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The Role of Biorefineries in the Transition to a Low Carbon Economy

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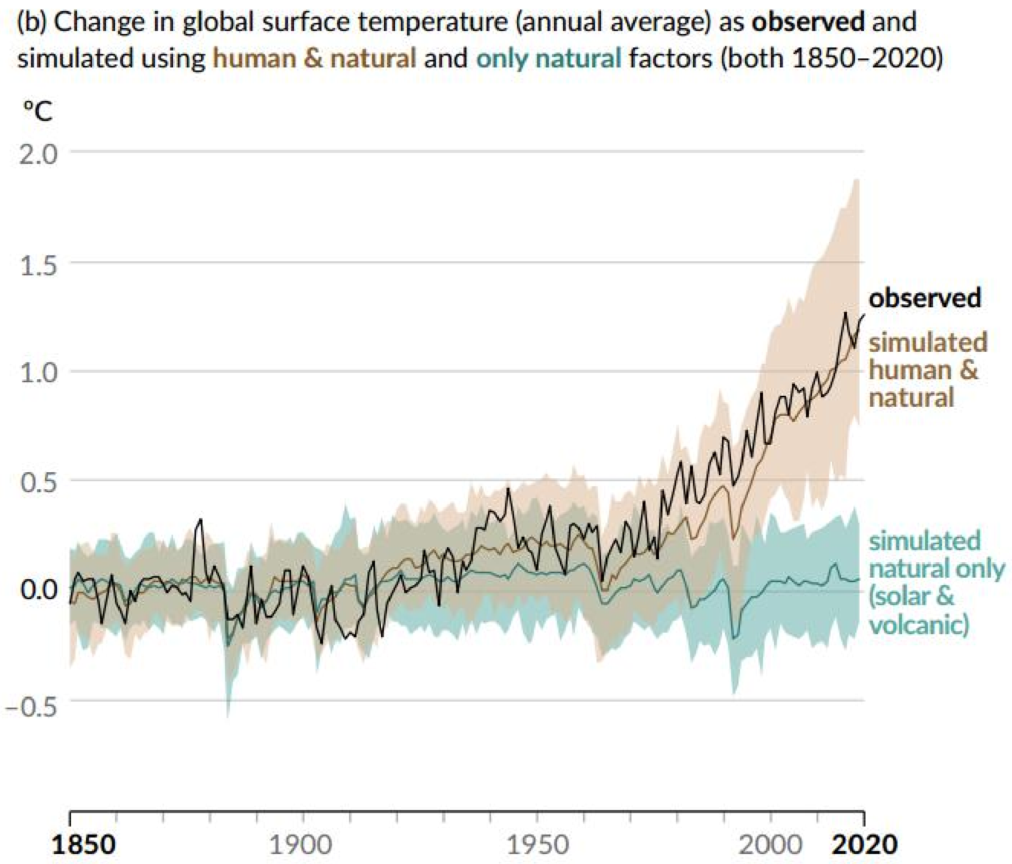
DEQ
DEPARTAMENTO DE
ENGENHARIA QUÍMICA

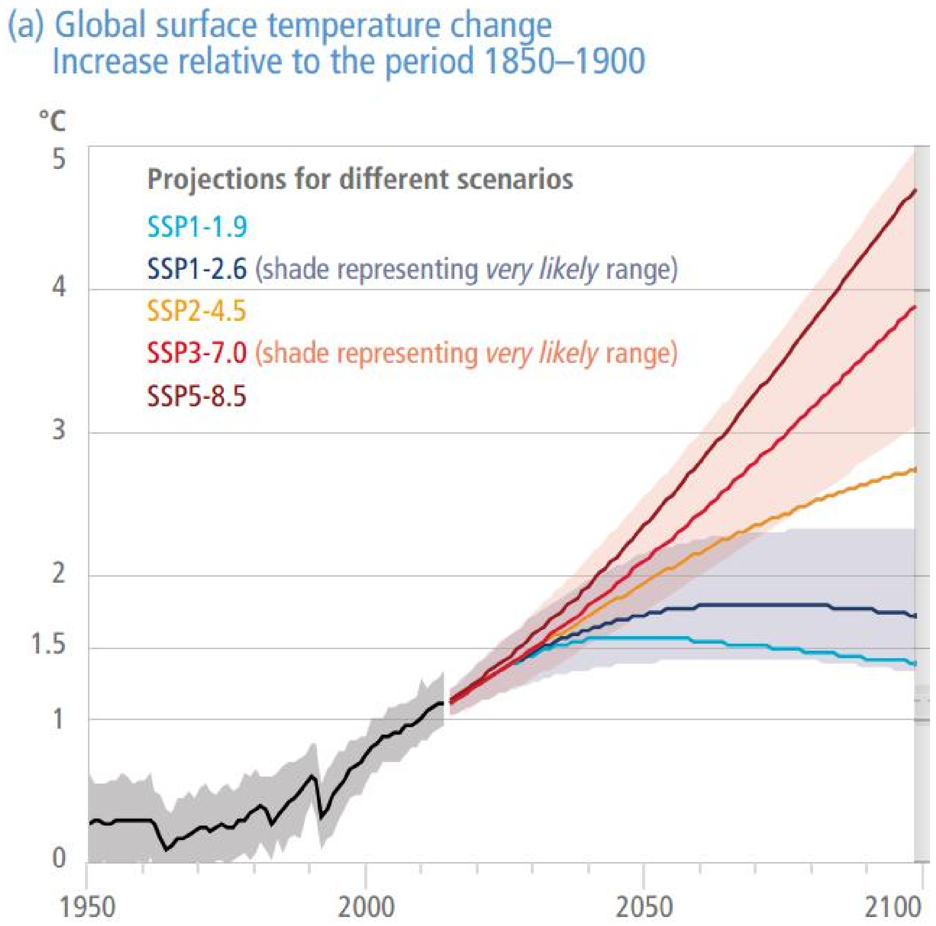
LaDABio

Energy Systems Initiative seminar Fall 2023

Climate Crisis



(b) Change in global surface temperature (annual average) as **observed** and simulated using human & natural and only natural factors (both 1850–2020)



(a) Global surface temperature change
Increase relative to the period 1850–1900

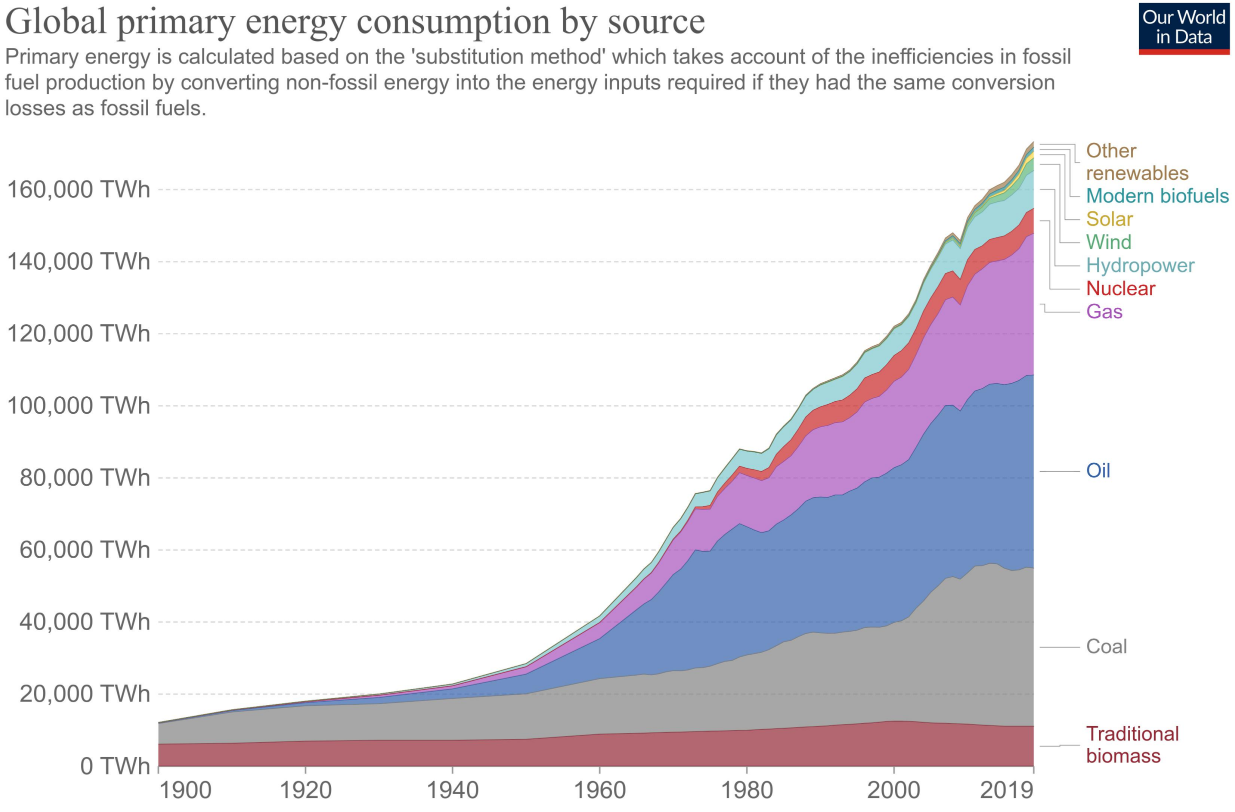
IPCC, 2021: Summary for Policymakers. In: Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change

IPCC, 2022: Summary for Policymakers. In: Climate Change 2022: Impacts, Adaptation, and Vulnerability. Contribution of Working Group II to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change

World’s energy matrix

Global primary energy consumption by source

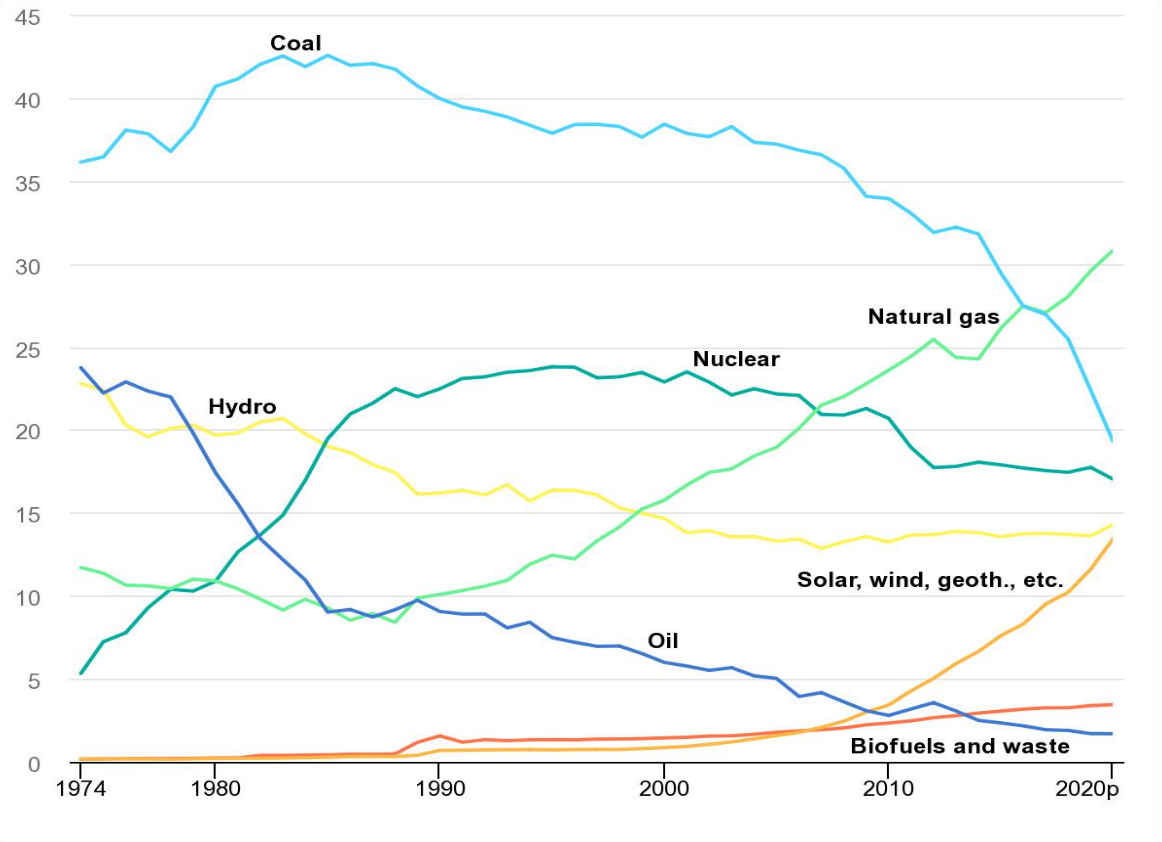
Primary energy is calculated based on the 'substitution method' which takes account of the inefficiencies in fossil fuel production by converting non-fossil energy into the energy inputs required if they had the same conversion losses as fossil fuels.



Source: Vaclav Smil (2017) & BP Statistical Review of World Energy

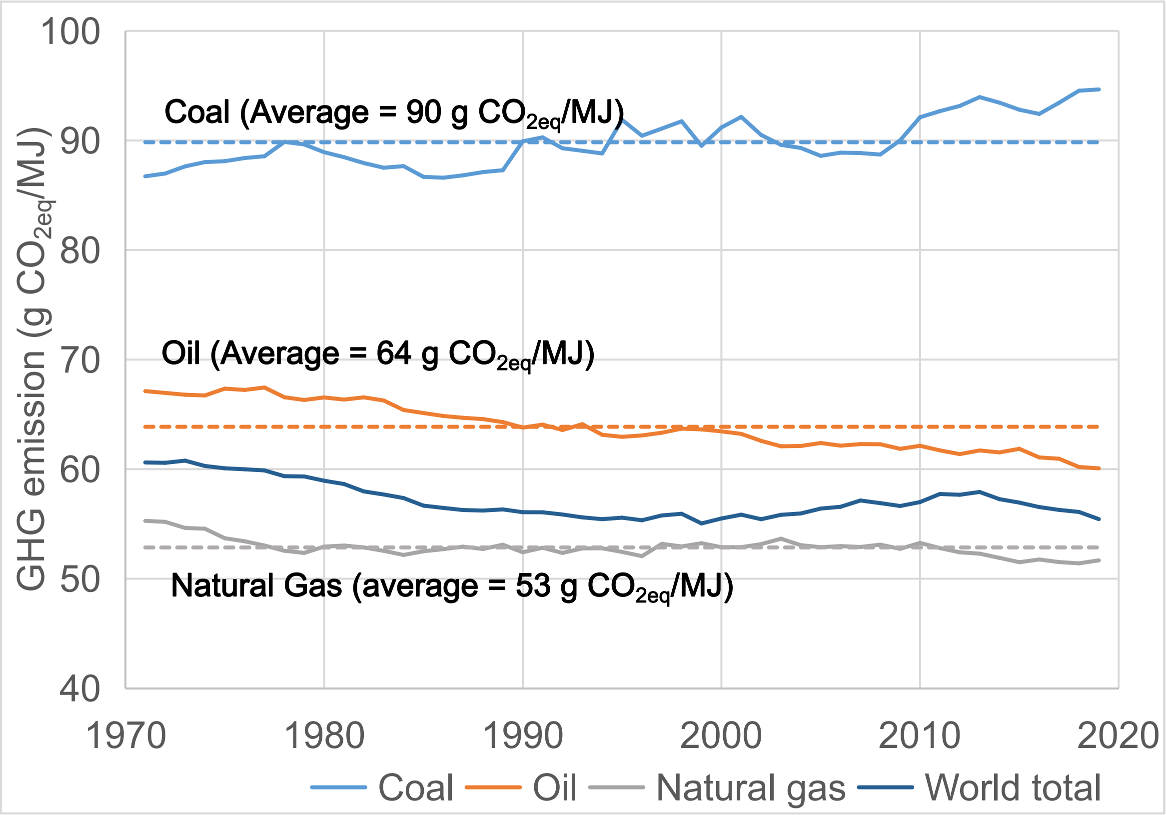
OurWorldInData.org/energy • CC BY

Contribution of different primary sources in electric energy production in OCDE countries.



IEA, Share of OECD gross electricity production by source, 1974-2020p, IEA, Paris https://www.iea.org/data-and-statistics/charts/share-of-oecd-gross-electricity-production-by-source-1974-2020p

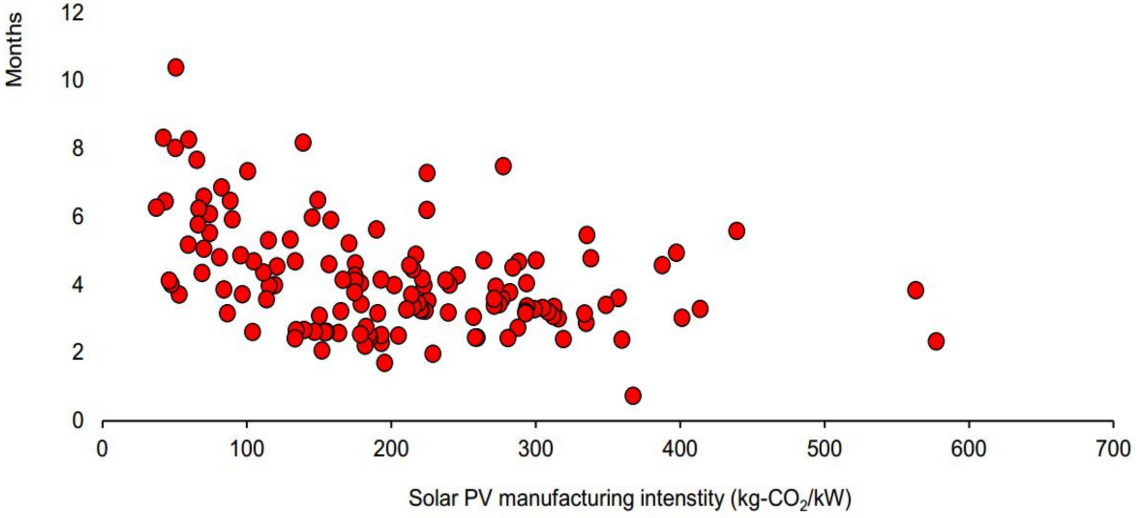
GHG in Energy production



IEA (2021), *Greenhouse Gas Emissions from Energy*

bp Statistical Review of World Energy, 71st edition, 2022

Solar photovoltaic carbon intensity and payback time (each point represents a country)



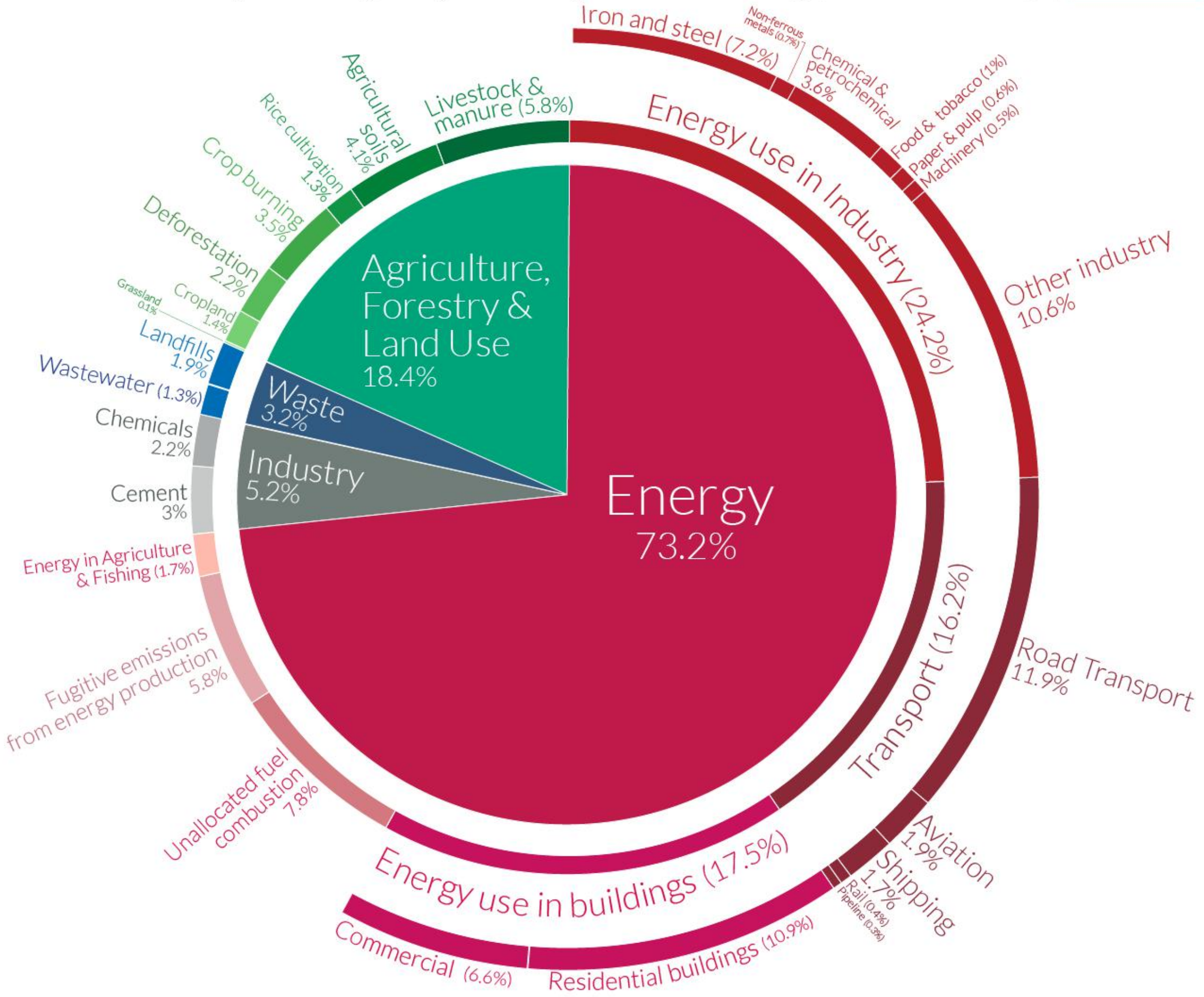
IEA, Solar PV manufacturing emissions intensity and payback period, IEA, Paris https://www.iea.org/data-and-statistics/charts/solar-pv-manufacturing-emissions-intensity-and-payback-period

Greenhouse gas emissions by sector

Global greenhouse gas emissions by sector

This is shown for the year 2016 – global greenhouse gas emissions were 49.4 billion tonnes CO_2eq.

Our World in Data

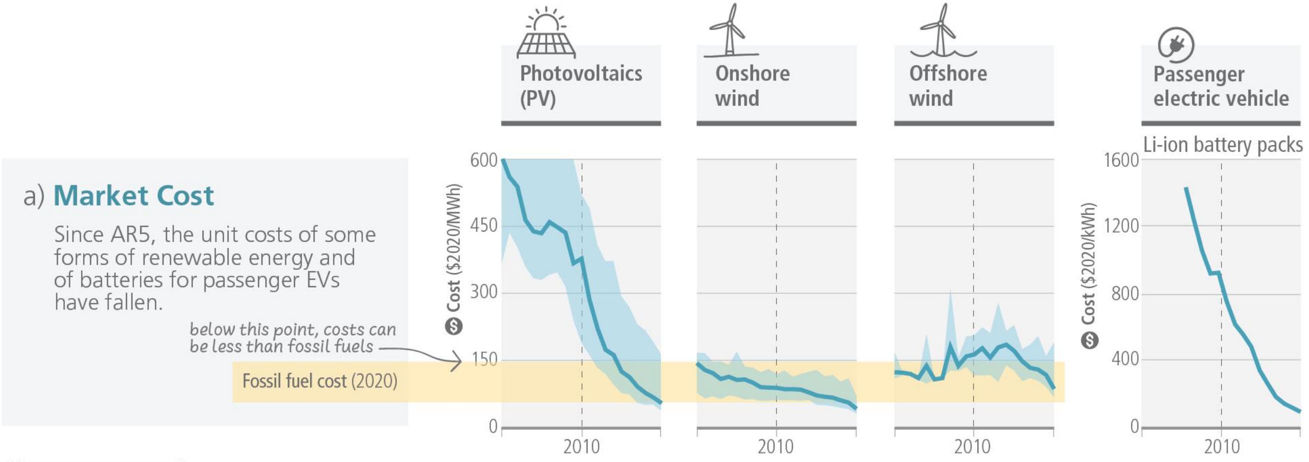


OurWorldinData.org – Research and data to make progress against the world's largest problems.
Source: Climate Watch, the World Resources Institute (2020).
Licensed under CC-BY by the author Hannah Ritchie (2020).

GHG in Electric Energy production

Electrification seems the answer. But car batteries will be a bottleneck in the near future.

Renewable electricity generation is increasingly price-competitive and some sectors are electrifying

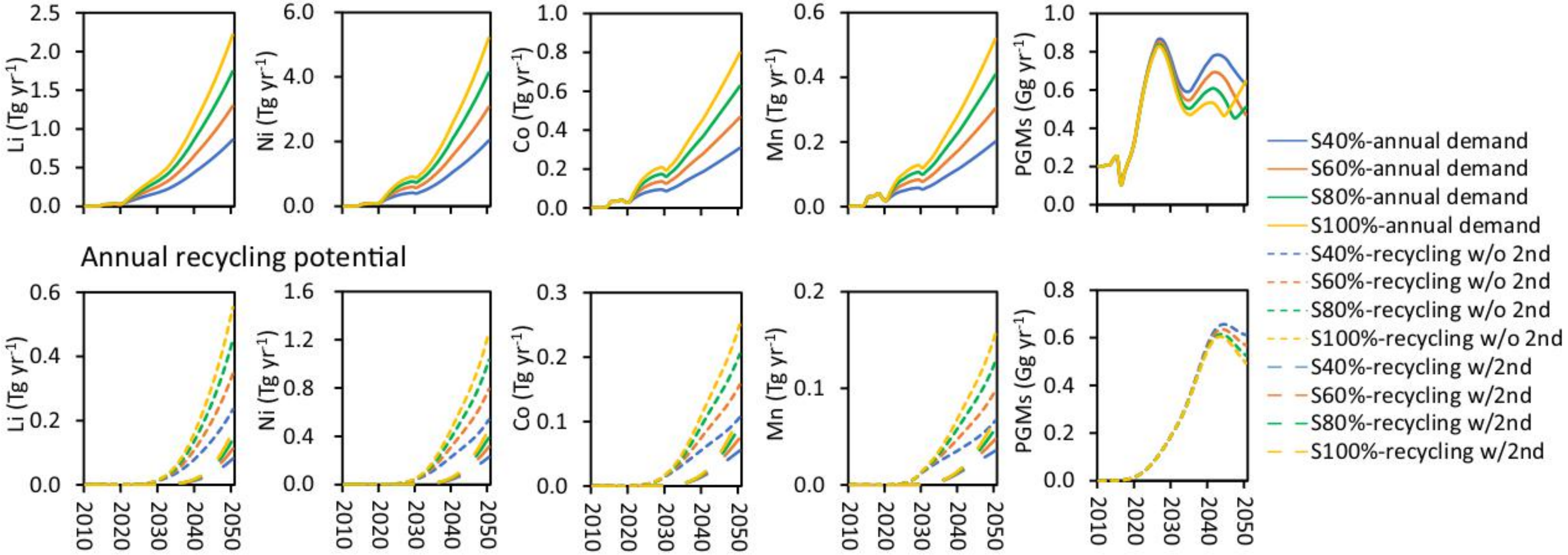


a) **Market Cost**

Since AR5, the unit costs of some forms of renewable energy and of batteries for passenger EVs have fallen.

below this point, costs can be less than fossil fuels

IPCC, 2023: Climate Change 2023: Synthesis Report of the IPCC Sixth Assessment Report (AR6).

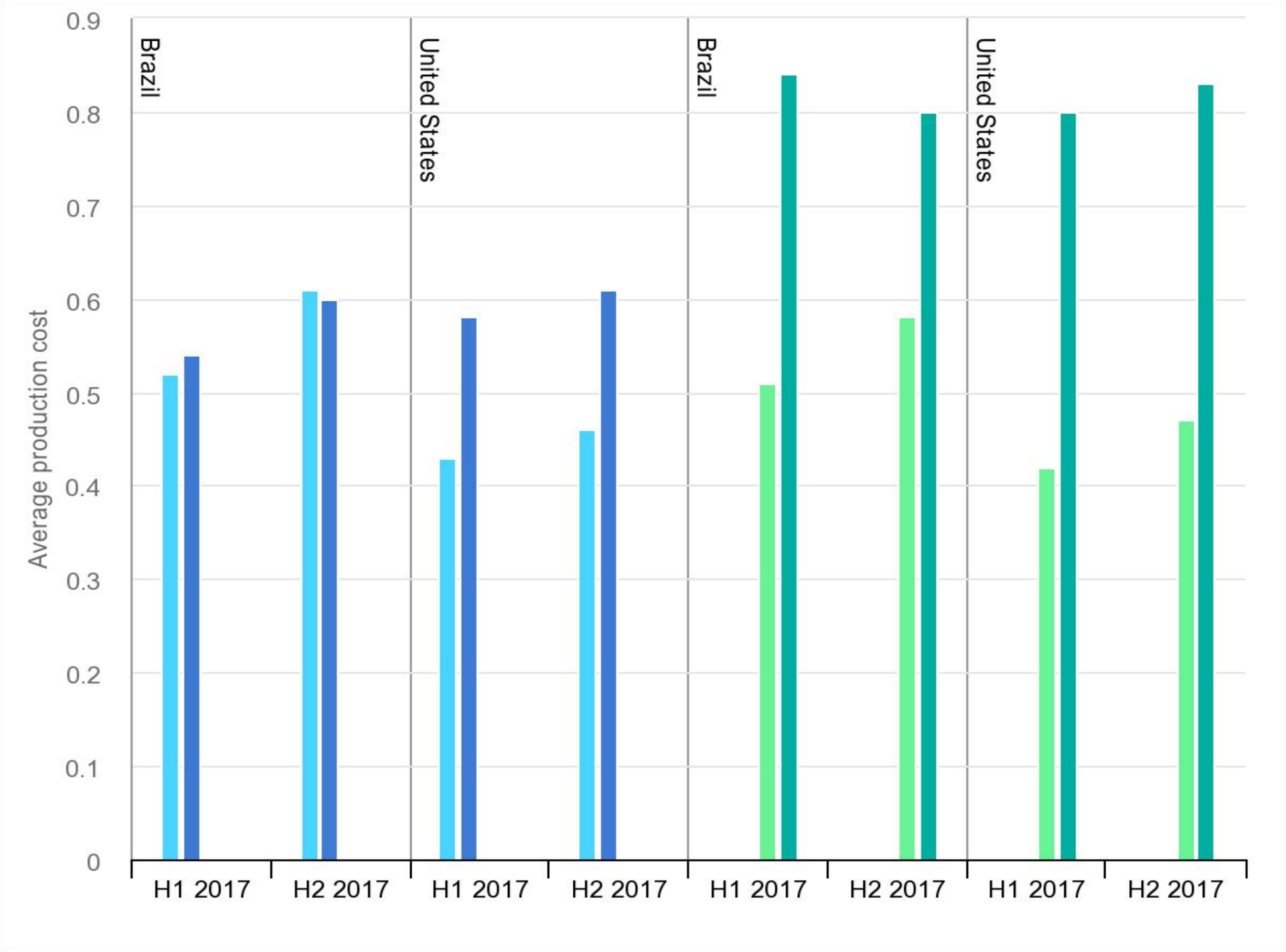


Annual recycling potential

Zhang C, Zhao X, Sacchi R, You F. Trade-off between critical metal requirement and transportation decarbonization in automotive electrification, 2023, nature communications, 14, 1616.

Economic feasibility of biofuels

Biofuels costs compared to fossil fuel alternatives:



H1: First half of the year, H2: second half

🟦 gasoline

🟦 ethanol

🟩 diesel

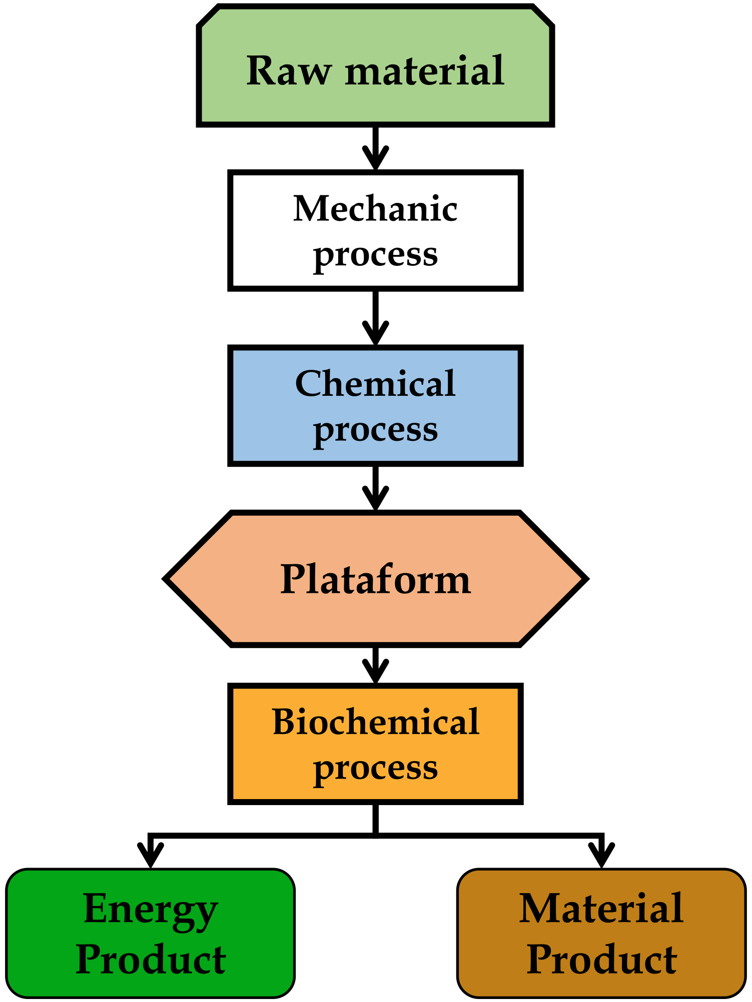
🟩 biodiesel

Europe (2014-2016):

- Ethanol: 15-22 €/GJ (gasoline: 12 €/GJ)
- Biodiesel: 16-21 €/GJ (diesel: 11 €/GJ)

IEA, Biofuel and fossil-based transport fuel production cost comparison, 2017, IEA, Paris https://www.iea.org/data-and-statistics/charts/biofuel-and-fossil-based-transport-fuel-production-cost-comparison-2017

Biorefineries



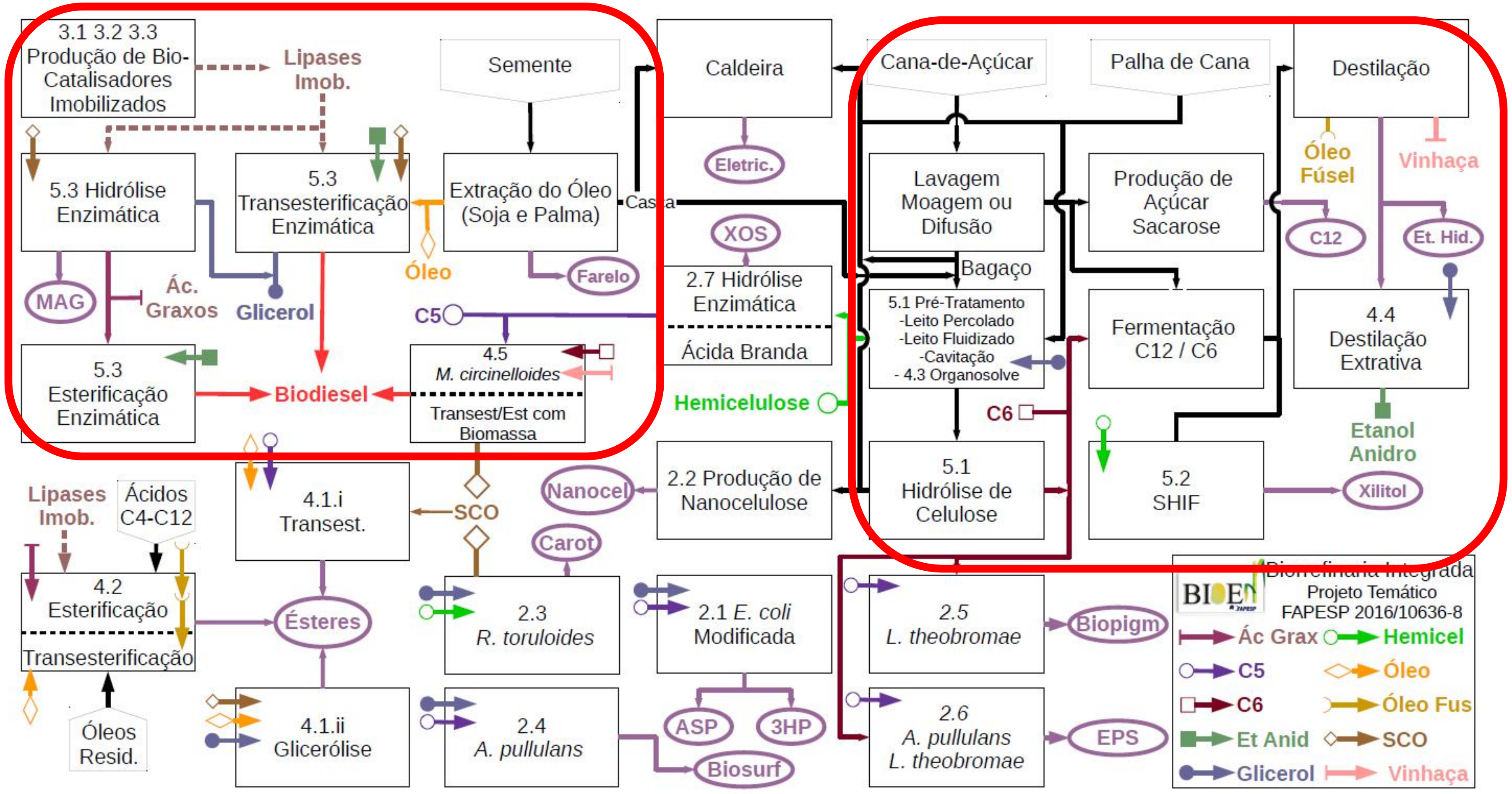
Acording to the International Energy Agency:

"Biorefinery is the sustainable processing of biomass into a spectrum of marketable products (food, feed, materials, chemicals) and energy (fuels, power, heat)"

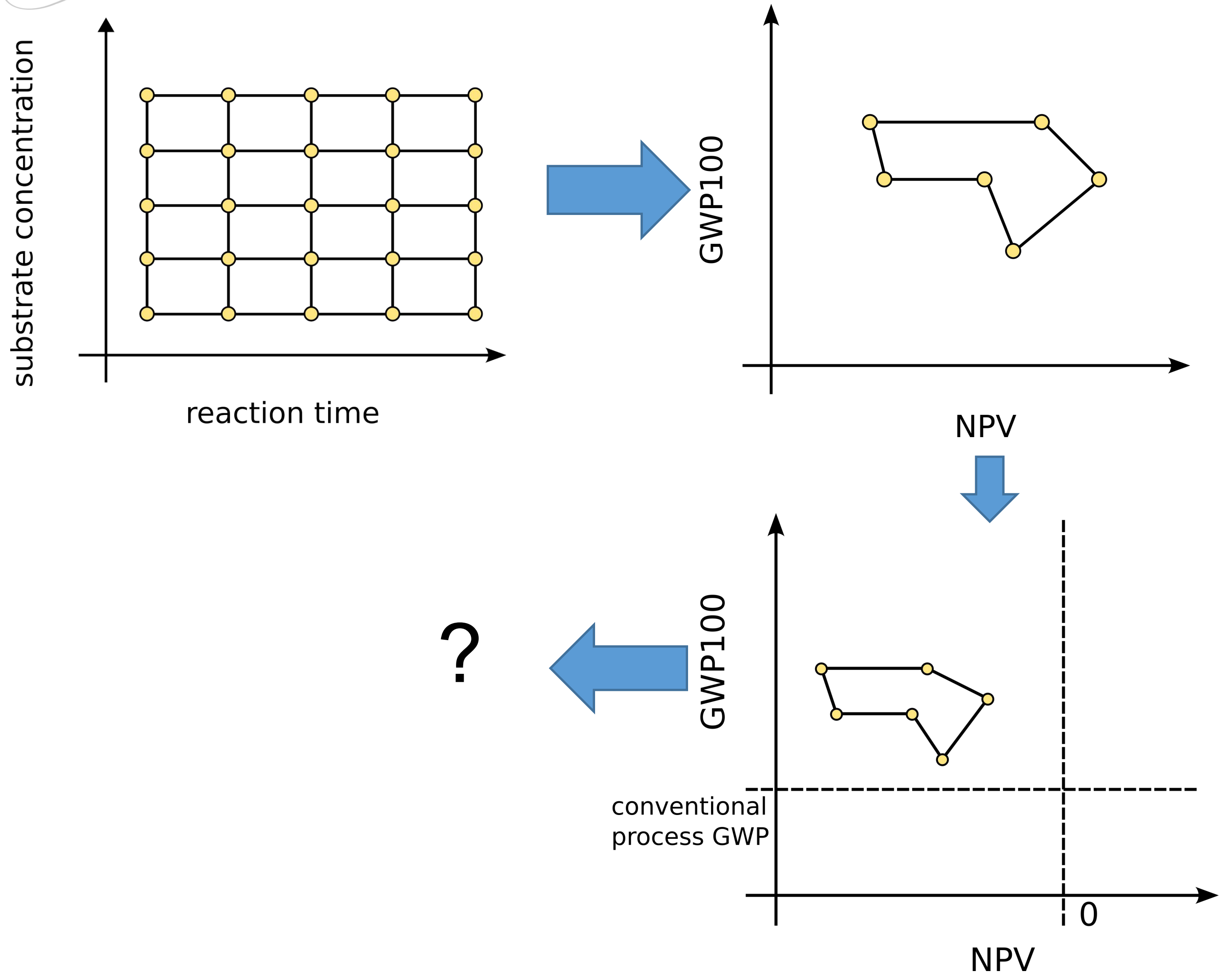
Biorefineries, similarly to oil refineries, are multipurpose plants, with a "backbone" (biofuels) and countless derivatives.

Cherubini, F.; Jungmeier, G.; Wellisch, M.; Willke, T.; Skiadas, I.; Van Ree, R.; Jong, E. Toward a common classification approach for biorefinery systems. Biofuels, Bioprod. Bioref. 2009, 3:534-546.

From cell factories to a biodiesel-bioethanol biorefinery



The problem: These processes are rarely feasible at the experimental conditions



- Optimization will find the best condition. But what if it is not feasible?
- Trying to find feasible conditions means extrapolating the models. Bad idea, specially for biochemical models.
- What information can we get to guide the experimental effort?

General metrics for biochemical processes

Process metrics	Cost	Annual Production	Biocatalyst yield	Reaction yield	Space-time yield	Product concentration	ee
Units	€/kg	ton/year	$g_{product}/g_{biocatalyst}$	%	$g_{product}/L_{reactor}/h$	$g_{product}/L_{reactor}$	%
Bulk chemical	0.5-10	10^4-10^6	10^3-10^5	>95	>20	>300	>90
Fine chemical	10-50	10^2-10^4	10^2-10^3	>90	>2.5	>150	>95
Pharmaceutical chemical	>100	10-10^3	10-10^2	>90	>1	>60	>95

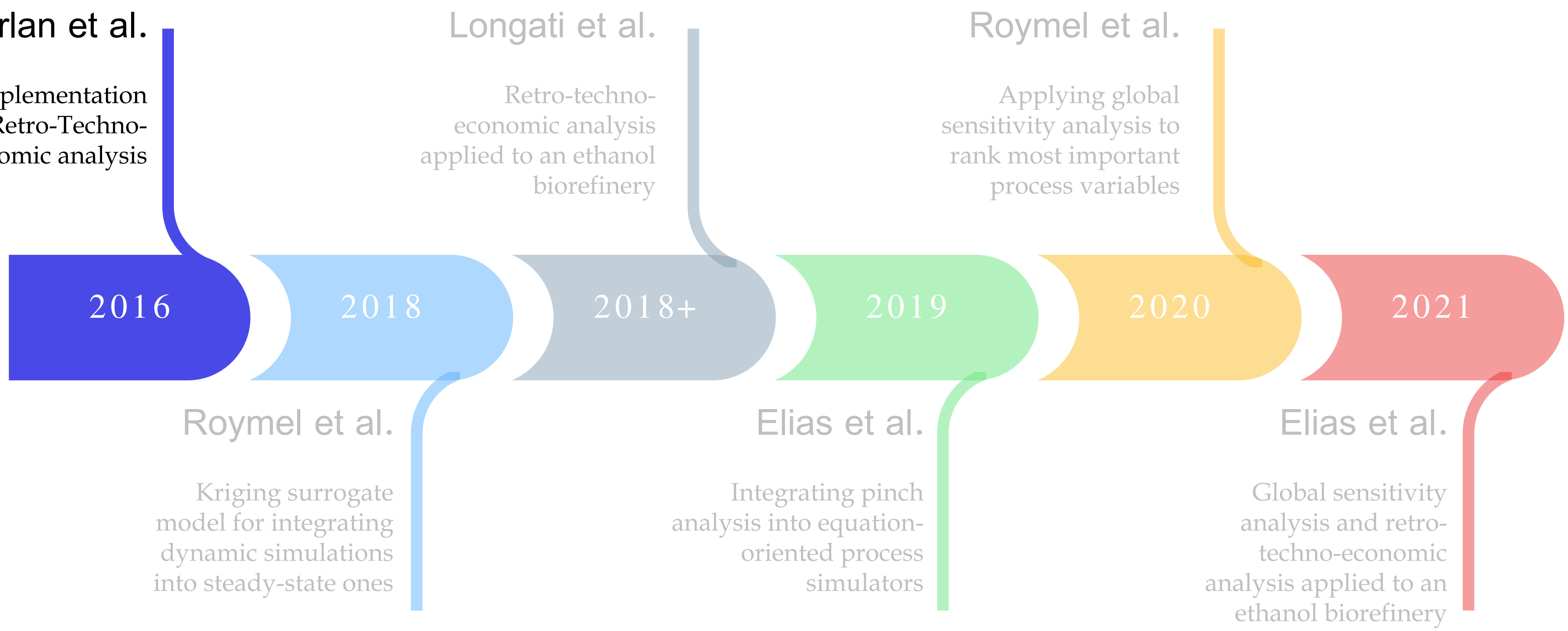
Lima-Ramos, J. A methodology for development of biocatalytic processes, PhD Thesis, Technical University of Denmark, 2013.

Retro-Techno-Economic-Environmental Analysis (RTEEA)

Turning the problem upside down!

http://kids.nationalgeographic.com/content/dam/kids/photos/articles/Other%20Explore%20Photos/R-Z/Wacky%20Weekend/Upside-Down%20Animals/ww-upside-down-animals-humpback-whale.adapt.945.1.jpg

The path we took



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Furlan: First RTEEA implementation and tests

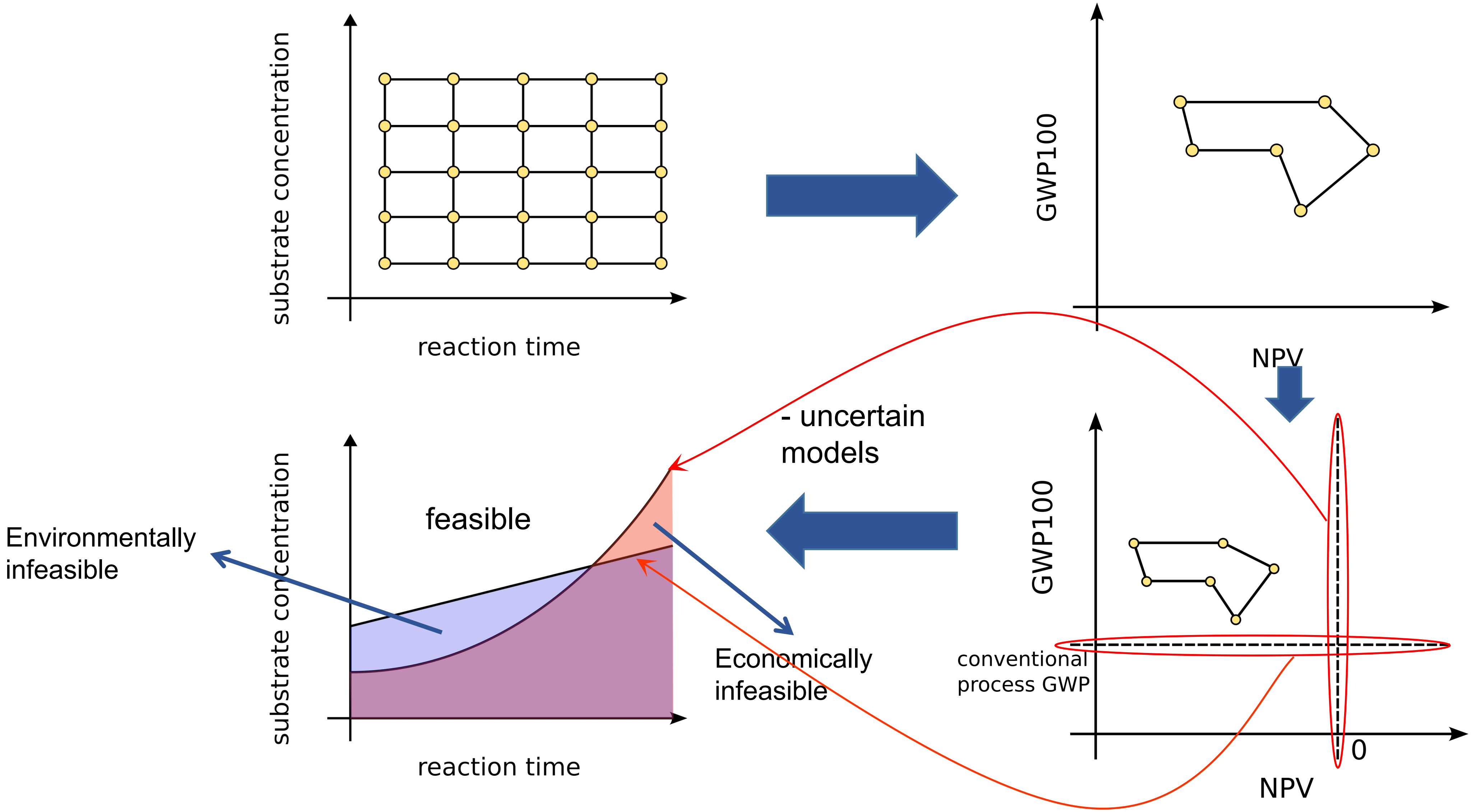
Economic and environmental analyses:

- Equations easy to solve, which does not impact the simulation convergence.

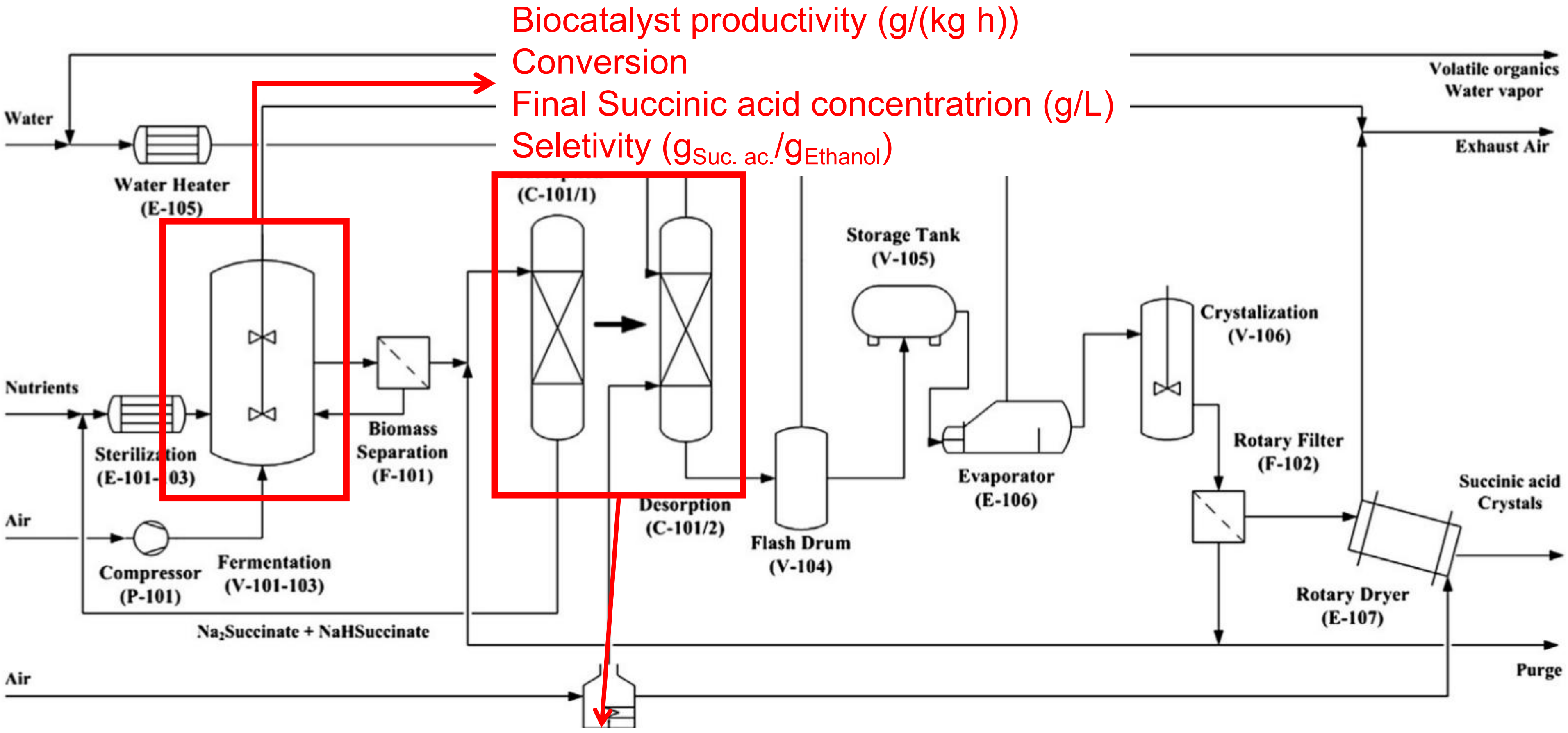
$$NPV = \sum_{i=1}^{Nt} \frac{CF_i(x)}{(1+r)^i} - \sum_{j=1}^{Neq} K_j(A_j(x))^{\alpha_j} \qquad I_i = \sum_{j=1}^{M} F_j \sum_{k=1}^{N} \theta_{ik} x_{jk}$$

- We include all equations responsible for both analysis in the simulation procedure, to be solved simultaneously to the process model equations.
- Knowledge about process economic feasibility and impacts are attained at simulation time.

Furlan: First RTEEA implementation and tests



Furlan: First RTEEA implementation and tests
Case study: Succinic acid production from glucose by *Sac. cerevisiae*



Biocatalyst productivity (g/(kg h))

Conversion

Final Succinic acid concentratrion (g/L)

Seletivity ($g_{Suc.\ ac.}/g_{Ethanol}$)

Adsorption selectivity ($g_{Suc.\ ac.}/g_{Ethanol}$)

Furlan FF, Costa CBB, Secchi AR, Woodley JM, Giordano RC. Retro-Techno-Economic Analysis: Using (Bio)Process Systems Engineering Tools to Attain Process Target Values. Industrial & Engineering Chemistry Research, 2016, 55, 9865-9872.

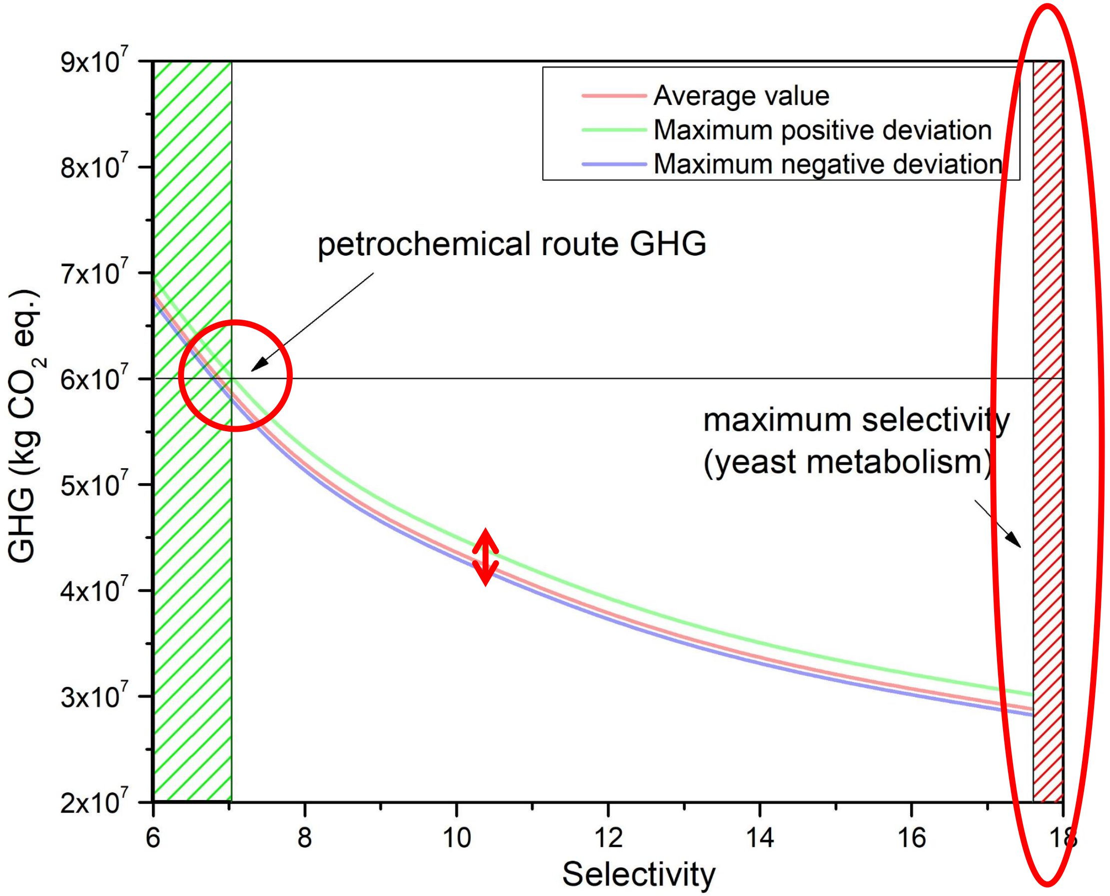
Furlan: First RTEEA implementation and tests
“Global” sensitivity analysis

Simultaneous modeled variables	variables considered					R^2	
	Csa	Pr	Conv	Selet	Sel_ad	NPV	GHG
5	1	1	1	1	1	0,996	0,994
4	1	1	1	1	0	0,996	0,994
3	1	1	0	1	0	0,996	0,994
2	1	1	0	0	0	0,923	0,086
	0	1	0	1	0	0,109	0,994
1	0	0	0	1	0	0,001	0,994
	1	0	0	0	0	0,672	0,039

Elias AM; Furlan FF, Ribeiro MPA, Giordano RC. Retro-Techno-Economic-Environmental Analysis (RTEEA) from the cradle: a new approach for process development. European Symposium on Computer Aided Process Engineering, 2018, Graz, Austria.

Furlan: First RTEEA implementation and tests

Results: GHG emission



Greenhouse gas emissions from petrochemical route = 1.94 kg CO_2eq/kg succinic acid. Equivalent to a selectivity of 7.0

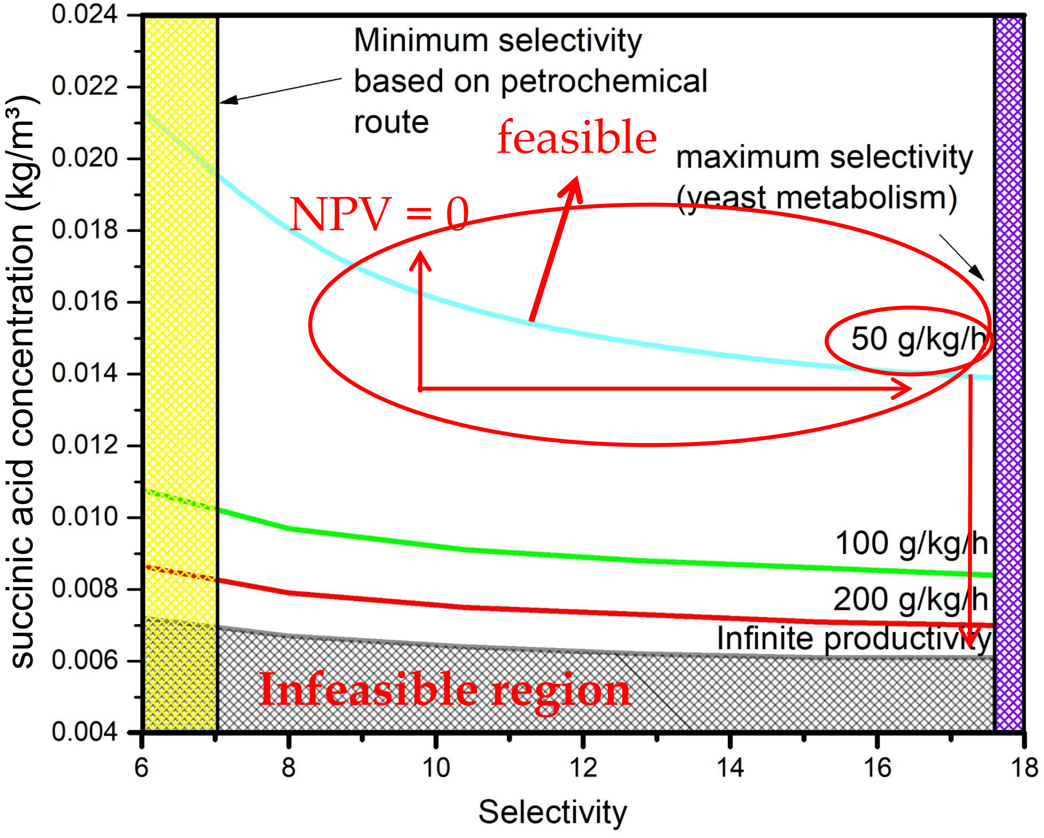
Limit imposed by the yeast metabolism on selectivity (equal to 17.6)

Effect on GHG caused by all the other variables

Elias AM; Furlan FF, Ribeiro MPA, Giordano RC. Retro-Techno-Economic-Environmental Analysis (RTEEA) from the cradle: a new approach for process development. European Symposium on Computer Aided Process Engineering, 2018, Graz, Austria.

Furlan: First RTEEA implementation and tests

Results: Economic feasibility



Biocatalyst productivity (g/(kg h)).

The effect of biocatalyst productivity decreases sharply. Hardly justify increasing it beyond 100 g/kg/h.

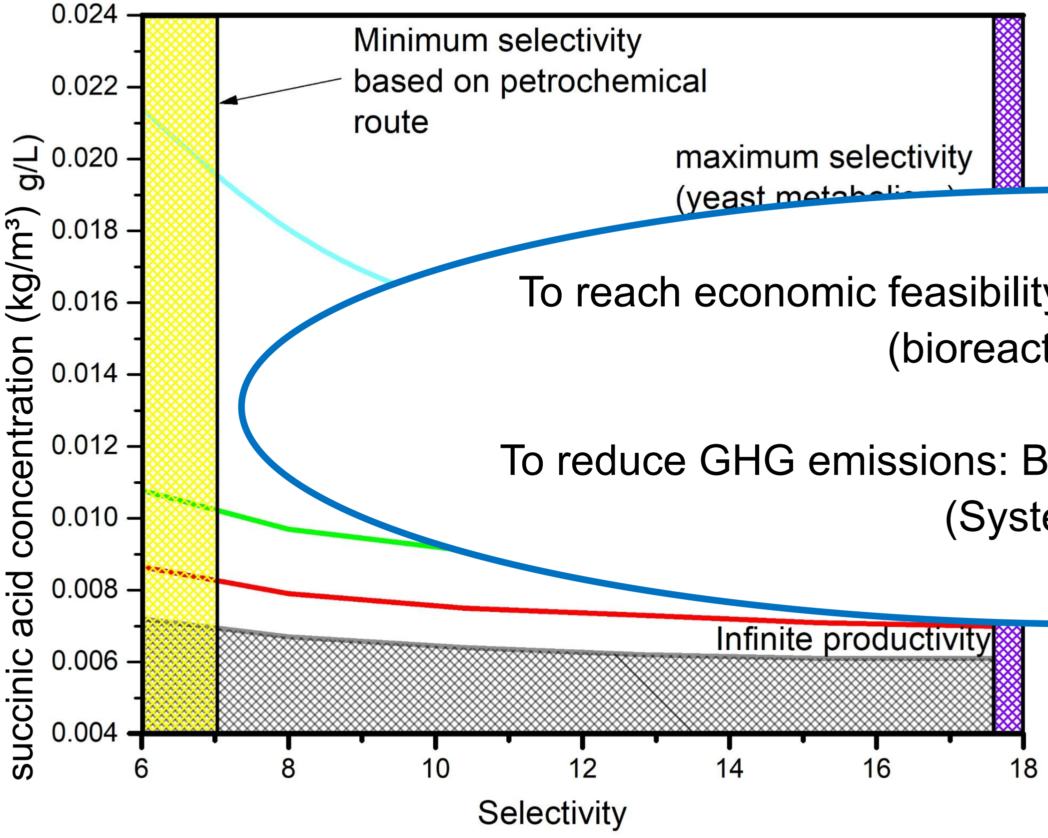
Infinit biocatalyst productivity limit (equals to a zero reaction time) Therefore, the minimum feasible product concentration is 7 g/L

Increasing selectivity does not help much. It's better to increase the maximum product concentration.

Elias AM; Furlan FF, Ribeiro MPA, Giordano RC. Retro-Techno-Economic-Environmental Analysis (RTEEA) from the cradle: a new approach for process development. European Symposium on Computer Aided Process Engineering, 2018, Graz, Austria.

Furlan: First RTEEA implementation and tests

Results: Economic feasibility

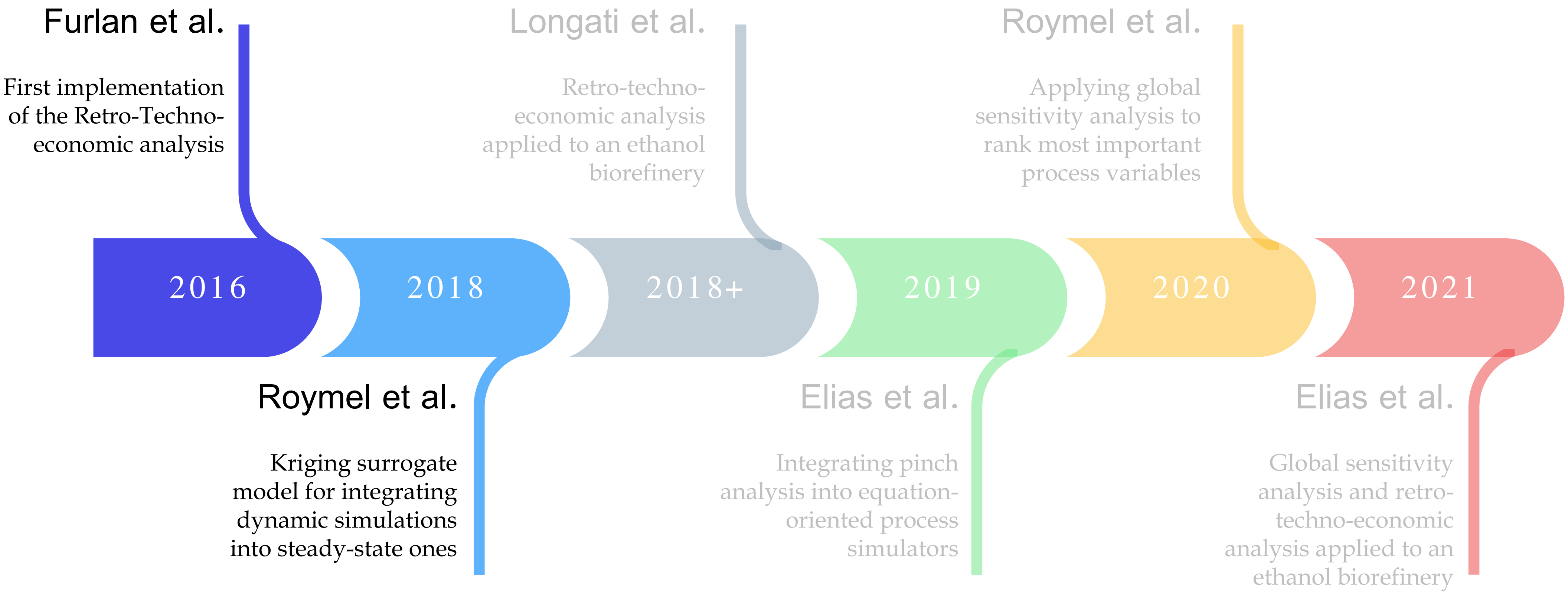


To reach economic feasibility: optimize the bioreactor operation (bioreactor engineering)

To reduce GHG emissions: Back to cloning to increase selectivity (Systems biology)

Elias AM; Furlan FF, Ribeiro MPA, Giordano RC. Retro-Techno-Economic-Environmental Analysis (RTEEA) from the cradle: a new approach for process development. European Symposium on Computer Aided Process Engineering, 2018, Graz, Austria.

The path we took



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Roymel: Kriging-based metamodels to integrate dynamic models into whole plant steady-state simulations

There are several types of models for Kriging, but to approximate the behavior of nonlinear systems, the most used are ordinary Kriging and universal Kriging.

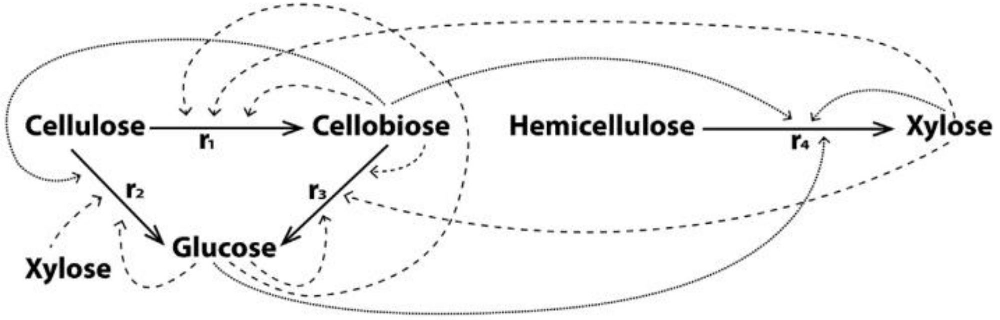
$$\hat{y}(x) = \mu(x) + z(x)$$

In this model, the first term represents the variation in the mean of the response variable and the second term represents the stochastic part of the response.

Characteristics:

- Perfect interpolator;
- μ(x) is normally a low order polinomial;
- z(x) is normally an exponencial function of the distance between points;

Roymel: Kriging-based metamodels to integrate dynamic models into whole plant steady-state simulations



Model of enzymatic hydrolysis of sugarcane bagasse describing the conversion of cellulose as a function of solids fraction, enzymatic load and reaction time.

$$\frac{dC}{dt} = -r_1 \text{-} r_2$$

$$\frac{dG2}{dt} = 1.056 r_1 \text{-} r_3$$

$$\frac{dG}{dt} = 1.111 r_2 + 1.053 r_3$$

$$\frac{dH}{dt} = -r_4$$

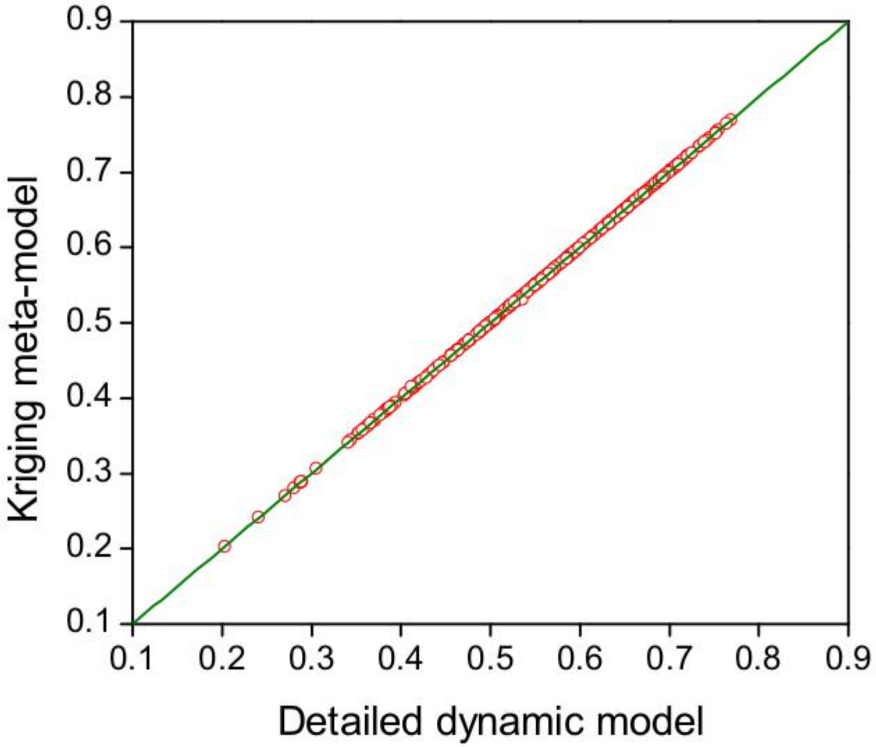
$$\frac{dX}{dt} = 1.136 r_4$$

$$r_i = \frac{k_{ir} E_{BC} R_s S}{1 + \frac{G2}{k_{iIG2}} + \frac{G}{k_{iIG}} + \frac{X}{k_{iIX}}}$$

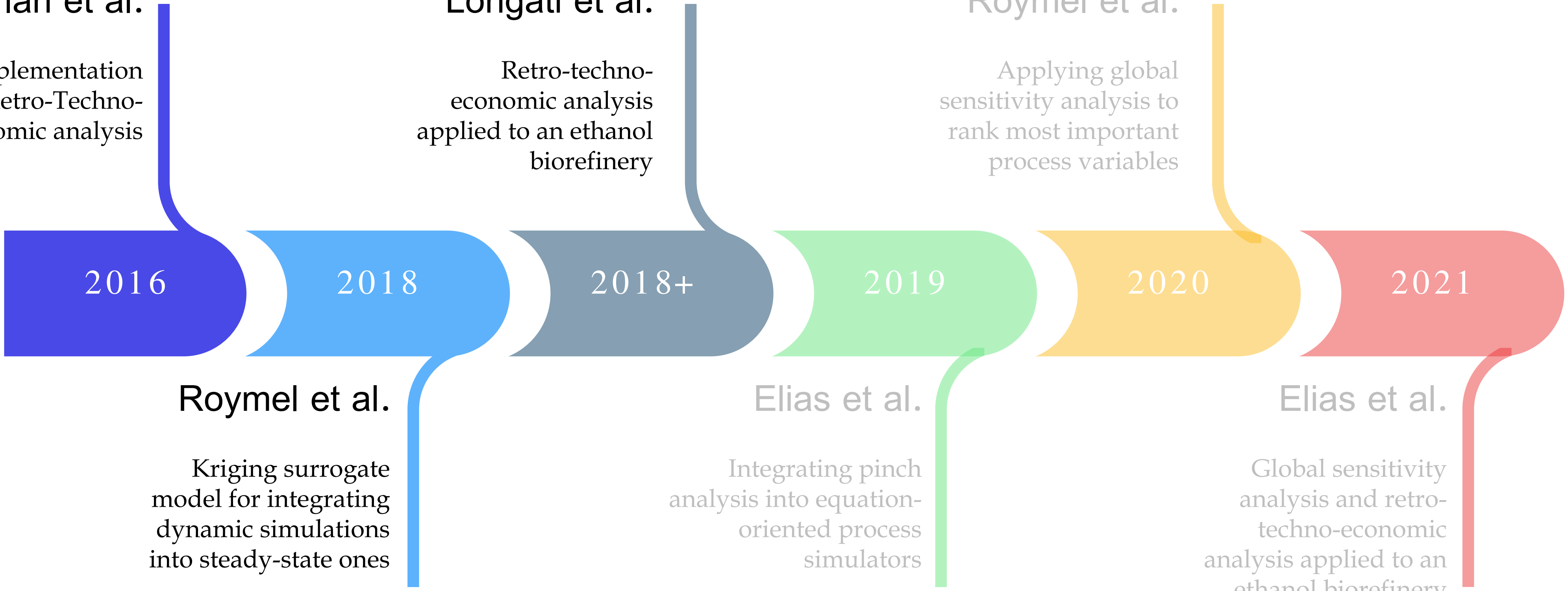
i = 1,2,4

$$r_3 = \frac{k_{2r} E_F G2}{K_{3M}\left(1 + \frac{G}{k_{3IG}} + \frac{X}{k_{3IX}}\right) + G2}$$

- Universal kriging using a second order polynomial for μ(x) and Gaussian function for z(x).
- Absolute acuracy of 10^{-2} mol/l.
- Kriging needed 500 points to achieve accuracy, while pure interpolation needed 2409 points to achieve the same result.



The path we took



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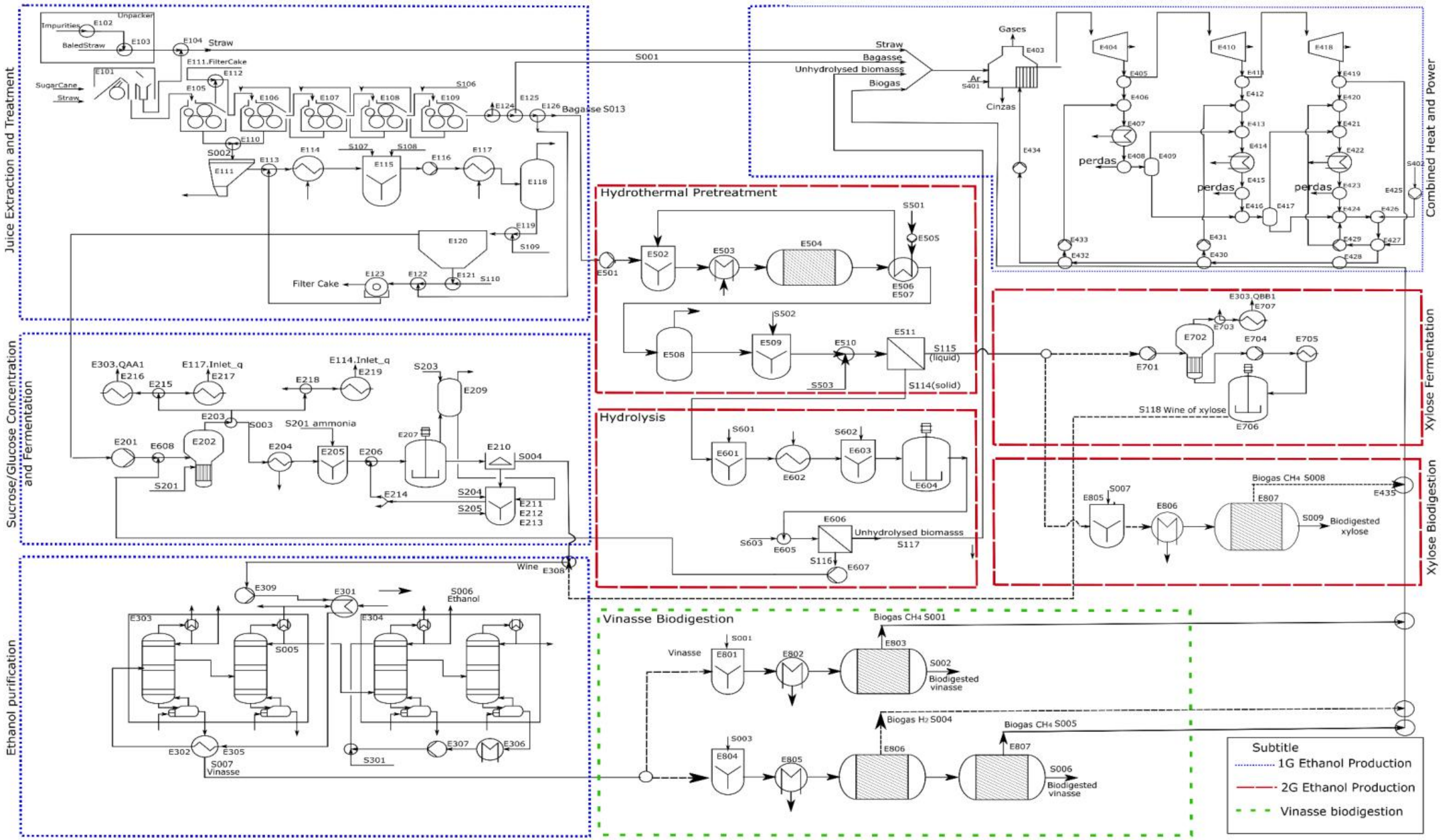
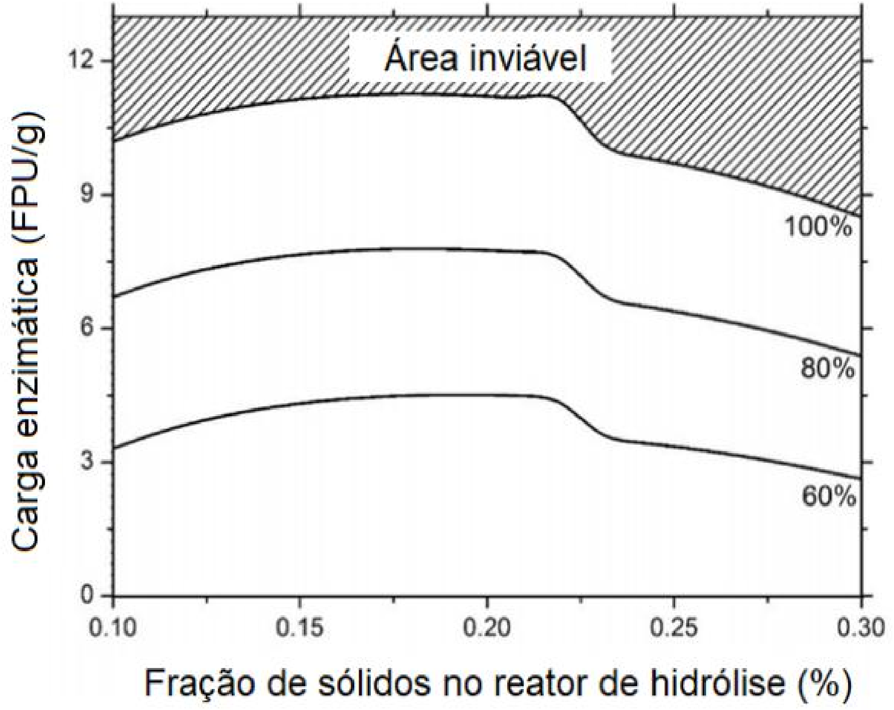
Longati: RTEA applied to 1G-2G Ethanol biorefinery



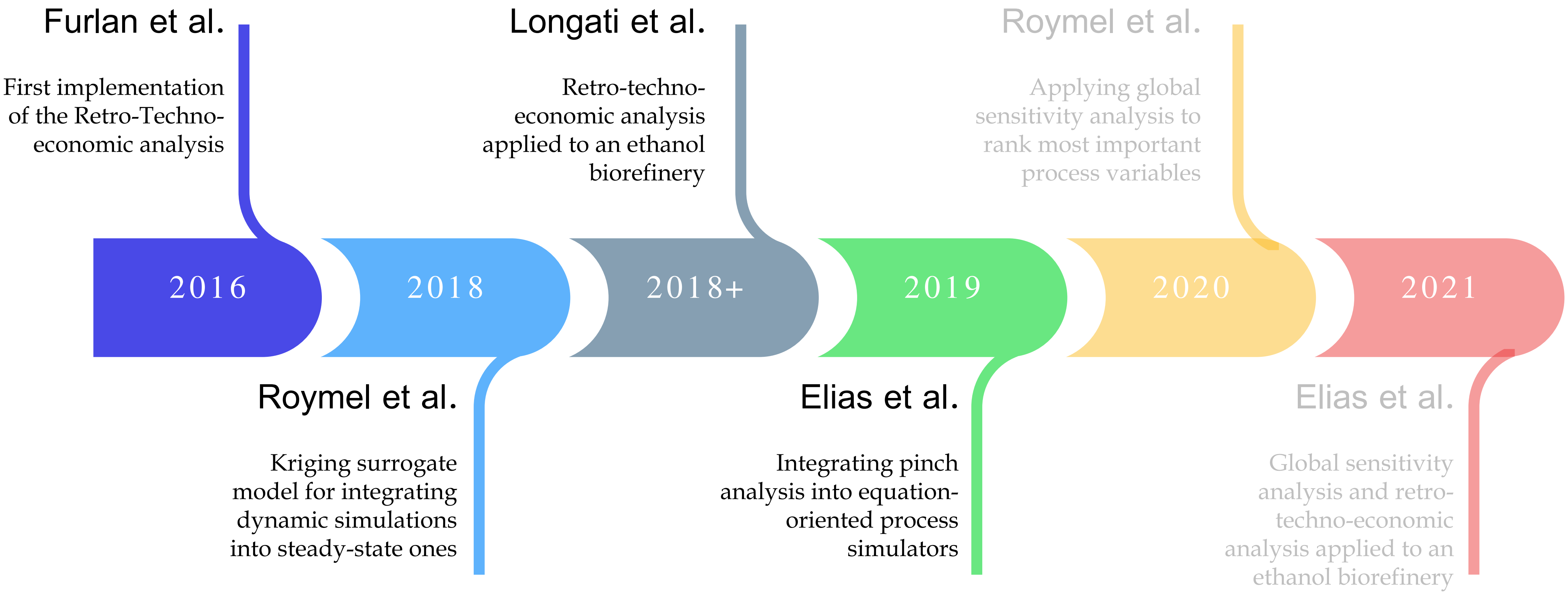
Longati, 2018

Longati: RTEA applied to 1G-2G Ethanol biorefinery



- Highest feasible enzyme load of 11.4 FPU/gcellulose.
- Negative curvature due to a tradeoff between solid load in the reactor (increasing final glucose concentration) and glucose recovery in the downstream stages.
- Discontinuities around 22% of solids are due to layout changes in the heat integration.

The path we took



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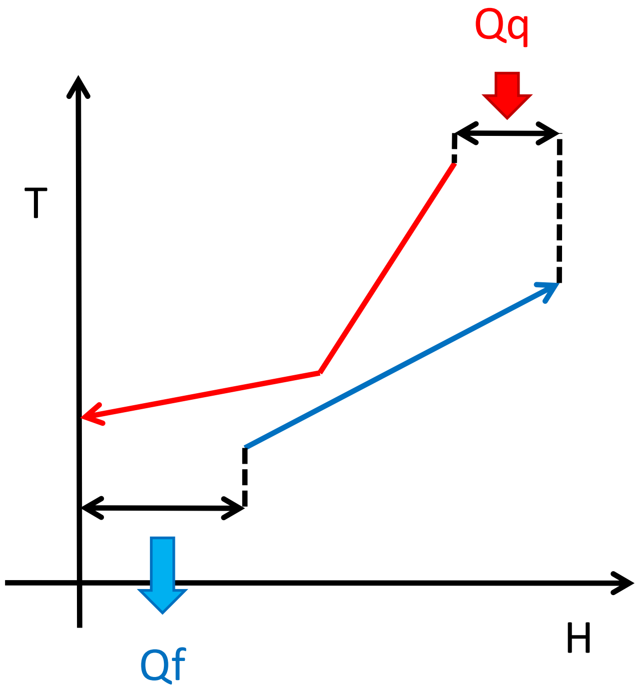
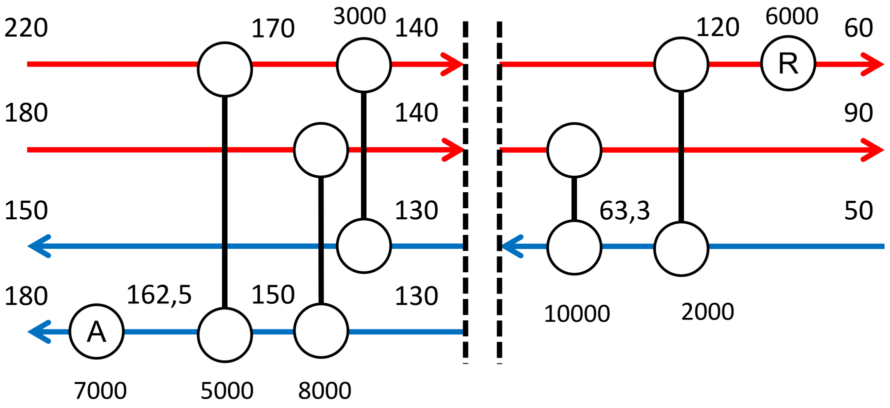
Elias: Integrating pinch analysis into equation-oriented process simulators

1- Minimum demands for hot and cold utilities



2- Construction of the heat exchanger network



3- Economic analysis

Approximate estimate based on the calculation of investment cost targets.

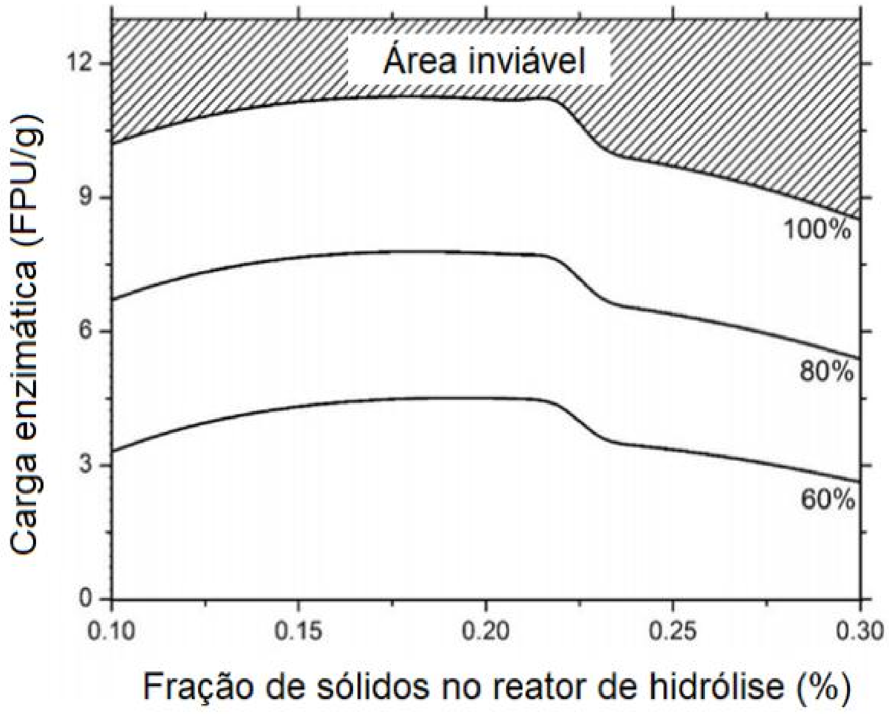
Elias: Integrating pinch analysis into equation-oriented process simulators
Results: Distance from the optimum

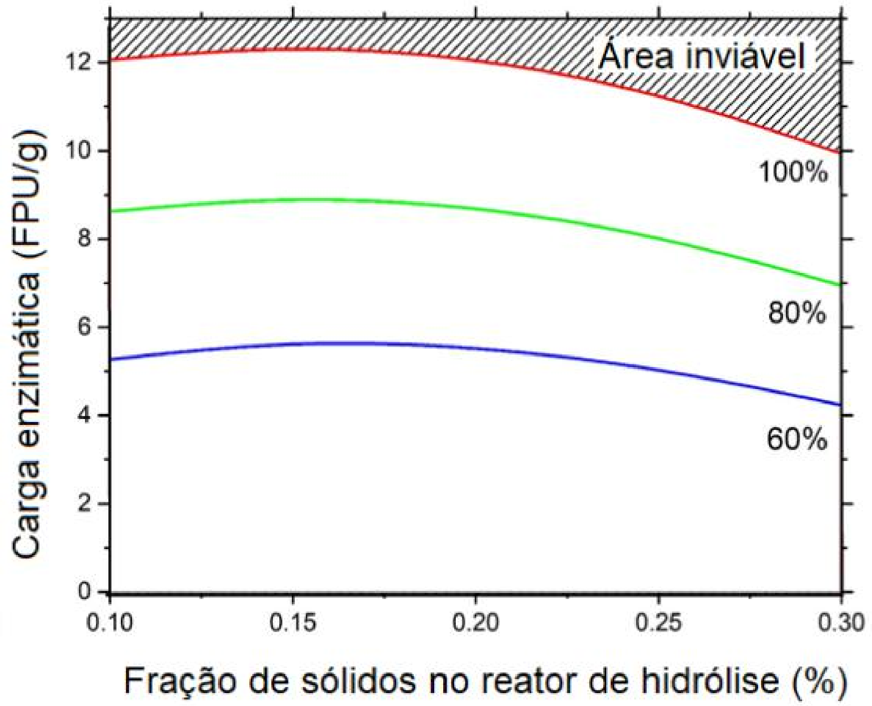
Case study	ΔT_{min}	# of units	Total annualized cost(US$/ano)		Deviation from optimum(%)
			Literature	Our work	
1	5	6	117.062,3	127.268,0	8,0
2	10	9	573.205,0	611.322,0	5,7
3	10	10	43.314,0	48.500,2	10,7
4	10	27	1.510.891,0	1.606.330,0	5,9

AM Elias, RC Giordano, AR Secchi, FF Furlan. Integrating pinch analysis and process simulation within equation-oriented simulators. Comp Chem Eng, 130, 106555, 2019.

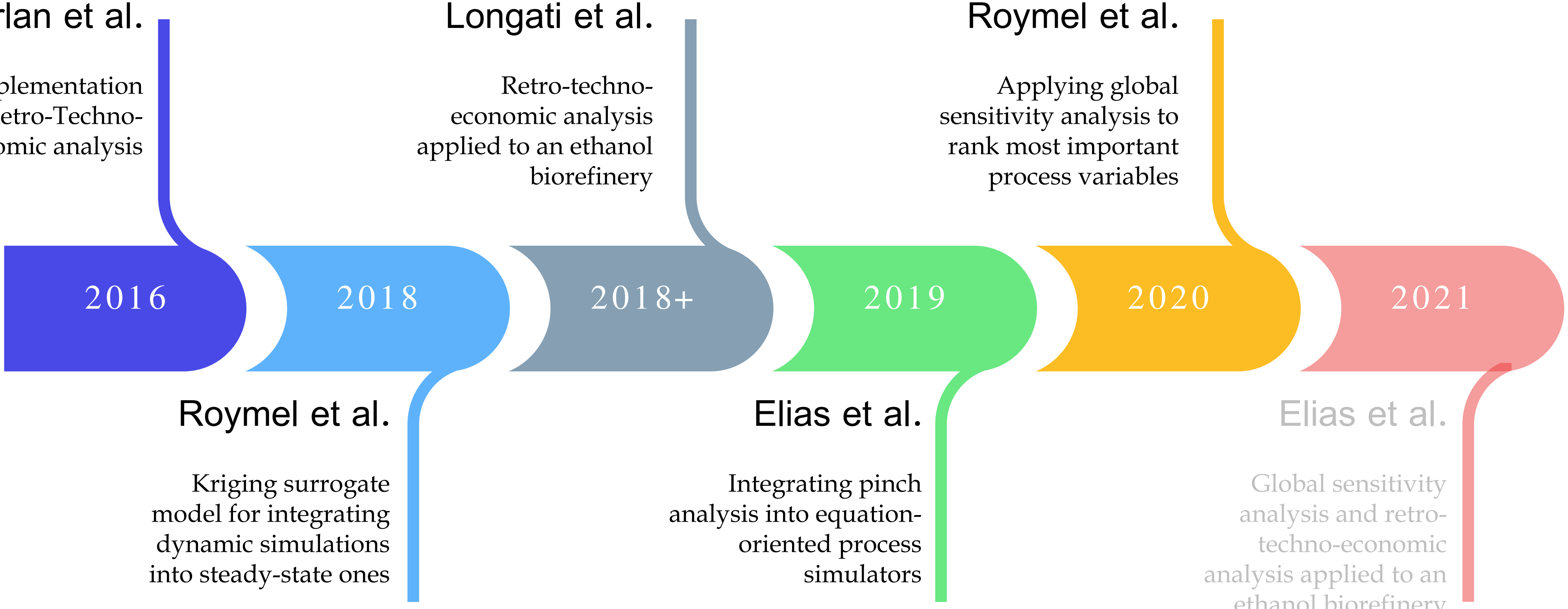
Elias: Integrating pinch analysis into equation-oriented process simulators
Results: Pinch analysis applied to a biorefinery

Extra advantage of using Pinch analysis:
Replaces the process heat exchanger network with a “virtual” network.
Increases simulation robustness and smoothes layout transitions.





The path we took



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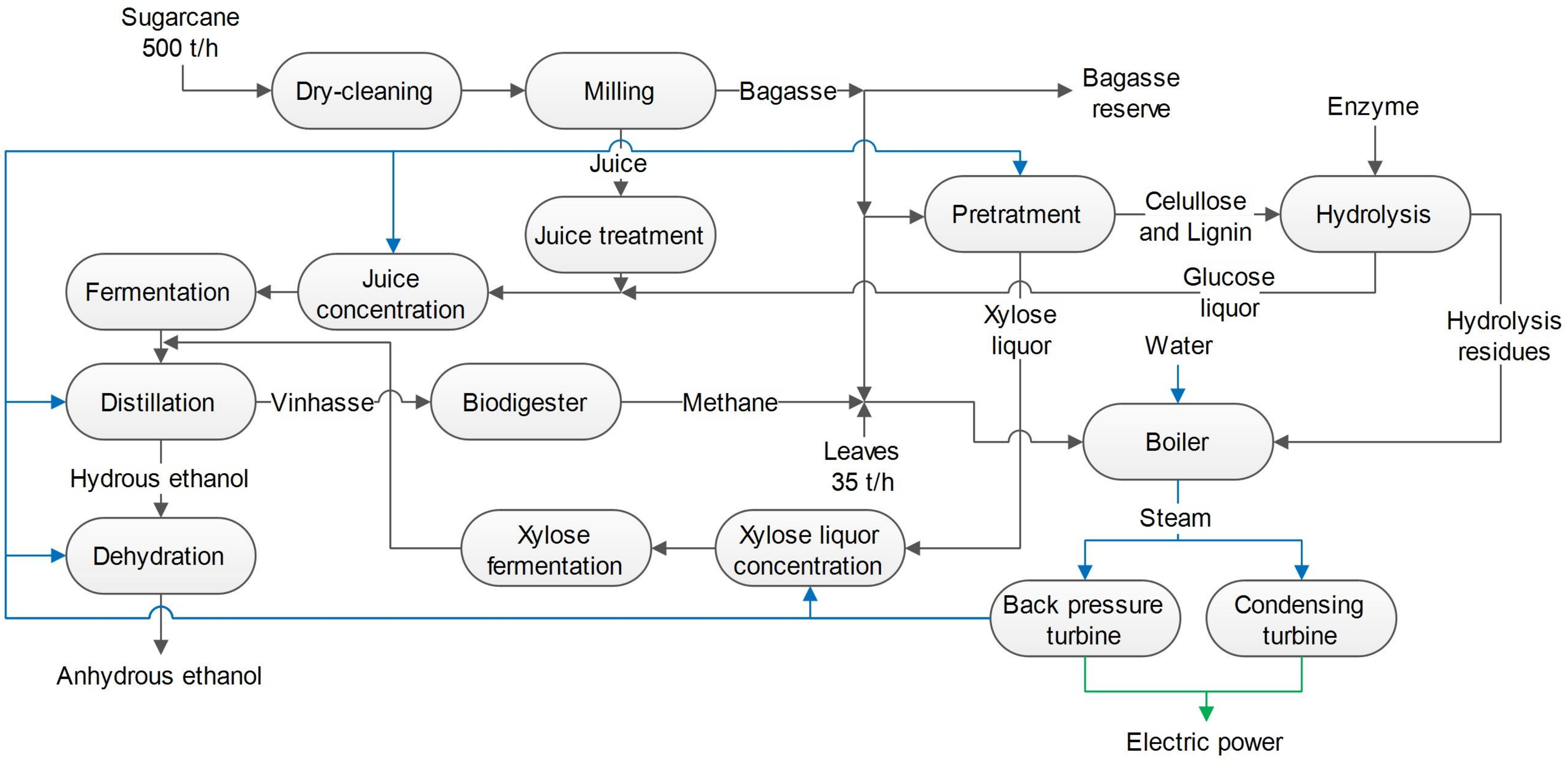


Roymel: Applying Global Sensitivity Analysis to rank most important variables
Morris Global sensitivity analysis

Elementary effects method:

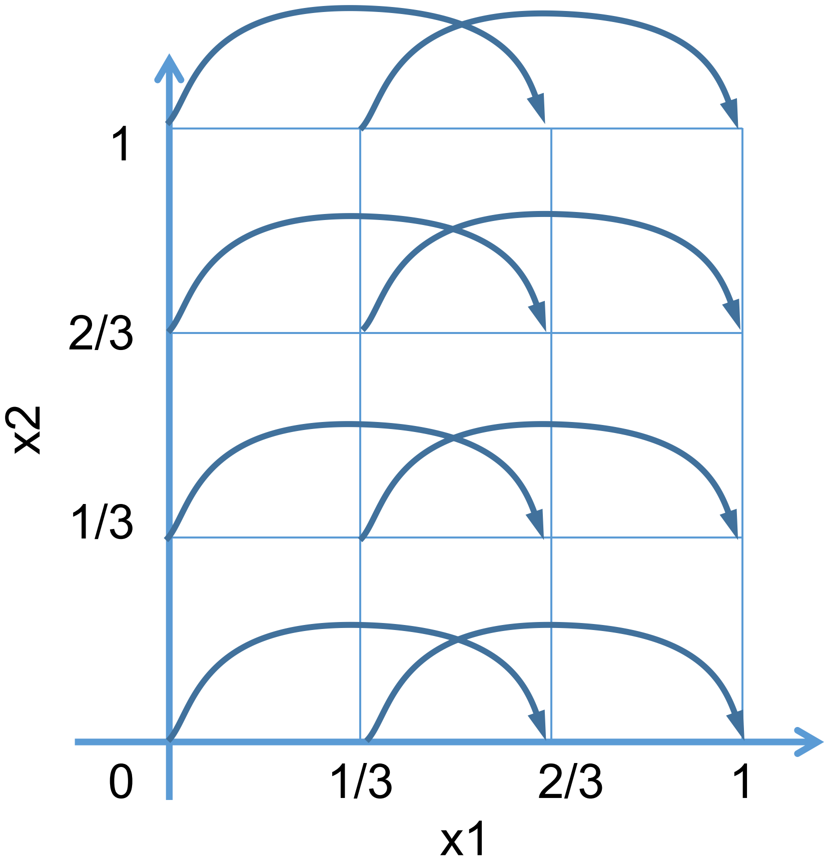
Based on the analysis of the elementary effects of the input variables on the output ones:

$$EE_i = \frac{[Y(X_1, X_2, .., X_i + \Delta, ..., X_k) - Y(X_1, X_2, ..., X_k)]}{\Delta}$$

$$\mu_i = \frac{1}{r}\sum_{j=1}^{r} EE_i^j$$

$$\mu_i^* = \frac{1}{r}\sum_{j=1}^{r} \left|EE_i^j\right|$$

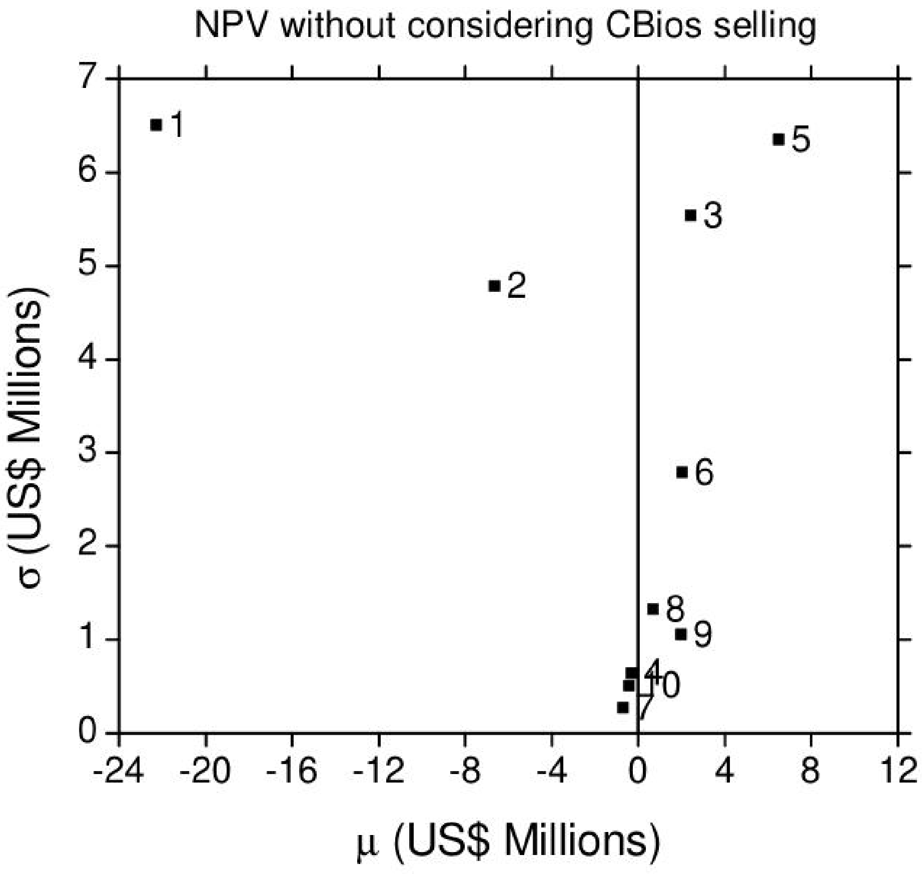
$$\sigma_i^2 = \frac{1}{r-1}\sum_{j=1}^{r} \left(EE_i^j - \mu_i\right)^2$$



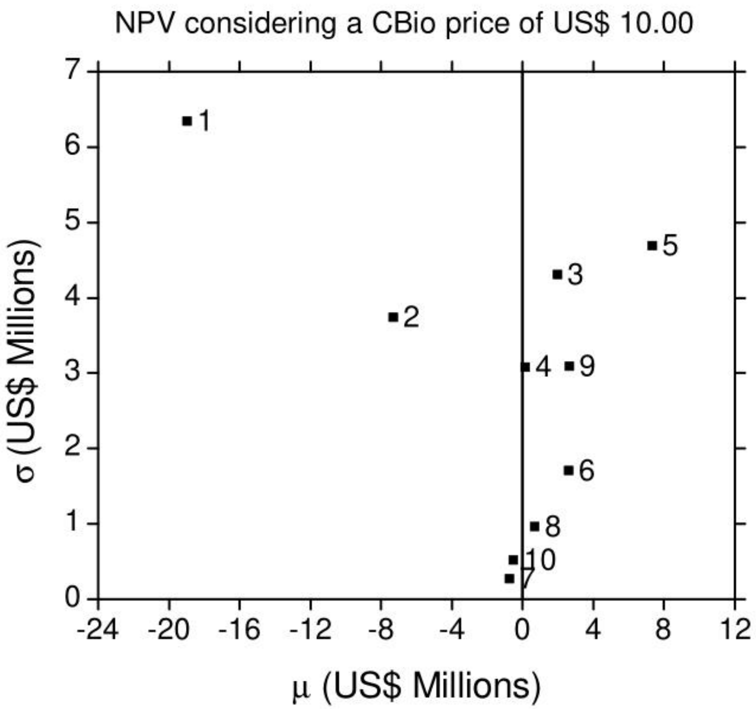
A Saltelli, et al. Global Sensitivity analysis: the primer. John Wiley & Sons, 2008

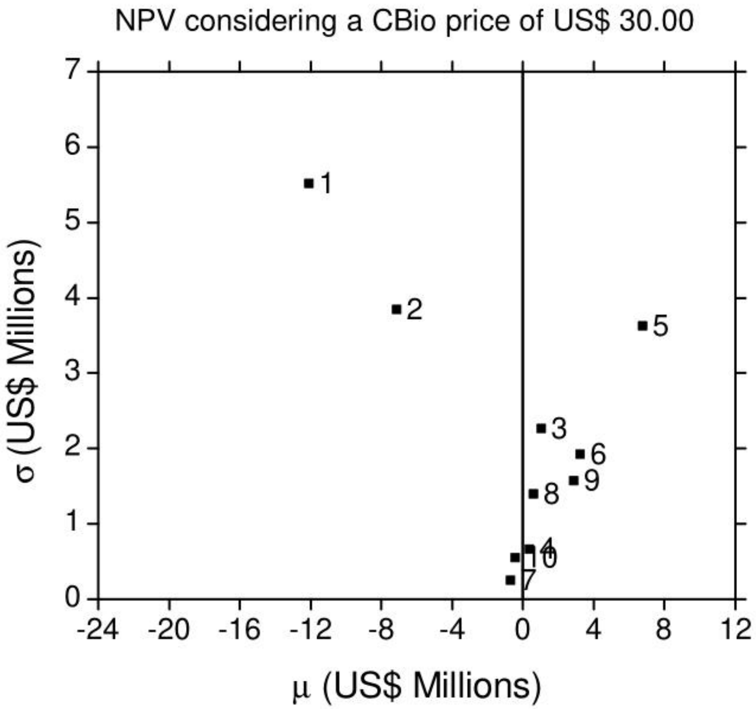
Roymel: Applying Global Sensitivity Analysis to rank most important variables
Results: Morris method

Code	Parameter	μ	σ
P1	Ratio of bagasse diverted to 2G	-22.25	6.50
P5	Solid fraction in pretreatment	6.52	6.35
P2	Enzyme load in hydrolysis	-6.63	4.78
P3	Solid fraction in hydrolysis	2.43	5.54
P6	Pretreatment yield	2.04	2.78
P9	Fermentation xylose yield	1.99	1.05
P8	Xylose concentration in fermentation	0.70	1.32
P7	Pretreatment residence time	-0.68	0.26
P4	Residence time in hydrolysis	-0.26	0.65
P10	Fermentation residence time	-0.43	0.51



Roymel: Applying Global Sensitivity Analysis to rank most important variables
Results: Influence of CBios price





	μ (CBios = 0)	μ (CBios = 10)	μ (CBios =30)	σ
P1	-22.25	-18.95	-12.07	~6

The path we took

2016

Furlan et al.

First implementation of the Retro-Techno-economic analysis

2018

Roymel et al.

Kriging surrogate model for integrating dynamic simulations into steady-state ones

2018+

Longati et al.

Retro-techno-economic analysis applied to an ethanol biorefinery

2019

Elias et al.

Integrating pinch analysis into equation-oriented process simulators

2020

Roymel et al.

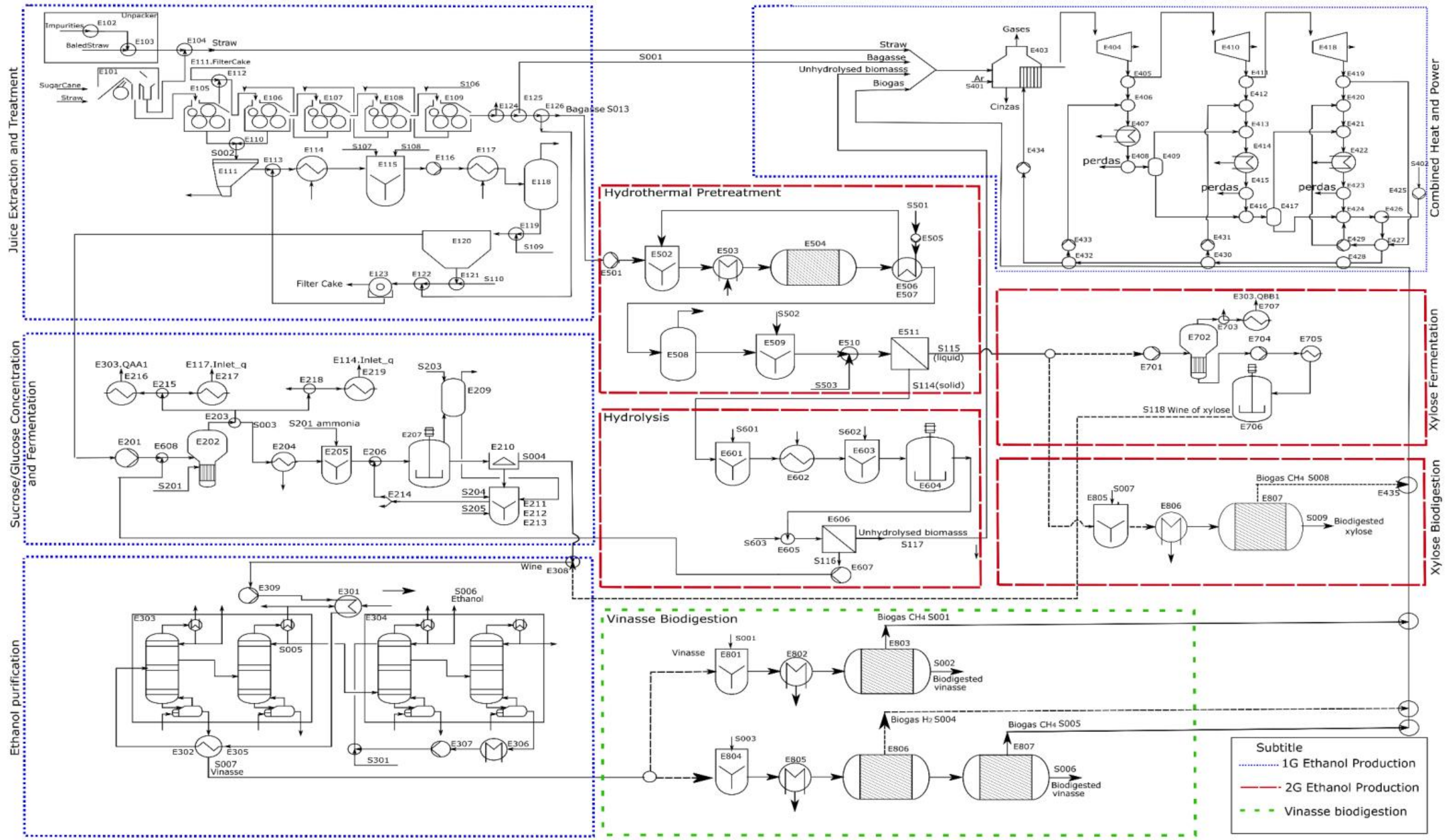
Applying global sensitivity analysis to rank most important process variables

2021

Elias et al.

Global sensitivity analysis and retro-techno-economic-environmental analysis applied to an ethanol biorefinery

Elias: GSA and RTEEA applied to an ethanol biorefinery



Elias: GSA and RTEEA applied to an ethanol biorefinery
Methods: Global sensitivity analysis

Variance based methods:

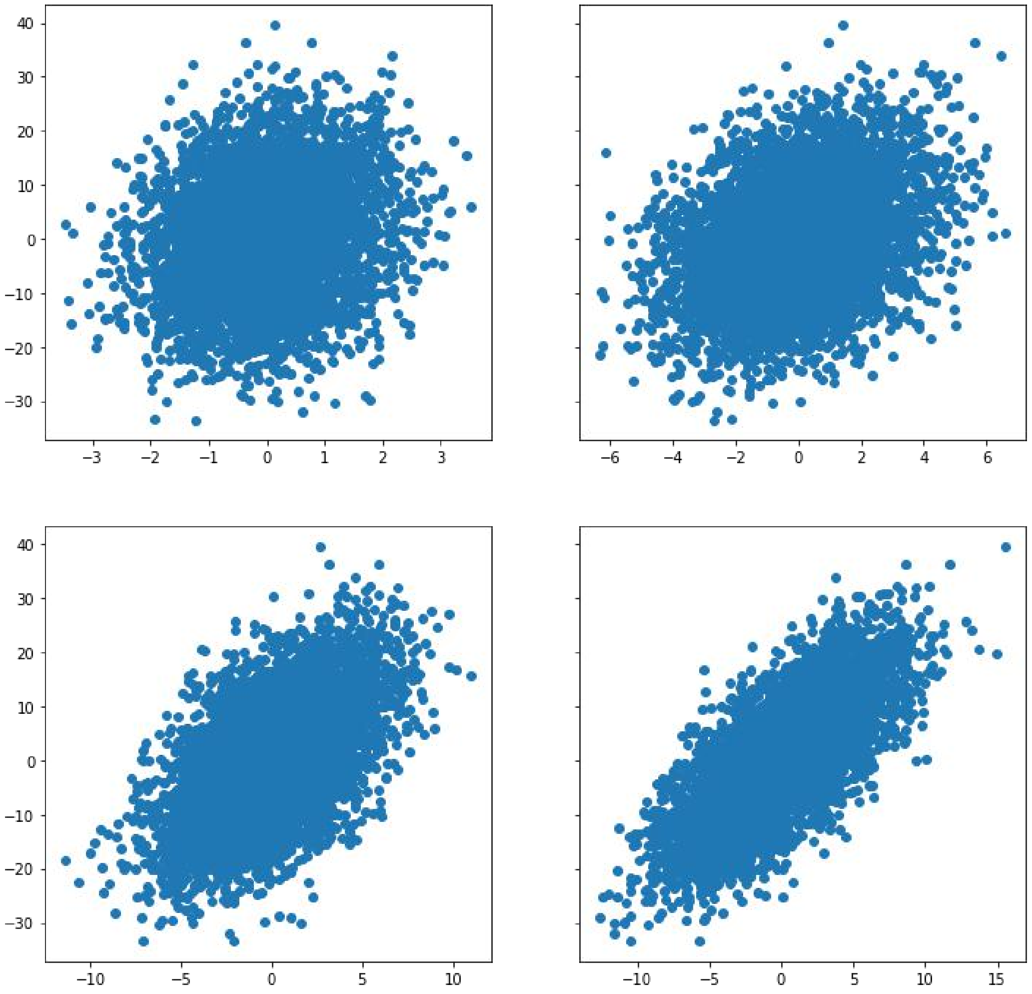
Estimates the sensitivity as the variance of the expected value of the output when the input changes (first order) or the expected decrease in the variance of the output when the input is fixed (total effect).

First-order sensitivity index:

$$S_i = \frac{V_{X_i}(E_{X_{\sim i}}(Y|X_i))}{V(Y)}$$

Total effect:

$$S_{Ti} = \frac{E_{\mathbf{X}_{\sim i}}(V_{X_i}(Y|\mathbf{X}_{\sim i}))}{V(Y)}$$



A Saltelli, et al. Global Sensitivity analysis: the primer. John Wiley & Sons, 2008

Elias: GSA and RTEEA applied to an ethanol biorefinery
Results: Global sensitivity analysis

Sobols total effects

Variables	Metrics										
	AD	ODP	HT	FWAET	MAET	TET	AC	EU	GWP100	PO	NPV
PSMF	0.35	0.44	0.47	0.40	0.40	0.50	0.36	0.33	0.28	0.00	0.00
PT	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00
PCGC	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.03	0.04	0.05
PHXC	0.03	0.03	0.04	0.03	0.03	0.04	0.04	0.04	0.03	0.01	0.00
HSMF	0.03	0.04	0.06	0.04	0.05	0.07	0.03	0.03	0.01	0.02	0.01
HEL	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.07	0.11	0.76	0.68
HC	0.43	0.35	0.34	0.39	0.39	0.32	0.41	0.42	0.41	0.15	0.17
HRT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07
XC	0.14	0.12	0.08	0.12	0.12	0.07	0.10	0.10	0.13	0.02	0.02

Elias AM, Longati AA, Giordano RC; Furlan FF. Retro-Techno-Economic-Environmental Analysis improves the operation efficiency of 1G-2G bioethanol and bioelectricity facilities. Applied Energy, 2021, 282, 116133.

Elias: GSA and RTEEA applied to an ethanol biorefinery
Results: Grouping metrics using K-means

	GROUP 1	GROUP 2	GROUP 3
PSMF	0.004	0.443	0.330
PT	0.000	0.010	0.010
PCGC	0.045	0.012	0.021
PHXC	0.005	0.034	0.034
HSMF	0.015	0.052	0.023
HEL	0.724	0.000	0.056
HC	0.158	0.357	0.417
XC	0.020	0.101	0.119
HRT	0.033	0.000	0.000

Group 1: NPV e PO

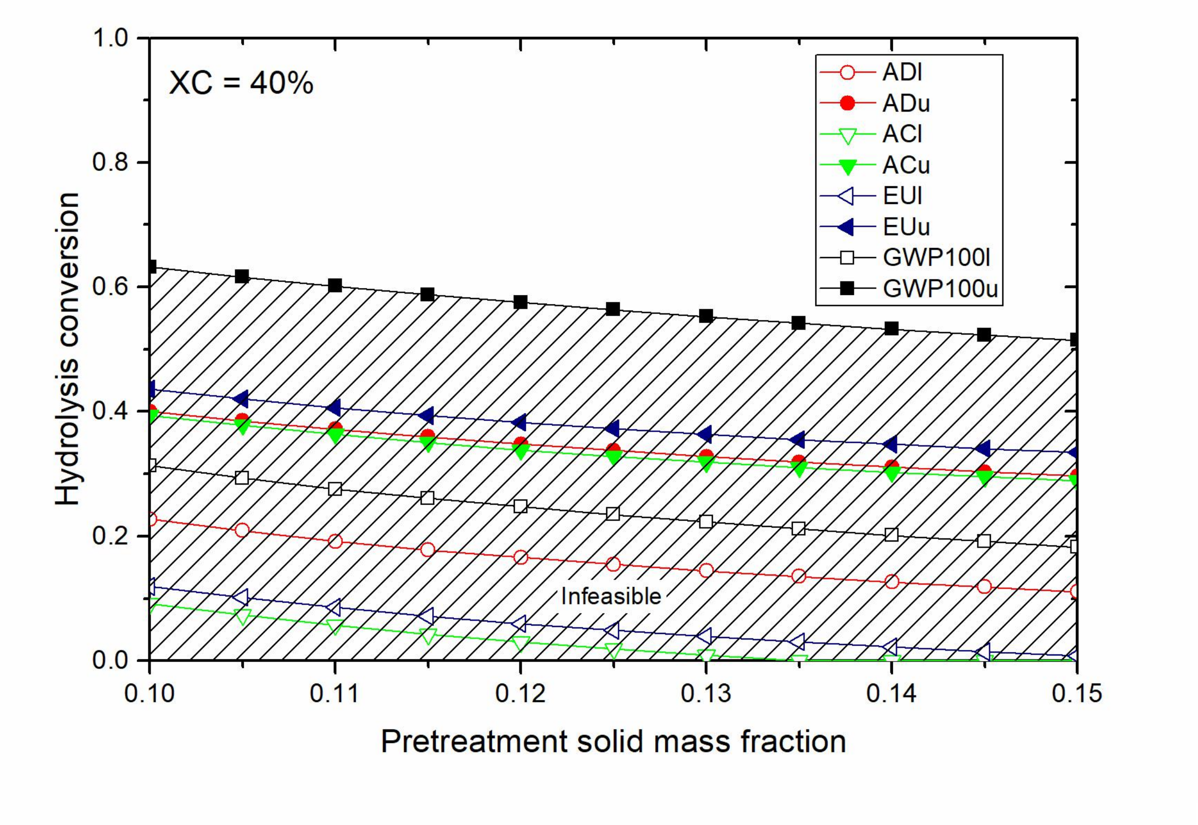
Group 2: ODP, HT, FWAET, MAET e TET

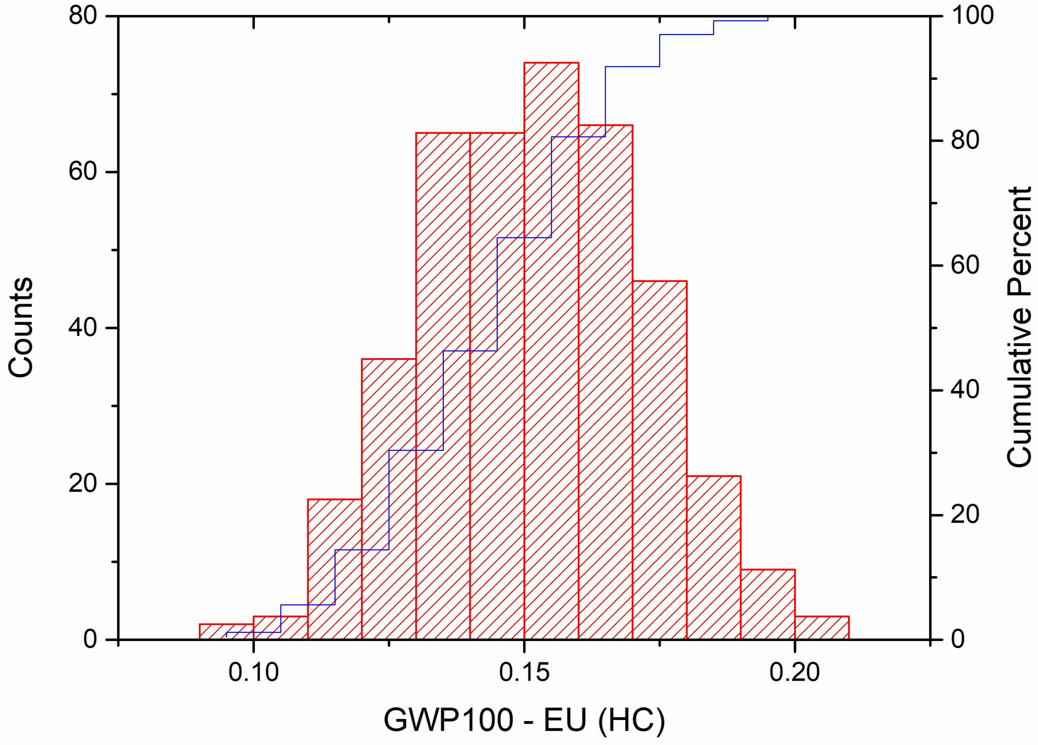
Group 3: AD, EU, AC e GWP100

Elias AM, Longati AA, Giordano RC; Furlan FF. Retro-Techno-Economic-Environmental Analysis improves the operation efficiency of 1G-2G bioethanol and bioelectricity facilities. Applied Energy, 2021, 282, 116133.

Elias: GSA and RTEEA applied to an ethanol biorefinery
Results: Isometric curves analyses

Group 3: AD, EU, AC e GWP100





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Elias: GSA and RTEEA applied to an ethanol biorefinery
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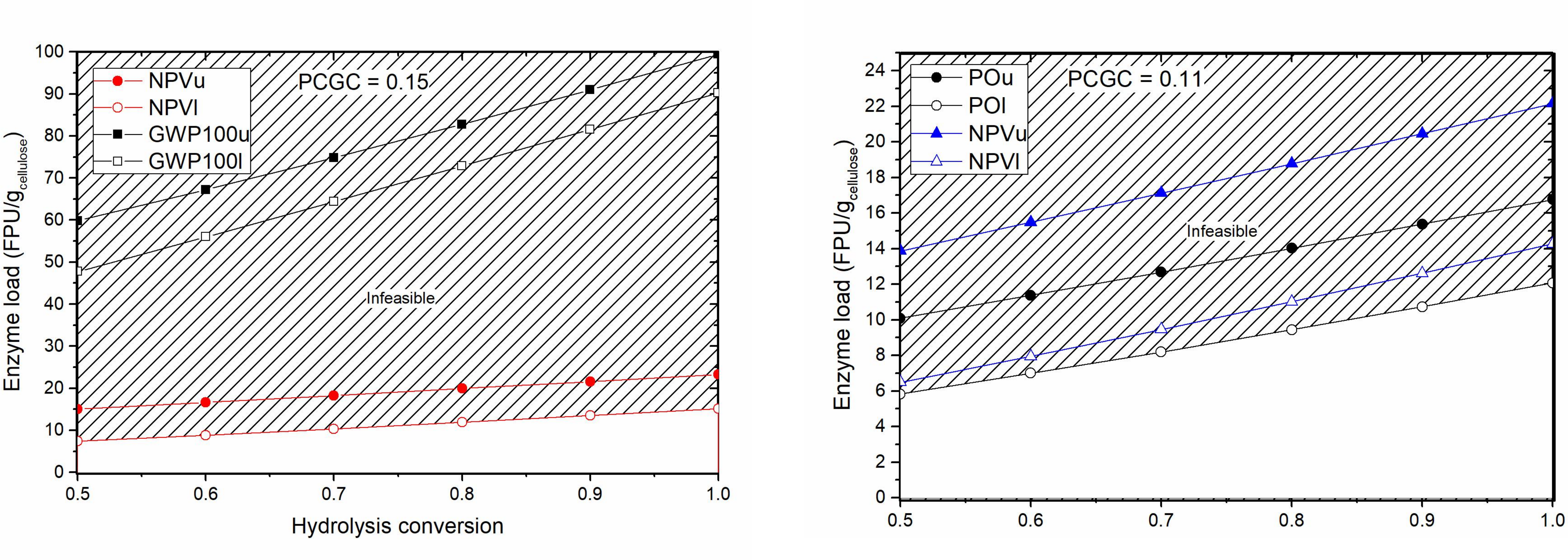

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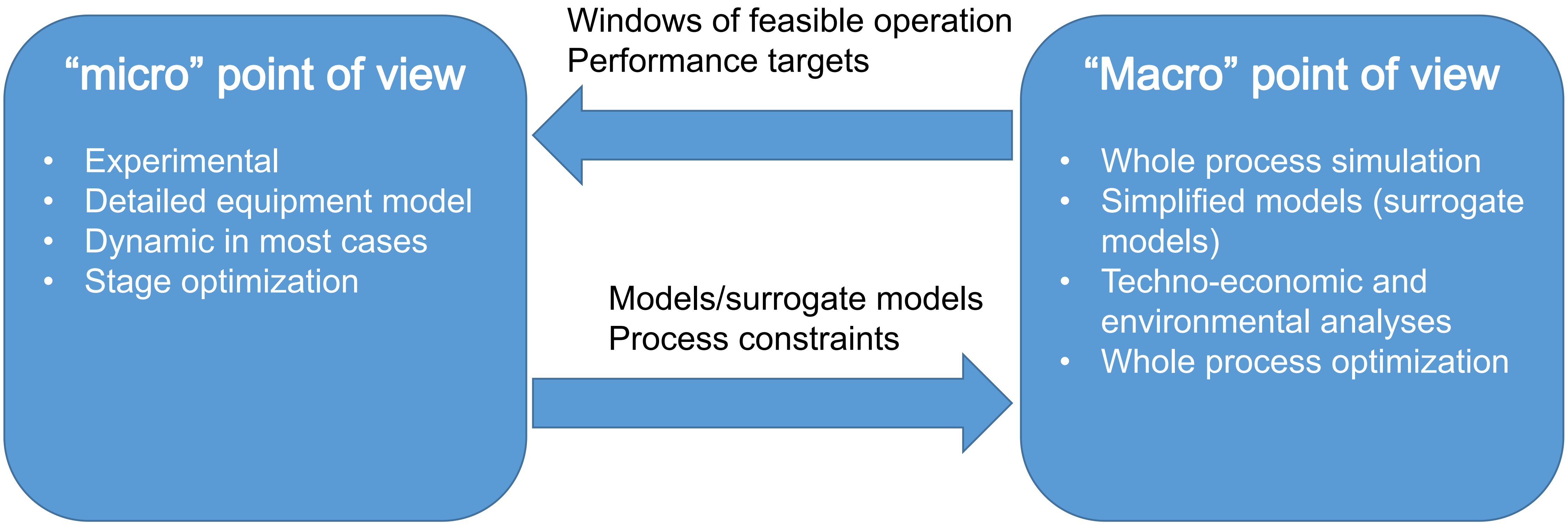
Connecting two points of view



“micro” point of view

- Experimental
- Detailed equipment model
- Dynamic in most cases
- Stage optimization

Windows of feasible operation
Performance targets

Models/surrogate models
Process constraints

“Macro” point of view

- Whole process simulation
- Simplified models (surrogate models)
- Techno-economic and environmental analyses
- Whole process optimization

Summary

- Transition to a low carbon economy, reaching net zero, is urgent;
- Biofuels, inside a biorefinery perspective, are/will be fundamental to this transition, substituting fossil fuels where electrification is (still) not feasible;
- Biorefineries can turn these biofuels feasible, by associating high added value product to its production process.
- These inovative processes/products under research are rarely studied at lab scale in industrialy feasible operating conditions;
- Construction of windows of feasible operation from process simulation and Techno-economic-environmental analysis, using preliminary experimental data, can guide future experiments towards more industrialy interesting and lower impact conditions.

Research Group

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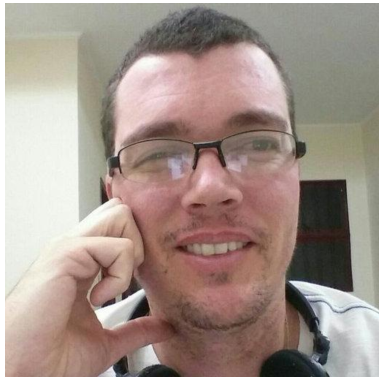

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