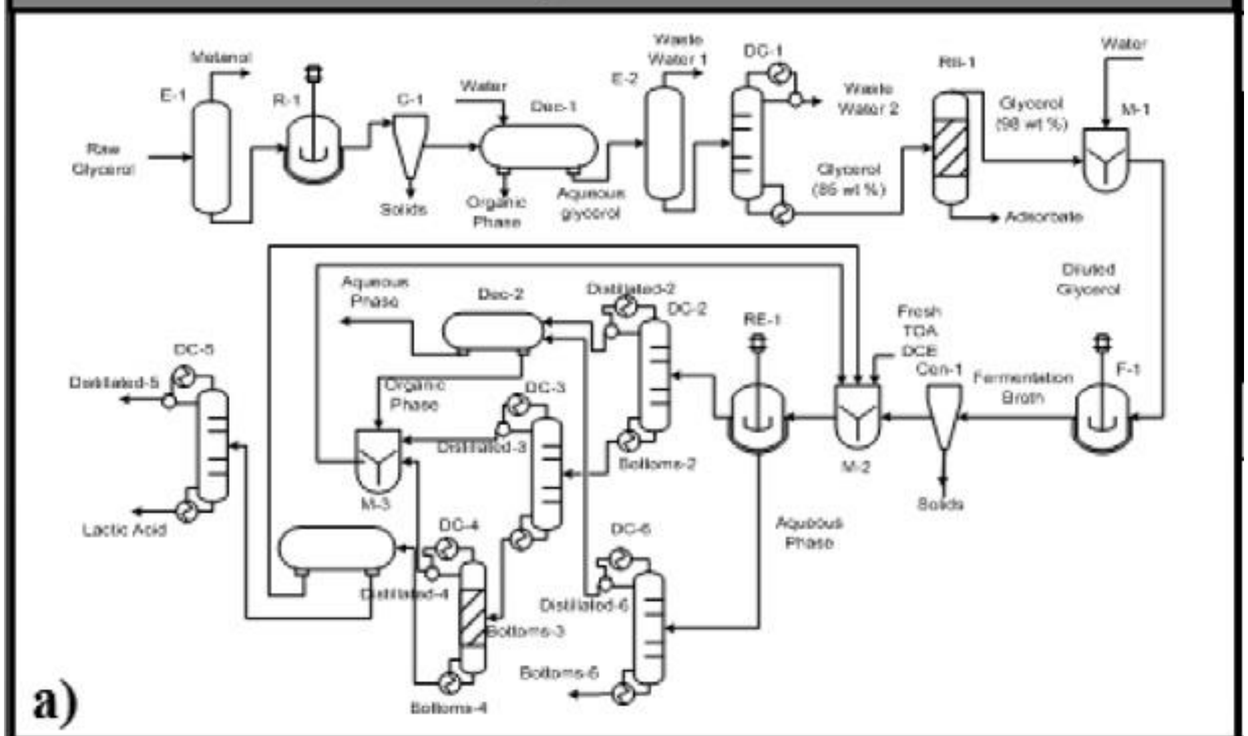
Techno-economic Analysis

- <u>case study</u>: derivatives of glycerol

Simplified flowsheet for raw glycerol purification



Case study IV: D-lactic acid



Techno-economic Analysis

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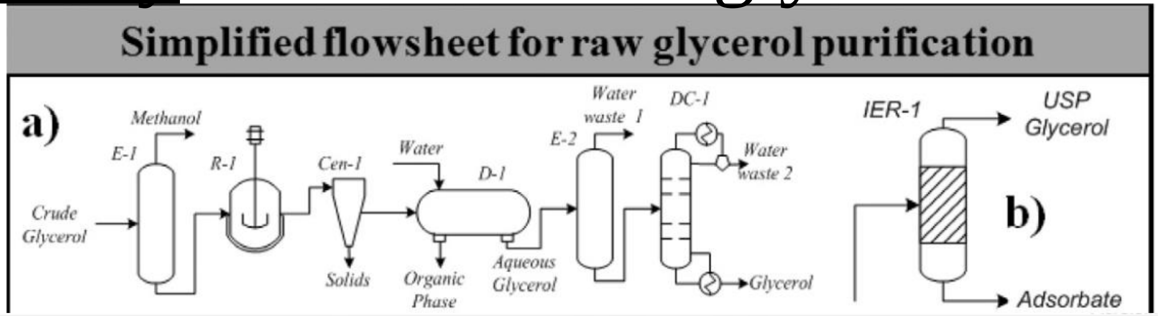
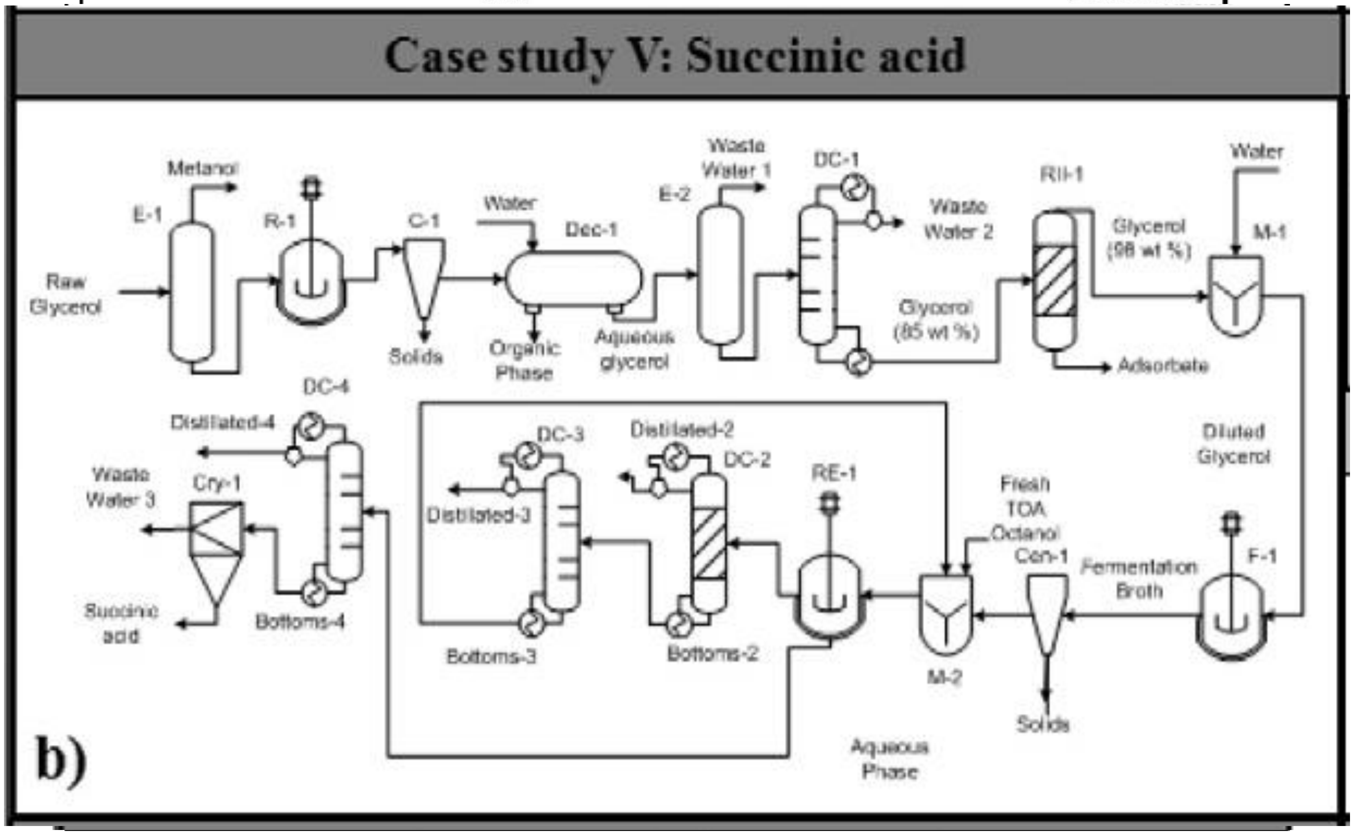
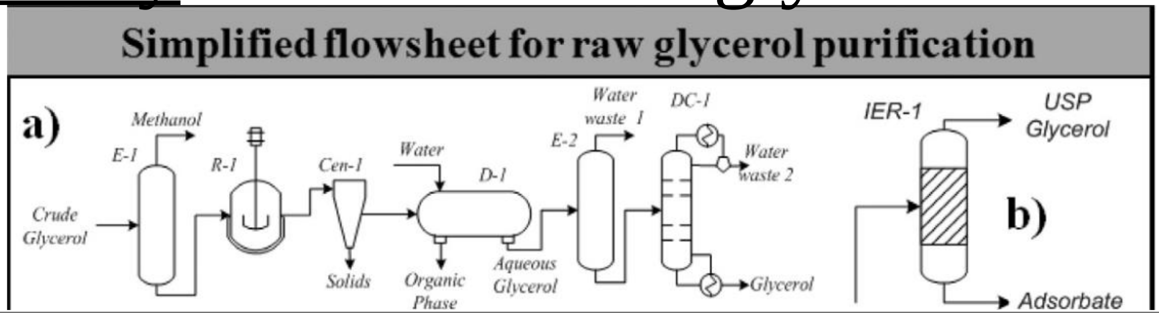
- <u>case study</u>: derivatives of glycerol

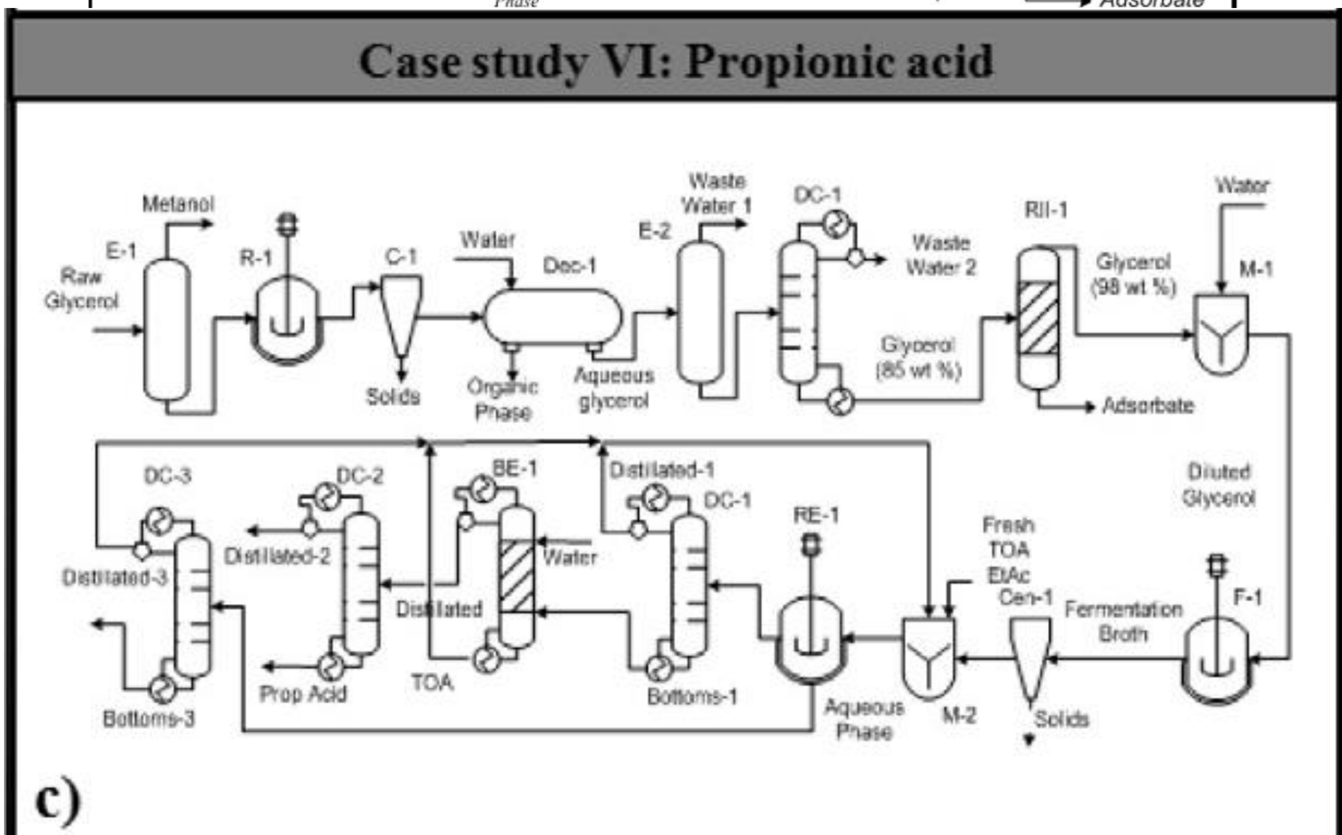




Techno-economic Analysis

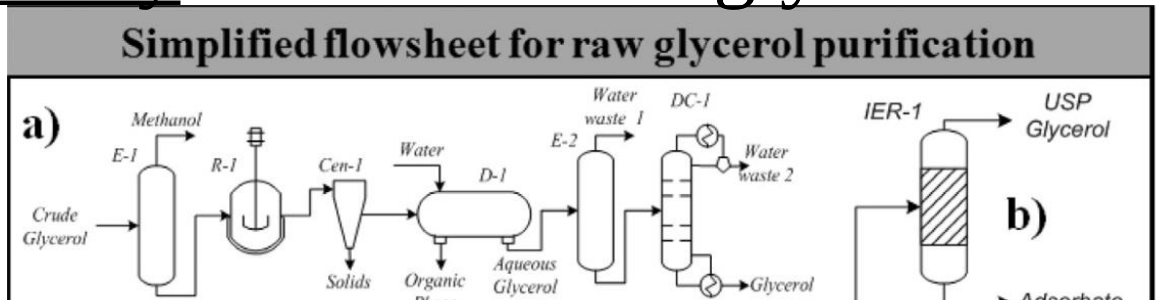
- case study: derivatives of glycerol

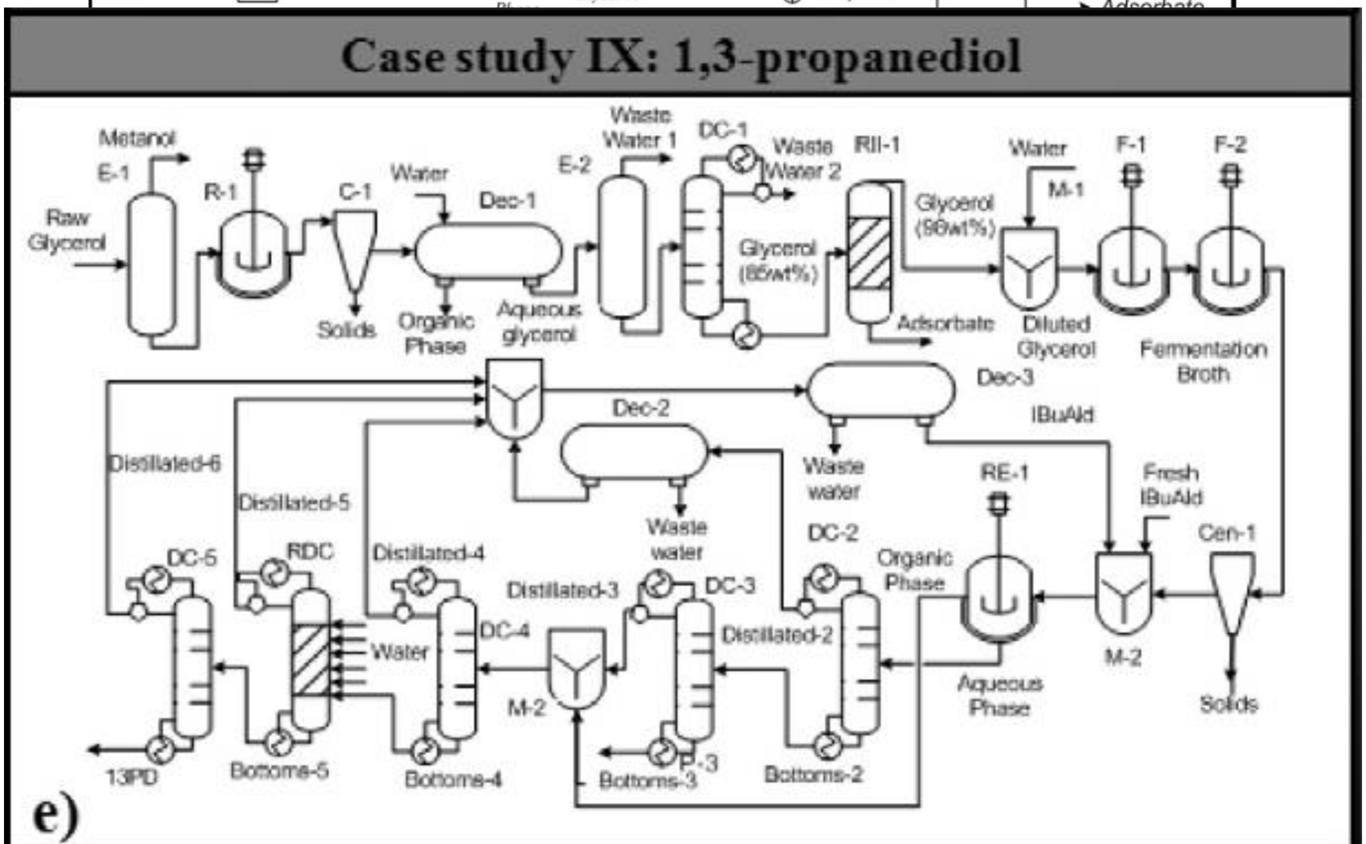




Techno-economic Analysis

- <u>case study</u>: derivatives of glycerol





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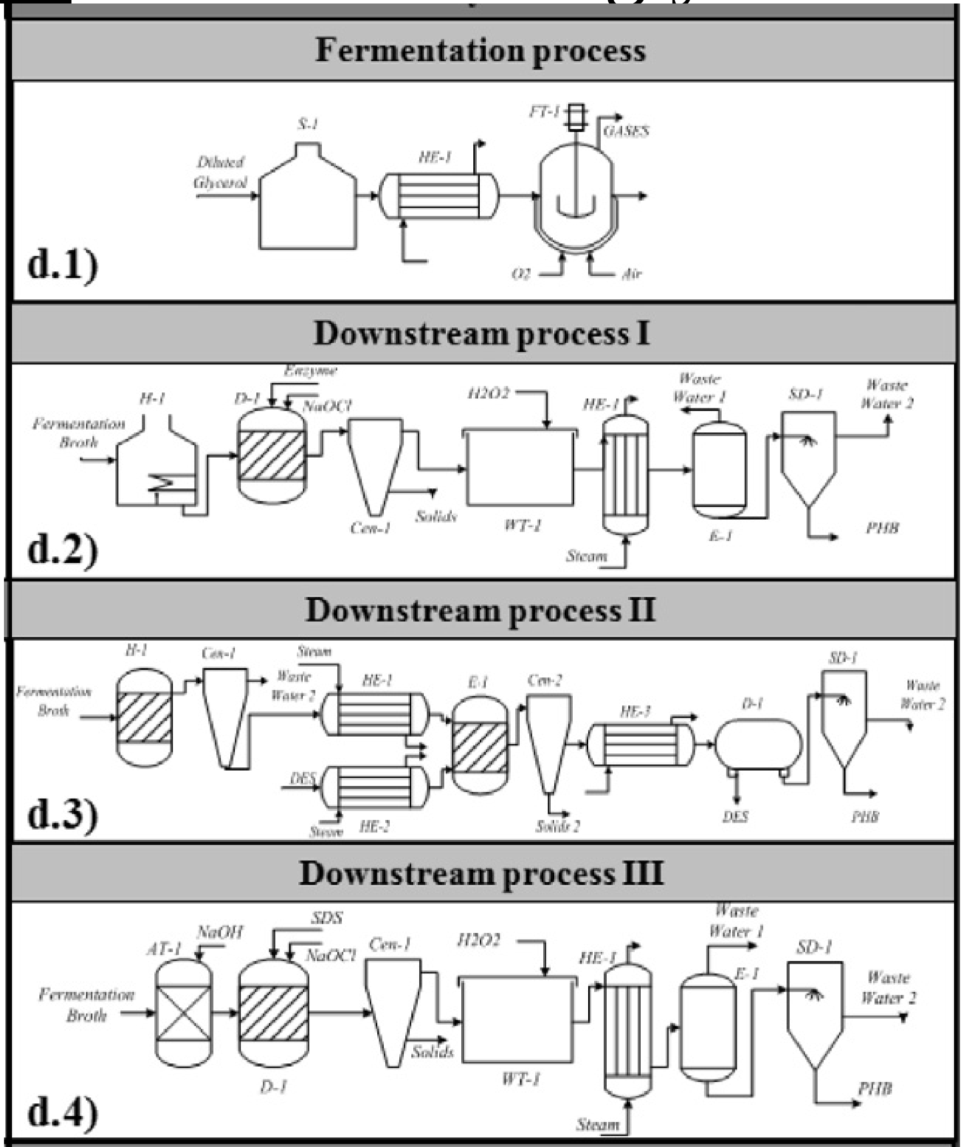
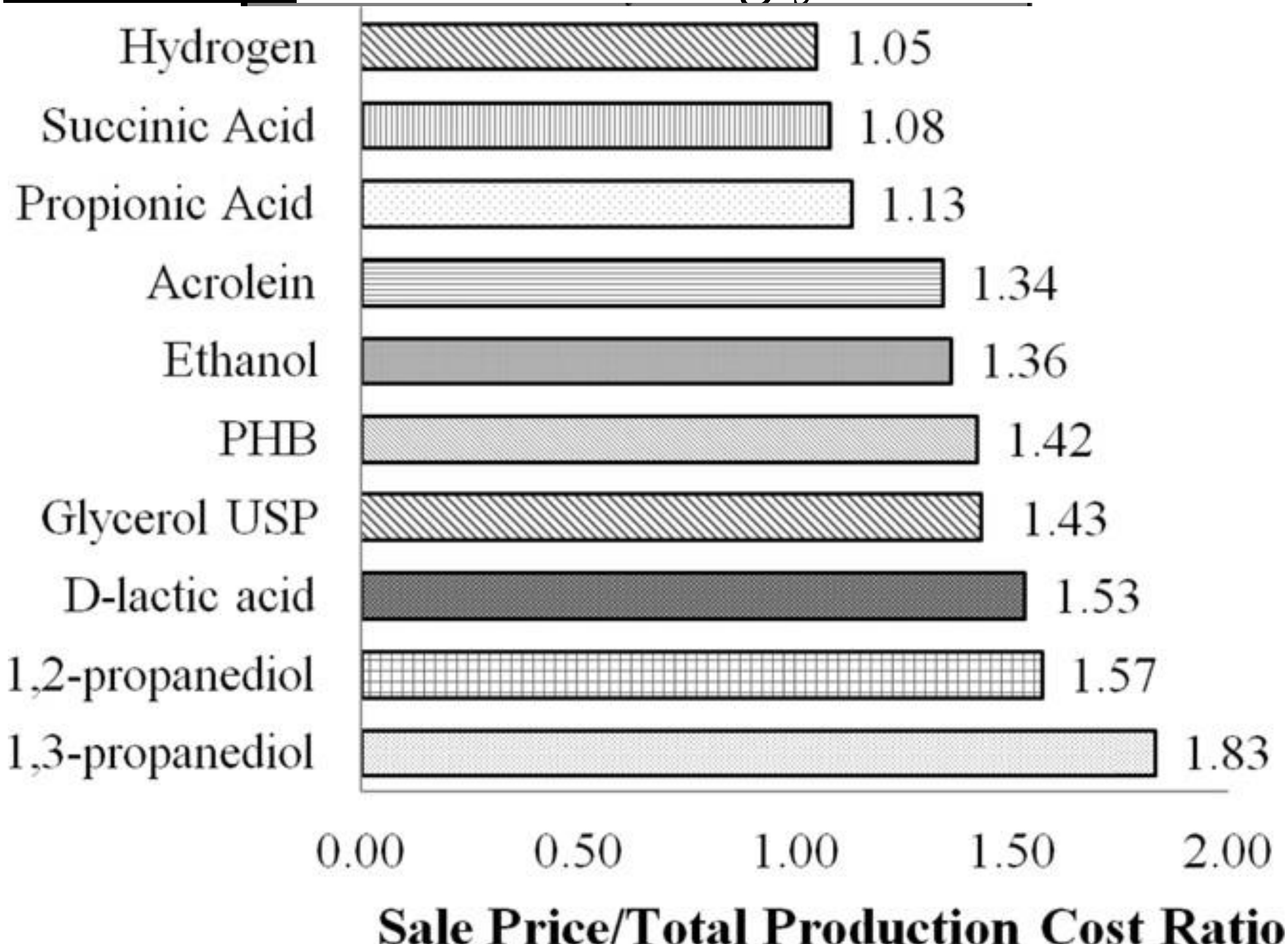
- case study: derivatives of glycerol



Techno-economic Analysis

- case study: derivatives of glycerol



Environmental Analysis

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- case study: microalgae biorefinery

system definition

- **Comparative cradle-to-gate LCA:**

  i) microalgae cultivation,
  ii) culture dewatering,
  iii) lipids extraction and purification,
  iv) fractions upgrading.

- **Impact categories:**
  - Non-renewable energy use (NREU) and net energy ratio (NER),
  - Greenhouse gas emissions (GHG) and net GHG ratio (N-GHG-R),

- **Functional unit:**
  - 1 MJ on main (energy) product (*i.e.*, biomass, oil, green diesel, biodiesel).

- **System expansion** for by-products (*i.e.*, Cake for fishmeal/soybean meal substitution, Oil for fish-oil substitution, Glycerol and Biogas).

- Intended to cover **different species and locations**.

Environmental Analysis

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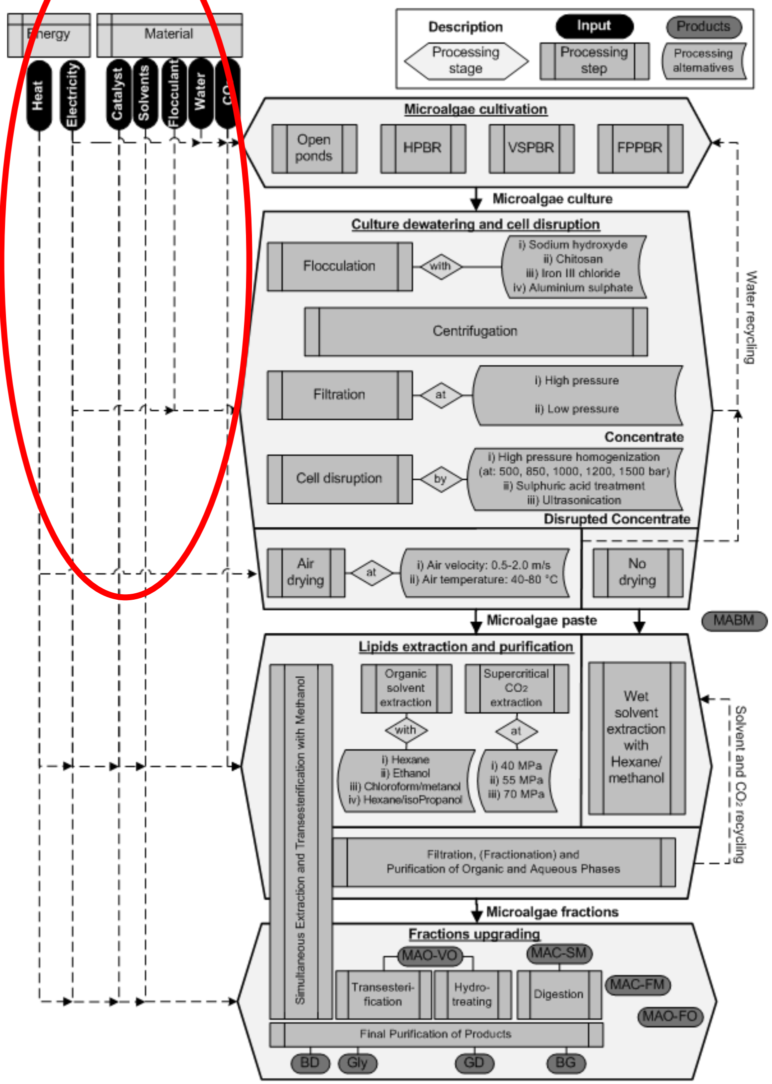
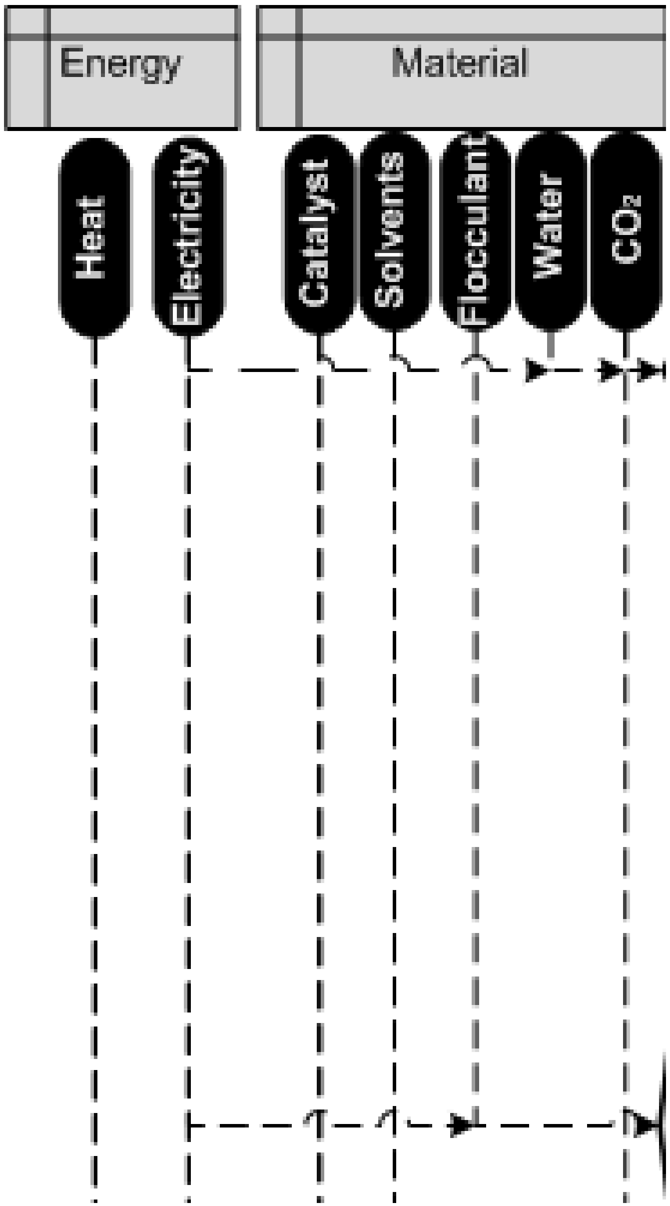
- case study: microalgae BR





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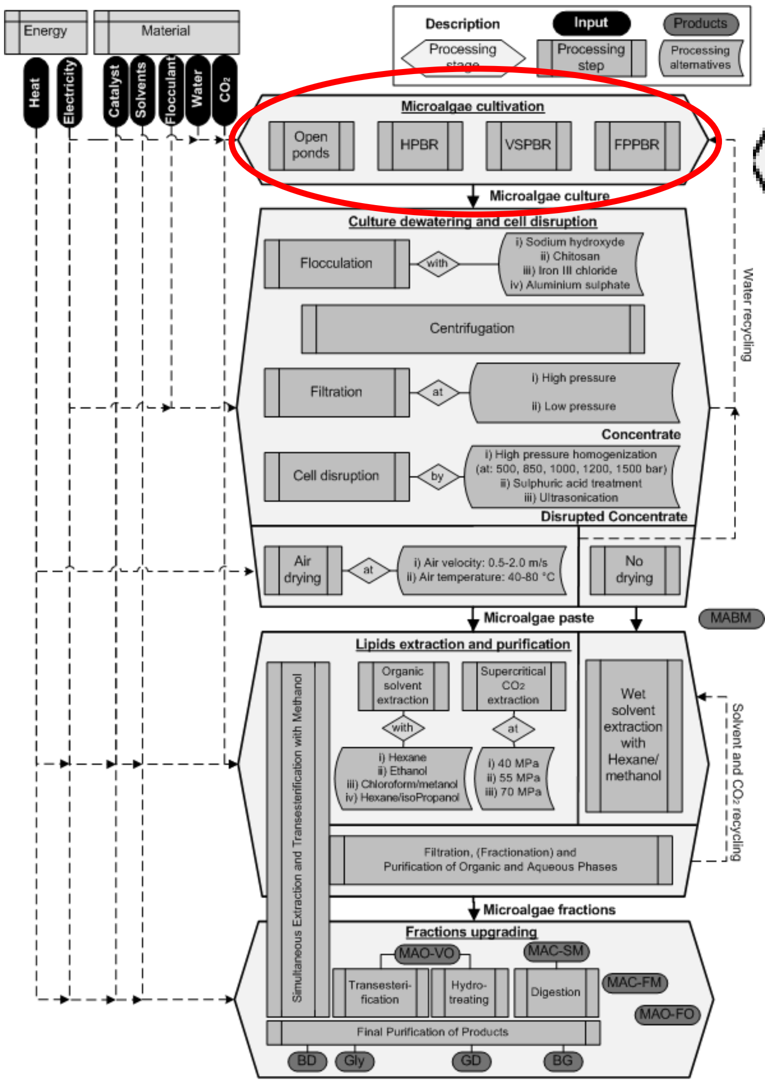
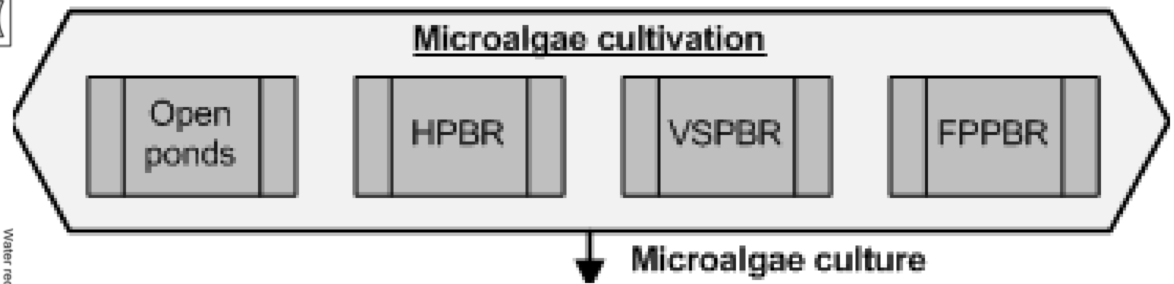
- <u>case study</u>: microalgae BR





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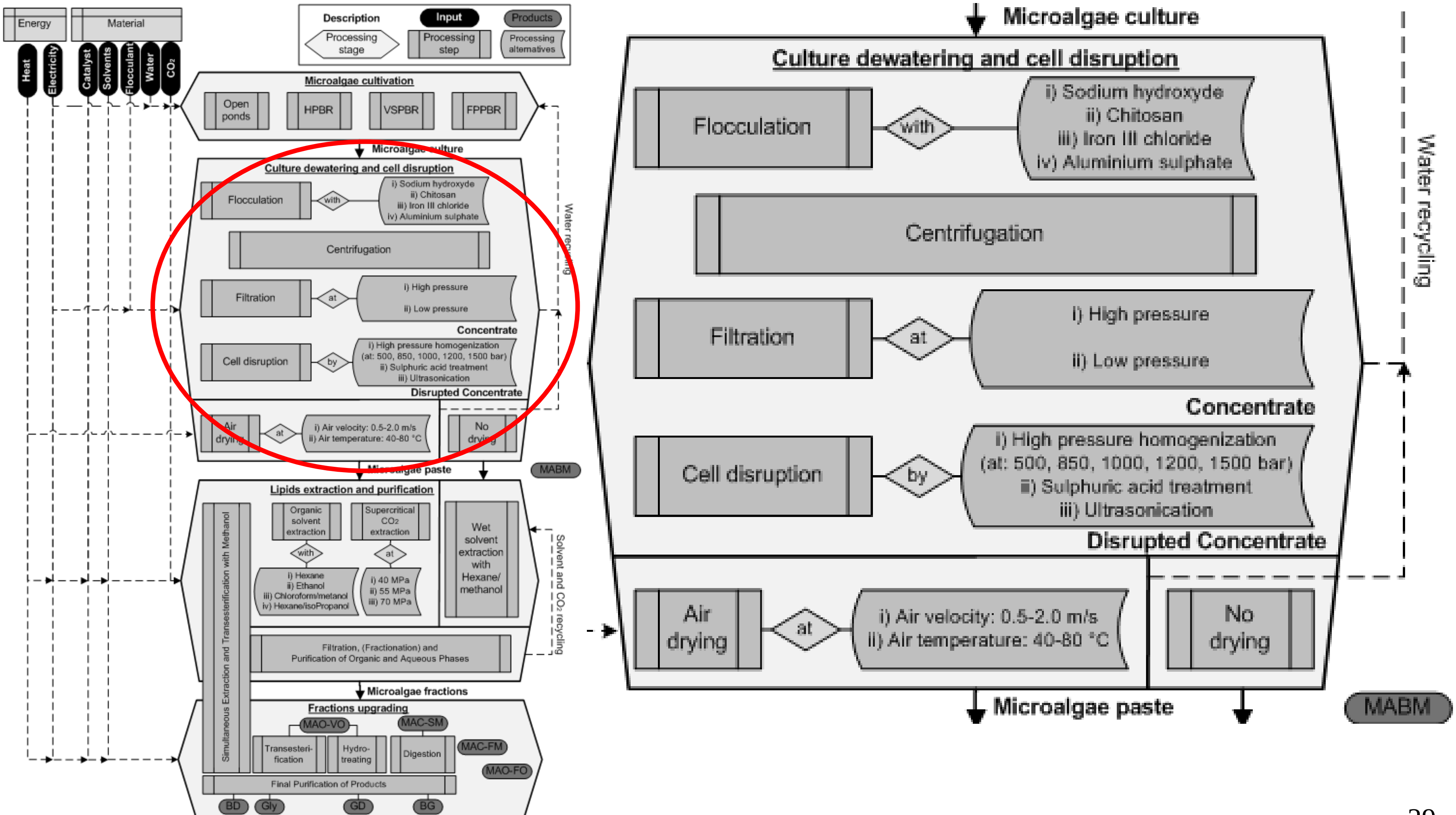
- <u>case study</u>: microalgae BR



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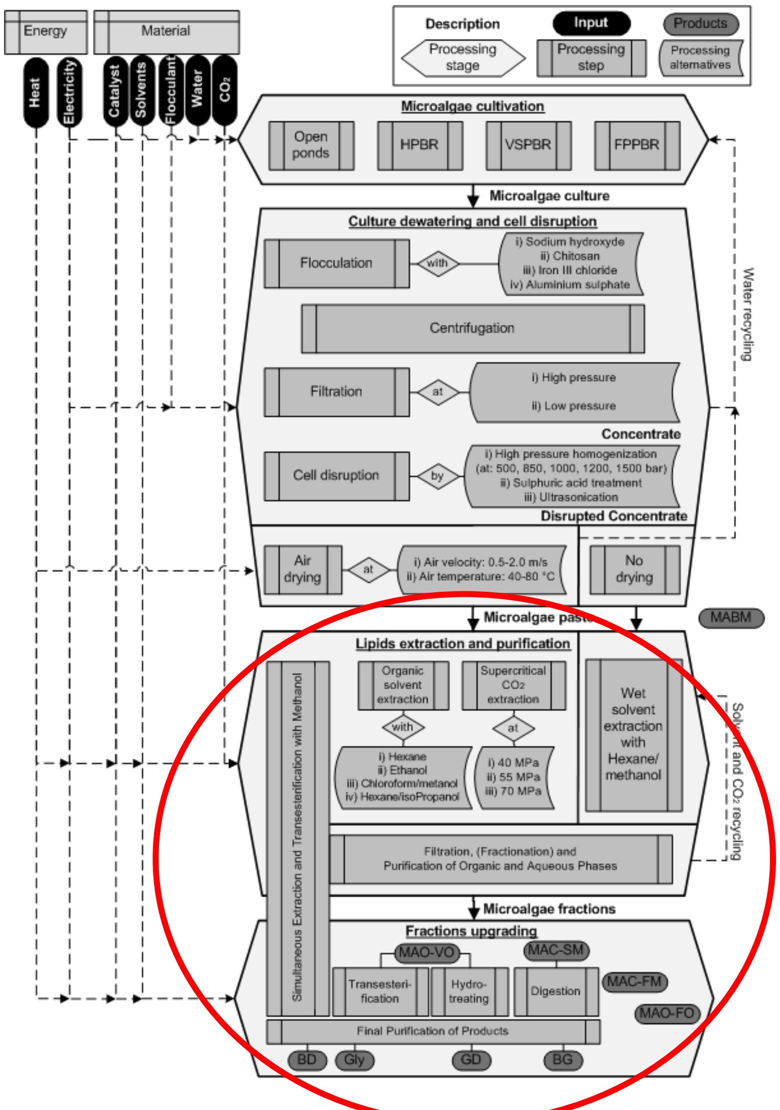
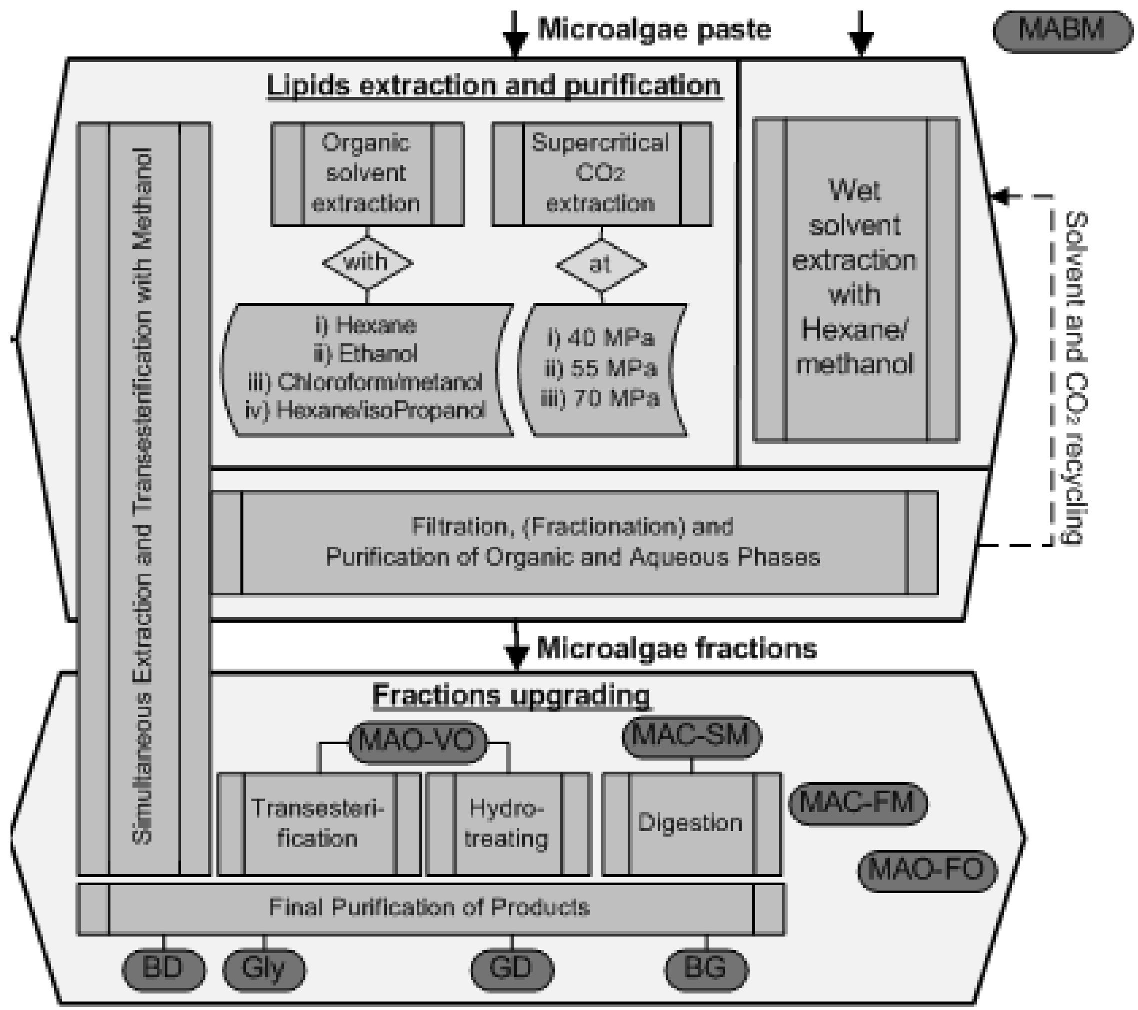
- case study: microalgae BR





Environmental Analysis

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- case study: microalgae BR

Table 1. Products distribution for MABRS

MABRS	MABM	MAC-FM	MAC-SBM	MAO-VO	MAO-FO	GD	BD	Gly	BG*
BR1	X								
BR2		X		X					
BR3			X	X	X				
BR4				X					X
BR5		X				X			
BR6			X		X	X			
BR7						X			X
BR8		X					X	X	
BR9			X		X		X	X	
BR10							X	X	X

Environmental Analysis

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- <u>case study</u>: microalgae BR

- All operation conditions and mass/energy balances are <u>based on design equations</u> and <u>actual lab/processing data</u>, *i.e.* process design approach.

- Parametric analysis.

Table 2. Microalgae productivities and culture concentration (at harvest)

Processing parameter	OP		HPBR		VPBR		FPPBR	
	Low Perform.	High Perform.	Low Perform.	High Perform.	Low Perform.	High Perform.	Low Perform.	High Perform.
Productivity (g m^{-2} day^{-1})	10	30	18	45	20	50	22	55
Culture con. (g l^{-1})	0.2	0.4	1.5	2.5	1.5	2.5	1.5	2.5

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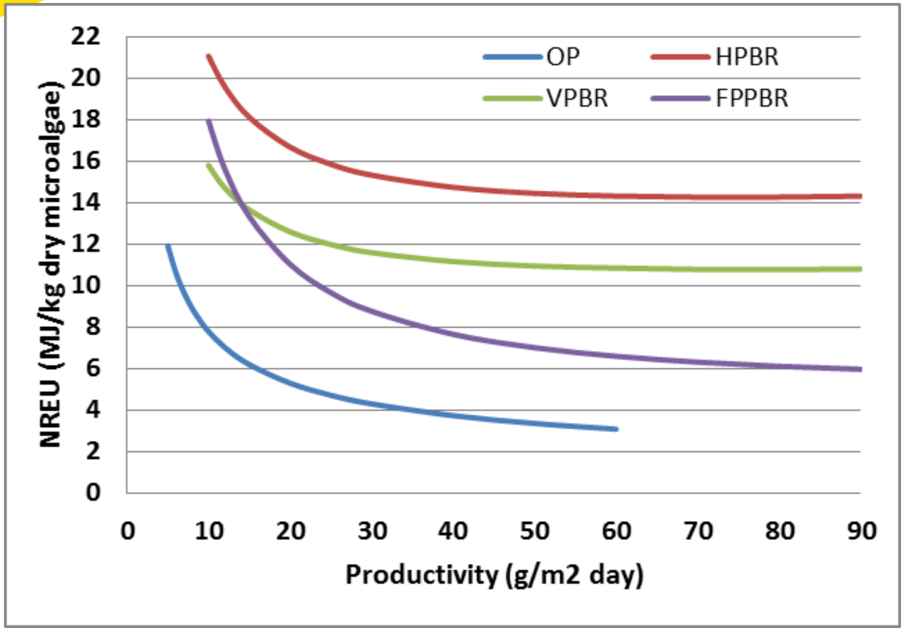

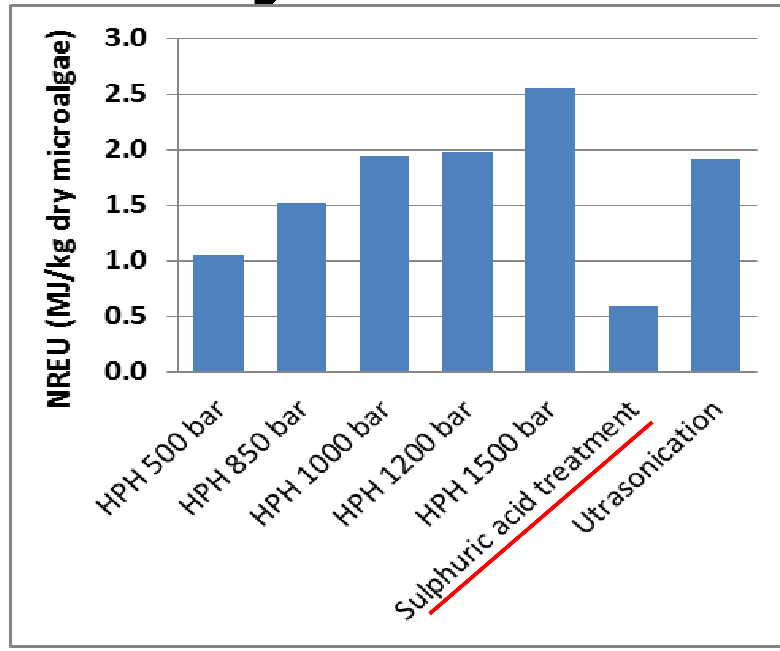

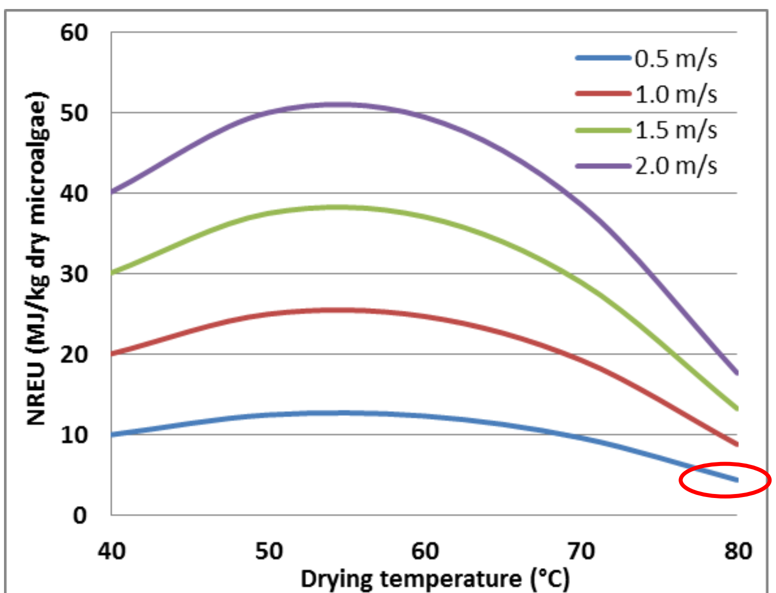

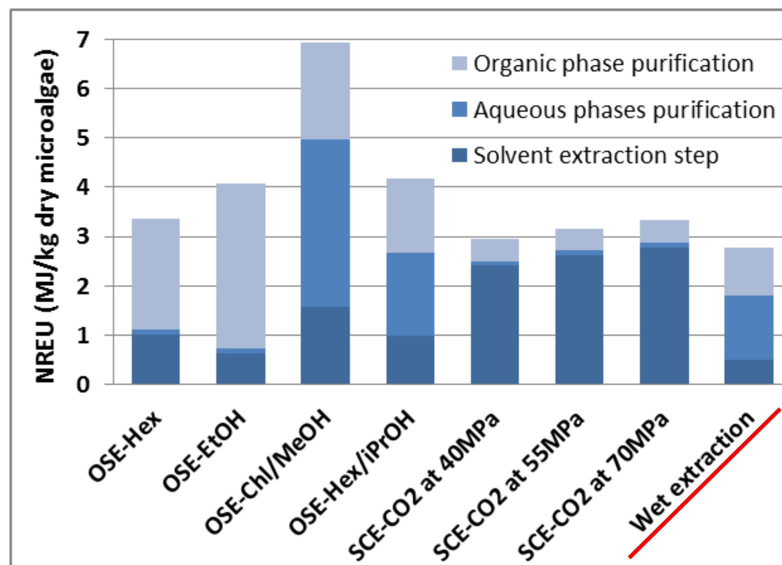

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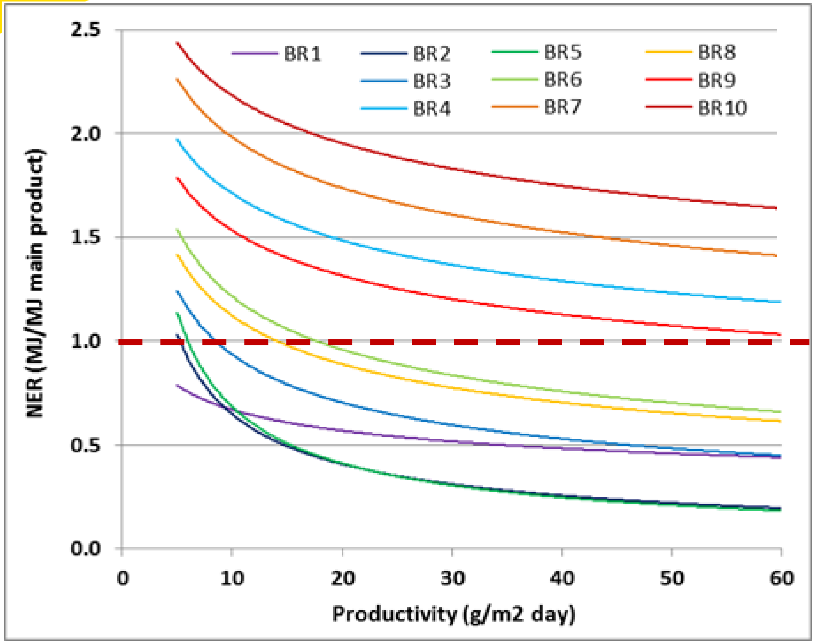

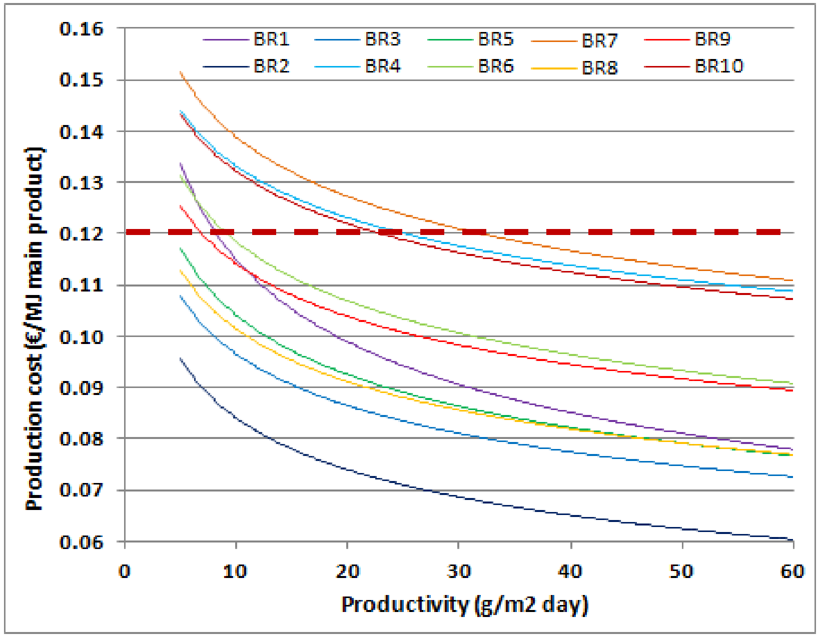

Ranking	OP	HBPR	VPBR	FPPBR	Group
1	BR2	BR2	BR2	BR2	
2	BR3	BR3	BR3	BR1	I
3	BR8	(BR1)*	(BR8)*	BR3	
4	BR5	BR5	BR5	BR5	II
5	BR1	(BR8)*	(BR1)*	BR8	
6	BR9	BR9	BR9	BR6	III
7	BR6	BR6	BR6	BR9	
8	BR10	BR10	BR10	BR10	
9	BR4	BR4	BR4	BR4	IV
10	BR7	BR7	BR7	BR7	

In summary

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- The early-stage sustainability assessment method is suitable to (quickly) screen different options of: raw materials, processing pathways, technologies and products arrangement.
  - The reference system is the fossil-based product
- In-depth analysis provides more technical, economic and environmental details.
  – It is very time intensive
  – It requires process related data
- The early-stage sustainability assessment method has been validated for two systems.

Thanks for your attention!

Are there any questions?

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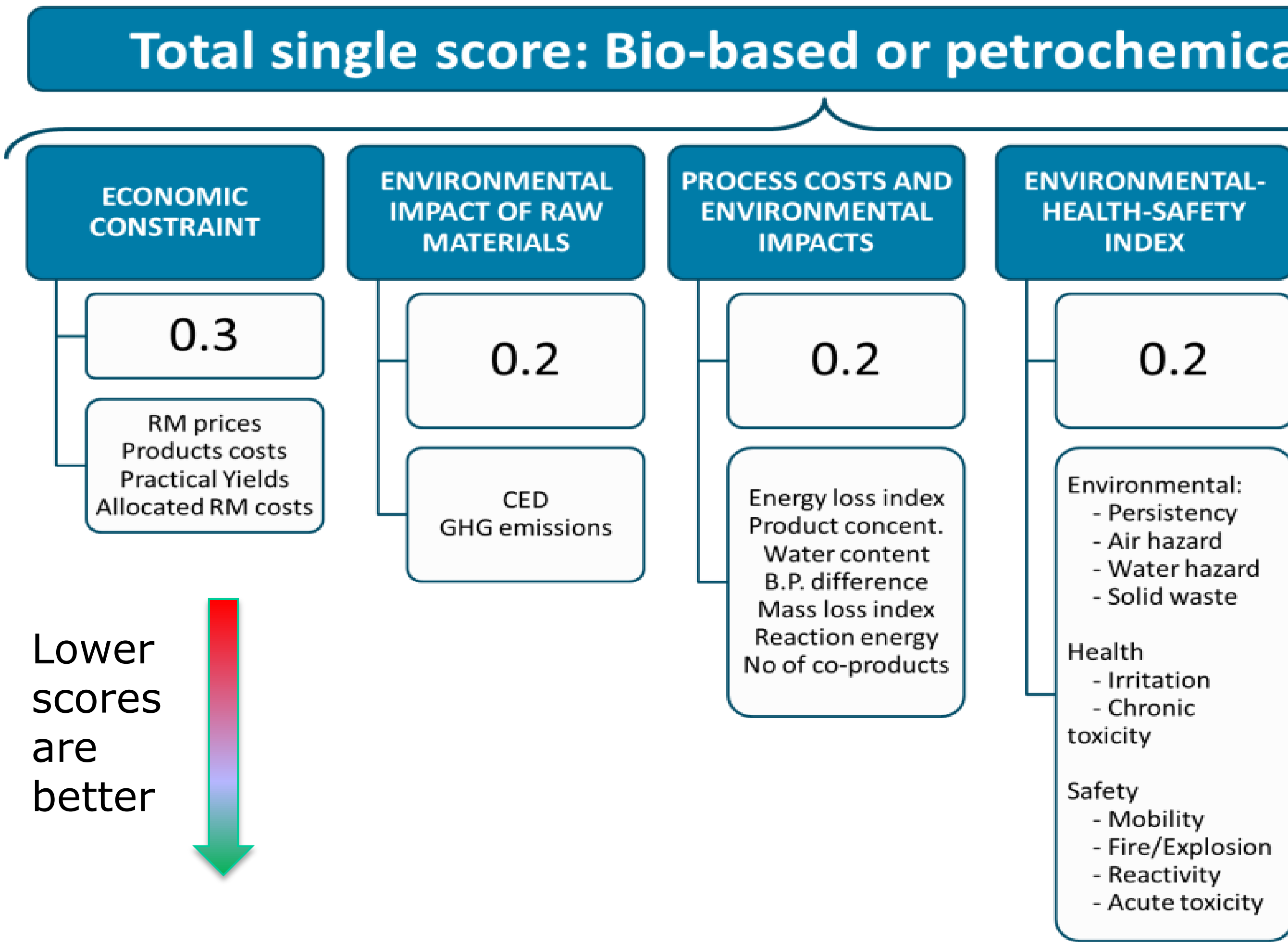
Economic constraint	$EC = \sum_{i=1}^{r} m_i^{RM} C_i^{RM} / \sum_{j=1}^{p} m_j^{P} C_j^{P}$	(1)	1.0	0.3
	$AF_n = m_n^{P} C_n^{P} / \sum_{j=1}^{p} m_j^{P} C_j^{P}$	(1.1)	NA	NA
Environmental impact of Raw material	$EIRM = CED_n + GHG_n$	(2)	1.0	0.2
	$CED_n = AF_n (1/m_n^{P}) \sum_{i=1}^{r} m_i^{RM} CED_i^{RM}$	(2.1)	0.5	
	$GHG_n = AF_n (1/m_n^{P}) \sum_{i=1}^{r} m_i^{RM} GHG_i^{RM}$	(2.2)	0.5	
Processing cost and environmental impacts	$PCEI = \sum_{i=1}^{PCEIc} IWF_i \cdot PCEI_i$	(3)	1.0	0.2
	$PCEI_1 = 0.0, \textit{ if water is NOT present}$ $0.5, \textit{ if water IS present}$ $1.0, \textit{ if water must be distilled}$	(3.1)	0.143	
	$PCEI_2 = 1 - (1/2)(\log_5(100 \cdot C_n))$	(3.2)	0.143	
	$PCEI_3 = 1 - (1/2)(\log_2(\Delta T_{bp}/5))$	(3.3)	0.143	
	$PCEI_4 = (1/2)(\log_{10} MLI + 1)$	(3.4)	0.143	
	$PCEI_5 = (\lvert\Delta H^0_{Rxn}\rvert - 100)/200, \textit{ if} : \Delta H^0_{Rxn} \geqslant 0$ $\textit{or if} : \Delta H^0_{Rxn} < 0 \textit{ and } T_R < 200^{0}C$ $+(100 - \lvert\Delta H^0_{Rxn}\rvert)/200, \textit{ when} : \Delta H^0_{Rxn} < 0 \textit{and } T_R > 200^{0}C$	(3.5)	0.143	
	$PCEI_6 = -0.015 \cdot N_{cp}^2 + 0.28 \cdot N_{cp} - 0.25$	(3.6)	0.143	
	$PCEI_7 = 0, \textit{ if feedstock pretreatment is NOT required}$ $1, \textit{ if feedstock pretreatment IS required}$	(3.7)	0.143	

Note: AF: allocation factor, C: commercial price or cost (€/kg), c: concentration (mol/mol), CCI: compatibility with current infrastructure, CED: cumulative energy demand (MJ/kg), EC: economic constraint, ECat: specific category of environmental hazards, EH: environmental hazards, EHSI: Environmental-Health-Safety Index, EIRM: environmental impact of raw materials, GFA: global feedstock availability, GHG: greenhouse gas (kg $CO_{2\ eq}$/kg), HCat: specific category of health hazards, HH: health hazards, I: index value of one specific component for either category (EH, HH or SH), IB: inherent benefits, IWF: internal weight factor, LFP: local feedstock potential, m: mass flow (kg/kg product), $L(E)C_{50}$ aquatic: aquatic lethal or effect concentration using daphnia magna, MLI: mass loss index, calculated as the ratio of the total mass of all components in the reactor outlet except for the main- and co-products, to the mass of main and co-products from the reaction, MS: market size, N_{cp}: number of co-products, PCEI: process costs and environmental impacts (1 to 7, see methodology), PCEIc: specific category of process costs and environmental impacts, p: number of products, r: number of raw materials, RA: risk aspects, SCat: specific category of safety hazards, SH: safety hazards, T_R: temperature of reaction (°C), Z: fraction of mass emitted to the environment in case of an accident from the maximum mass present in the overall process (=0.1), ΔH^0_{rxn}: standard enthalpy of reaction (kJ/mol), ΔT_{bp} = smallest absolute difference between the boiling point of the product and another substance that has to be separated from this product (°C). *Sub-indexes:* i, j, n: counter for species i, j and main product; cp: number of co-products. *Super indexes:* F: refers to a any internal stream in the process, Out: refers the stream leaving the process (contains main product and co-products), P: refers to the main stream leaving the process (contains the main product), RM: refers to the stream feeding the process (contains the raw materials), UN: refers to a unit mass stream (i.e., 1 kg of each substance).

Hazard Index	$EHSI = AF_n \cdot (IWF_{EH} \cdot EH + IWF_{HH} \cdot HH + IWF_{SH} \cdot SH)$	(4)	1.0	0.2
	$EH = \sum_{ECat}\sum_i (Z \cdot \max_F(m_i^F) I_i^{ECat}) + \sum_{Ecat}\sum_j (m_j^{Out} I_j^{ECat})$	(4.1)	0.4	
	$HH = \sum_{HCat} \max_i (m_i^{UN} I_i^{HCat})$	(4.2)	0.2	
	$SH = \sum_{SCat} \max_F (\max_i (m_i^F I_i^{SCat}))$	(4.3)	0.4	
Risk aspects	$RA = IWF_{GFA} \cdot GFA + IWF_{LFP} \cdot LFP + IWF_{MS} \cdot MS + IWF_{CCI} \cdot CCI + IWF_{IB} \cdot IB$	(5)	1.0	0.1
	GFA = 0.0, for Large scale availability(Commodity chemical or fuel). 0.5, for Potential for near term bulk availability. 1.0, for Conceptual feedstock(Needs fundamental development).	(5.1)	0.25	
	LFP = 0.0, for Feedstock is locally available in bulk quantities. 0.5, for Feedstock available in other parts of the world in free and open markets. 1.0, for Feedstock primarily available in regulated markets with limited global market access.	(5.2)	0.15	
	MS = 0.00, for Existing bulk chemical/fuel market. 0.33, for Existing commodity(ex.Lacticacid, levulinic acid). 0.66, for Near term bulk chemical/fuel market potential. 1.00, for Long term market potential, possibly accelerated by interesting properties.	(5.3)	0.25	
	CCI = 0.00, Process can be integrated or retrofitted into existing processing infrastructure, and the existing target product enters existing processing and supply chains. 0.33, New processing plants required based on known technologies, and the existing target product enters existing processing and supply chains. 0.66, New processing plants required based on known technologies, and new target product which would need new processing and supply chains. 1.00, New greenfield process plants built with new technologies, and new target product which would need new processing and supply chains.	(5.4)	0.20	
	IB, Chemicals, Functional groups, = 0.0, Between2*and*4functional groups.Platform molecule. = 0.5, More than 4 functional groups.Difficult platform molecule to work with. = 1.0, One functional group.Limited potential for platform chemical. Retention of raw material functionality, = 0.0, Complete functionality is preserved. = 0.5, Limited modification of functionality. = 1.0, All functionality stripped off. *or* Fuels, Energy density, = 0.0, High energy density, more than or equivalent to gasoline = 0.5, Energy content80 – 90%that of gasoline. = 1.0, Energy content below80%of gasoline. Engine compativility, = 0.0, Perfectly compatible.Gasoline/Diesel equivalent. = 0.5, Potential for use in existing engines in mixture with gasoline. = 1.0, Engine modification necessary for use.	(5.5)	0.15 or 0.15	

Early stage analysis

- Case study: Derivatives of bioethanol[3,4,5].



(half-life in water).
(index value of chronic toxicity).
($L(E)C_{50}$ aquatic, R-codes).
(based on substance class).

(EU-class, R-codes, LD50dermal).
(EU-class, GK, R-codes)

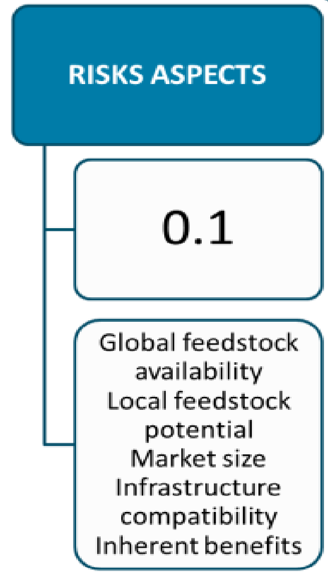
partial pressure, boiling point).
(flash point, R-codes).
(NFPA reactivity, R-codes).
(IDLH, EU-class, GK, R-codes).

3. Posada et al., Bioresource Technology 135 (2013) 490–499;
4. Pater et al.., Energy Environ. Sci., 2012, 5 (9), 8430–8444 ;
5. Sugityama et al., AIChE Journal. 54 (2008) 1037-1053

Early stage analysis

- Case study: Derivatives of bioethanol[3,4,5].

Total single score: Bio-based or petrochemical process



Feedstock supply risk – 0.25.
Regional feedstock availability – 0.15.
Market risk – 0.25.
Infrastructure (availability) risk – 0.2.
Application-technical aspects – 0.15.
+ Chemicals: functional groups – 0.5.
+ Chemicals: retention of raw material functionality – 0.5.
+ Fuels: high energy content – 0.5.
+ Fuels: engine compatibility – 0.5.

3. Posada et al., Bioresource Technology 135 (2013) 490–499;
4. Pater et al.., Energy Environ. Sci., 2012, 5 (9), 8430–8444 ;
5. Sugityama et al., AIChE Journal. 54 (2008) 1037-1053

Techno-economic analysis

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