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Development of a methodology for the sustainability evaluation of biodiesel production process

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Introduction

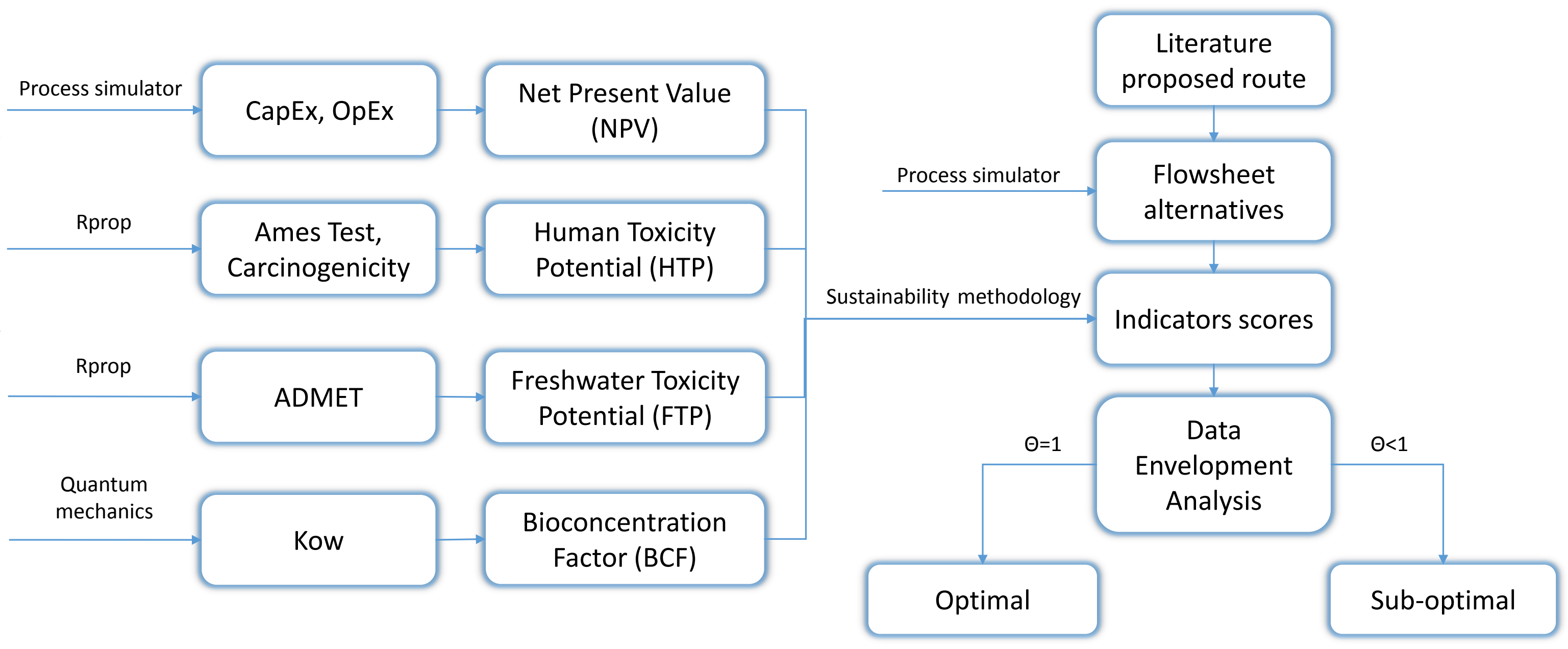
This work extends a general framework for the prediction of industrial sustainability, *i.e.* Process Sustainability Prediction (PSP) Framework proposed by Fermeglia et al. [1] for continuous design processes, implementing features for sustainability evaluation of batch pharmaceutical and biodiesel industrial processes. Our approach allows a proper selection among different process conditions, employing a broad methodology that comprehend the three sustainability pillars of sustainability, *i.e.* economy, environment and society. Each aspect of sustainability has been evaluated using a specific indicator, followed by a global estimation of sustainability performance of process designs. The resulting procedure allows performing a sustainability evaluation on different industrial plants operative conditions using representative indicators and metrics to identify the most sustainable design, therefore is suitable for a preliminary screening of process alternatives before performing well-established methodologies, *e.g.* Life Cycle Assessment (LCA).

Sustainability Evaluation Methodology

Our methodology takes into consideration the following characteristics:

- *Economic*: **Net Present Value (NPV)** as economical evaluator is a well-establish index for the estimation of the profitability of an investment.
- *Social*: **Human Toxicity Potential (HTP)** adopts *in-silico* estimations of Ames Test for human toxicity and carcinogenicity of rodents by backward elimination and Rprop neural net method
- *Environmental:* **Freshwater Toxicity Potential (FTP)** employs the results from in-silico evaluations on acute toxicity threshold for algae, daphnia magna, feathed minnow and medaka.
- *Socio-Enviromental:* **Bioconcentration Factor (BCF)** is related to the accumulation of substances in organism so it affects both human and environmental impacts

The 3D-indicators are calculated using the results obtained from process simulation coupled with an in-house procedure for the estimation of toxicological properties based on molecular structure and quantum-mechanics

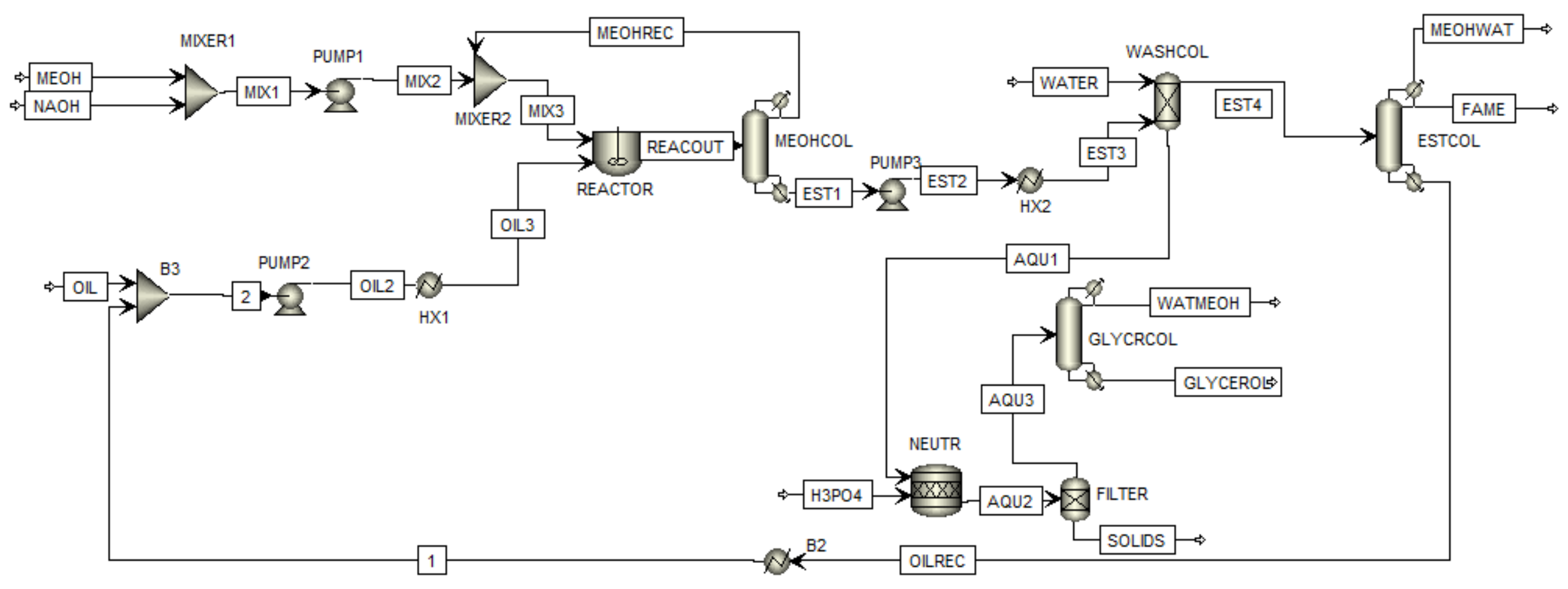


Case study

The transformation process of palm oil into biodiesel [2] has been investigated in order to identify the best process conditions. A reliable model has already been created in a process simulator (Aspen Plus), which includes transesterification, methanol recovery, water washing, fatty acid methyl ester (FAME) purification, catalyst removal and glycerol purification. Vegetable oil is the mixture of triglycerides (TG) as specified in [3], while the composition profile of palm oil feedstock is determined by Che Man[4].

In order to evaluate the sustainability indicators, the variables and the parameters involved in their calculation have to be retrieved.

- **NPV**: Capital Expenditures (CapEx) and Utilities Expenditures (UtEx) as well as mass and energy balances have been calculated using Aspen Plus flowsheet. Market prices of raw materials and products have been retrieved on different web sources related to commodity chemicals market prices. The lifetime of the project has been set to 15 years, while the discount rate has been defined as 7%.
- **HTP & FTP:** the hazard classes related to these indicators have been evaluated using PreADMET , a web-based application for predicting ADMET properties using *in-silico* method.
- **BCF:** this indicator is strongly dependent on Kow, that is related to the hydro solubility of compounds and is adopted to evaluate whether a compound is more likely to reside in organic phase or in aquatic one. We adopted COSMO-RS to calculate this parameter using a quantum-mechanic approach related to the calculation of σ-profiles of the molecules involved.



We performed a sensitivity analysis to identify the best operating conditions for the trasesterification reactor. We selected temperature, pressure and residence time as variables and the minimization of our set of indicators (-NPV, HTP, FTP and BCF), as optimal target. The selection of the best performing process design has been carried out using Data Envelopment Analysis (DEA), a mathematical tool that employs linear programming (LP) techniques for the assessment and the evaluation of the efficiency of a group of homogeneous units considering multiple criteria simultaneously [5]

Temperature [°C]	Pressure [bar]	Residence Time [hours]
50	3	1
60	4	2
70	5	3

Sustainability Indicators

Four indicators have been selected in order to evaluate the sustainability performance of the different process conditions considering all impacts to sustainability at once.

Net Present Value (NPV)

NPV evaluates the economic performances of each process design considering Capital (CapEx) and Operative Costs (OpEx), the latter comprehending raw materials and utilities cost (UtEx).

$$OpEx = \sum_j m_j^{in} * price_j + UtEx$$

m_j^{in}: j^{th} chemical inlet masslow (kg/yr)

$$NPV = -(CapEx) + \sum_{i=1}^{\tau} \left\{ \frac{-(OpEx)}{(1+r_d)^i} + \frac{revenue}{(1+r_d)^i} \right\}$$

τ: project lifetime (yr); r_d: discount rate

Human Toxicity Potential (HTP)

Human Toxicity Potential (HTP) addresses hazards and risks for human related to chemicals involved within a chemical plant in order to exhibit the social contribution of a process design to sustainability. It takes into account the specific maximum mass per mass of product times an Hazard Class [2] based on positivity for *in-silico* estimation of Ames test, carcinogenity for rodents and hERG inhibition.

$$\mathrm{HTP} = \sum_j \frac{m_j^{max}}{m_{prod}} * H_{Cl_j}^{H}$$

Freshwater Toxicity Potential (FTP)

FTP inspects the environmental issues on freshwater sources due to polluting chemicals. The indicator considers the specific maximum mass per mass of product, times an Hazard Class based on *in-silico* estimated concentration acute toxicity threshold for algae, daphnia magna, feathed minnow and medaka.

$$\mathrm{FTP} = \sum_j \frac{m_j^{max}}{m_{prod}} * H_{Cl_j}^{F}$$

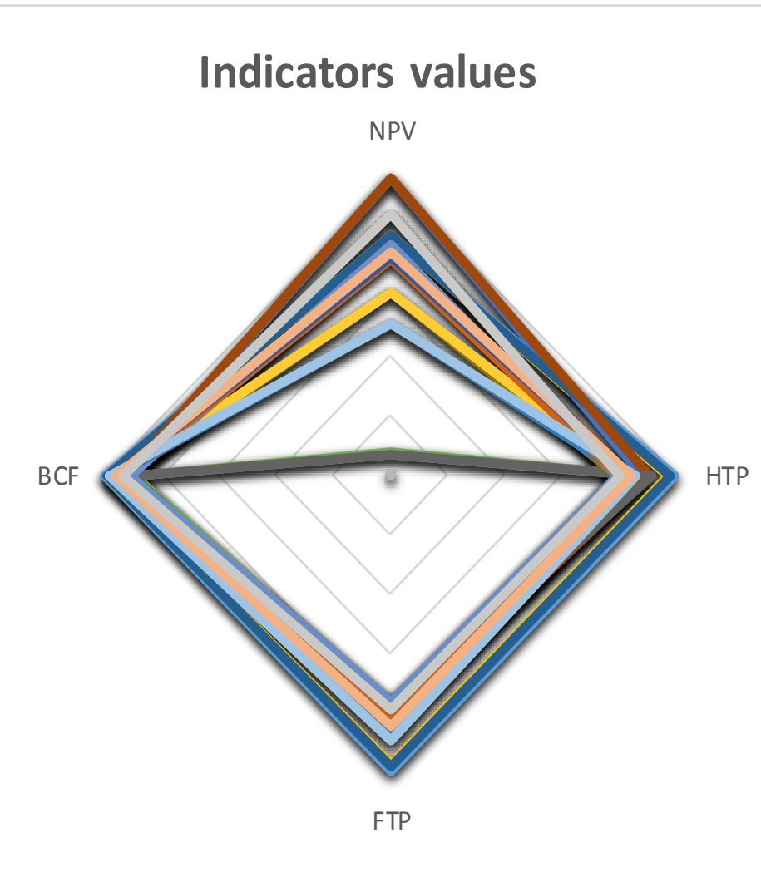
Bioconcentration Factor (BCF)

BCF is the ratio of the chemical concentration in an organism to the concentration in water and can be related to the octanol-water partition coefficient, Kow, using the following relationships:

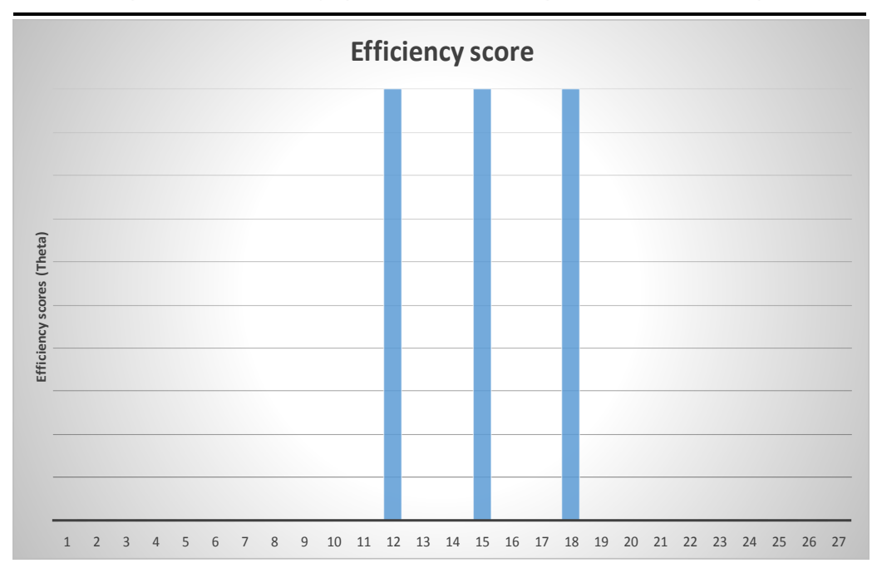
$$logBCF = 0.15\ if\ logKow < 1$$
$$logBCF = 0.85 * \mathrm{logKow} - 0.7 \text{ if } 1 \leq logKow \leq 6$$
$$logBCF = -0.2 * (logKow)^2 + 2.74 * logKow - 4.72\ if\ 6 < logKow < 10$$
$$logBCF = 2.68\ if\ logKow \geq 10$$

Indicators calculation

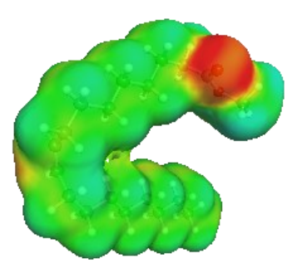
The combination of Temperature, Pressure and Residence Time variations gave rise to 27 (3^3) alternatives. Our sensitivity analysis induced a modification on the amount of substances in speficic streams (FAME, SOLIDS, GLYCEROL), while the nature of the 38 implemented chemicals has been preserved. The radar plot shows the scores attained by each flosheet (27) for each indicator (4), while the efficiency scores are reported in the column plot. It is therefore clear how three alternatives perform efficiently (they are overlapping on the central dot in the radar plot), while the others are far from the optimal score (1) for Theta. It is still hard to recognize the best alternative, as none of the efficient design performed better on each aspect of sustainability simutaneously.

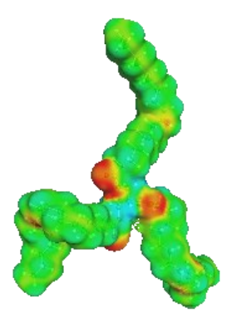


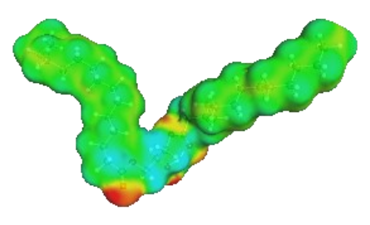
DESIGN	TEMP	PRES	RES-TIME
	C	BAR	HR
12	60	3	3
15	60	4	3
18	60	5	3

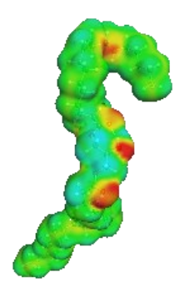


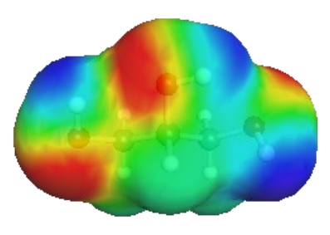
The estimation of logKow has been performed using COSMO-RS quantum-mechanical approach for computation of distribution of charges on the molecular surface (σ-surface).

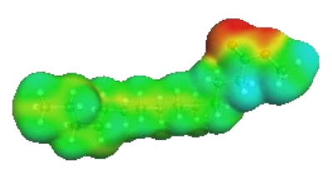

Methy oleate


Glycerin trioleate


1,3-Dimyristin


1-Linoleic-3-olein


Glycerol


Methyl tetradecanoate

ID	logKow	ID	logKow	ID	logKow
1-LI	5.405	METHYL-S	7.137	OS	16.246
1-M	6.301	MLI	13.137	PLI	14.050
1-O	6.771	MM	12.164	PLIO	20.689
1-P	6.832	MMM	17.321	PO	13.846
1-S	6.960	MMP	18.758	POO	20.730
GLYCEROL	-1.086	MP	12.430	POS	20.956
H3PO4	-2.392	MPLI	19.911	PP	14.832
LIO	15.370	NAOH	-3.888	PPLI	20.793
METHANOL	-0.650	NA3PO4	-10.388	PPO	19.684
METHY-LI	7.188	OO	14.202	PPP	21.000
METHYL-M	5.131	OOLI	20.354	PPS	20.539
METHYL-O	7.797	OOO	20.114	PS	13.972
METHYL-P	6.489	OOS	23.147		

Results and Conclusions

DEA Results

DEA Dual super-efficiency model has been performed once again in order to identify the most sustainable design among the efficient ones. This approach follows the *leave-one-out* rule, quantifying the performances of efficient designs whether one of them is removed from the analysis. Thus the most influencing design can be recognized.

DESIGN	Theta_sup
12	0.000056
15	1.858976
18	0.00016

We can then define the best performing operating condition for the transesterification reactor (temperature of 60°C, pressure of 4 bar and residence time of 3 hours) which will guarantee the lowest sustainability impact considering the three pillars of sustainability. The operating conditions previously adopted by the simulation base case were the same for temperature and pressure (60°C, 4 bar), while the residence time was set to 1 hour, lowering the overall reaction yield.

Therefore, our methodology arises as a valuable contribution to sustainability assessment of chemical and biochemical processes, as it provides a quick sustainability estimation of different process alternatives. We still encourage the adoption of well-established and more comprehensive methodologies (*e.g.* Life Cycle Assessment), which are able to take into account the total impact related to the production of a chemical (from cradle to grave), while our methodology becomes useful in case of lack of data in LCA database and for a preliminary screening of process designs.

References

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[2] Y. Zhang, M.A. Dube, D.D. McLean, M. Kates, "Biodiesel Production from Waste Cooking Oil: 1. Process Design and Technological Assessment", Bioresource Techchnology, 89:1- 16, 2003.

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[4] Y.B. Che Man, T. Haryati, H.M. Ghazali, B.A. Asbi, "Composition and Thermal Profile of Crude Palm Oil and Its Products", Journal of American Oil Chemical Society, 76:237-242, 1999.

[5] Cooper, W.W., Seiford, L.M., Tone, K., "Data Envelopment Analysis: A Comprehensive Text with Models, Applications, References and DEA-Solver Software: Second Edition" pp. 1-490, 2007