Electronic Supplementary Material (ESI) for Energy & Environmental Science

Sustainability Assessment of Novel Chemical Processes at Early-stage: Application to Biobased Processes

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Electronic supplementary information

Economic constraint

In the EC parameter, in effect gives an indication of the ratio of the raw material cost of the main product to the market price of the main product. This is achieved by use of allocation which enables comparison on the basis of one unit of main product which in essence is the functional unit for the assessment. Given the nature of this calculation, any of the products from the process could be chosen as the main product regardless of its mass or economic value. In our case economic allocation is used to distribute raw material costs over all the products and co-products. In the special case of the EC parameter the use of economic allocation leads to the simplified calculation as represented by equation 1 in the article. The steps leading to equation 1 are as follows:

$$A_{fn} = \frac{x_{fn} \times y_{fn}}{\sum_{n=1}^{n} x_n \times y_n} \qquad (S1)$$

$$r_{fn} = \frac{A_{fn}}{y_{fn}} \times \sum_{m=1}^{m} x_m \times y_m \qquad (S2)$$

$$EC_{fn} = \frac{r_{fn}}{x_{fn}} \qquad (S3)$$

In equation S1, S2 and S3, *fn* stands for the main product which is the functional unit for our calculations. x_{fn} and y_{fn} are the price and mass flows respectively of the main product while x_n and y_n are the respective price and mass flow of the n^{th} product. A_{fn} is

the allocation factor for allocating the costs to the main product. x_m and y_m are the price and mass flows respectively of the m^{th} raw material respectively. r_{fn} is the allocated raw material cost of the main product. Thus, EC gives the ratio of raw material cost of the main product to that of the market price of the main product. If one combines the three equations, one can see that the use of economic allocation results in the equation 1, which is used in the article.

EHS index calculation

The EHS index is used to evaluate the inherent hazards associated with the chemical conversion. In estimation of the EHS index, the mass flows of all the chemicals (or representative chemicals) within the process are considered. This estimation methodology follows from the thesis of H. Sugiyama[17]. The process streams considered are as shown in figure 2 in the article. So overall the chemicals present in each of these 7 streams and their mass flows are taken into account.

Equation 4 in the article represents the final calculation of the EHS index value. The estimation of *E*, *H* and *S* scores in this equation is based on the following equations and chemical hazard indices. These equations and hazard indices are based on the thesis of H. Sugiyama[17] and have been reproduced with permission.

The calculation of environment index (*E*) is based on four sub-categories (*cE*) that include persistency, air hazard, water hazard and solid waste. In equation S4, m_k^F is the specific mass flow of k^{th} chemical in the flow *F*. The specific mass flow is the mass flow of the particular chemical per unit mass of the main product (flow F6) (kg/kg product). I_k^{cE} is the hazard index value of the k^{th} chemical in the relevant sub-category. *z* is the fraction of overall mass emitted to the environment in case of an accident. m_k^{Out} is the specific mass flow of the k^{th} chemical leaving the process as waste through flow F7.

$$E = \sum_{cE=1}^{4}\sum_{k=1}^{k}\left[z \times \max_{F}(m_k^F) \times I_k^{cE}\right] + \sum_{cE=1}^{4}\sum_{k=1}^{k}[m_k^{Out} \times I_k^{cE}] \qquad (S4)$$

The hazard index value in different environment sub-categories is calculated based on the scales shown in figure S1.

Sub-categories	Prio-rity		
Persistency	1	Halflife$_{water}$ (days)	1 — 3.2 — 10 — 32 — 100
Air hazard	1	Index value of chronic toxicity	0 — 0.5 — 1
Water hazard	1	L(E)C$_{50\ aquatic}$ (mg/l)	1000 — 10 — 1
	2*	R-codes	Other R-codes — 52 — 51 — 50
	2*	WGK	1 — 2 — 3
Solid waste	1	Substance class	H_2O, organics, gases — Other substances

WGK: German water hazard class (Wassergefahrdungsklasse)
L(E)C$_{50\ aquatic}$: Aquatic lethal or effect concentration using daphnia magna
*take maximum index value when more than one parameter has same priority

Figure S1: Hazard index values for sub-categories in environment index (*E*)

The health index (*H*) is based on two sub-categories (*cH*) that include irritation and chronic toxicity. In equation S5, m_k^{un} is unit mass (*un*) and is equal to 1, while I_k^{cH} is the hazard index value of the k^{th} chemical in the relevant sub-category.

$$H = \sum_{cH=1}^{2} \max_{k}[m_k^{UN} \times I_k^{cH}] \qquad (S5)$$

The hazard index value in different health sub-categories is calculated based on the scales shown in figure S2.

Sub-categories	Prio-rity		
Irritation	1	EU-class	Xi — C — 100
	1*	R-codes	Other R-codes** — 36,37,38 — 34 — 35
	2	LD$_{50\ dermal}$ (mg/kg)	50000 — 5000 — 500 — 50 — 5
Chronic toxicity	1	MAK-CH (mg/m^3)	10000 — 100 — 1 — 0.1
	2*	EU-class	Xn — T — T+
	2*	GK	no — 5 — 4 — 3 — 2 — 1
	2*	R-codes	Other R-codes — 31,33 — 42,43 — 29,32, 48 — 40,62, 63,64 — 45,46,47 49,60,61

LD$_{50\ dermal}$: Lethal dose via dermal exposure using rat, mouse, rabbit
MAK: Workplace threshold value (Maximale Arbeitsplatz Konzentration)
GK: Giftklasse (Swiss poison class)
*take maximum index value when more than one parameter has same priority
** use only when there is no LD$_{50}$ value available

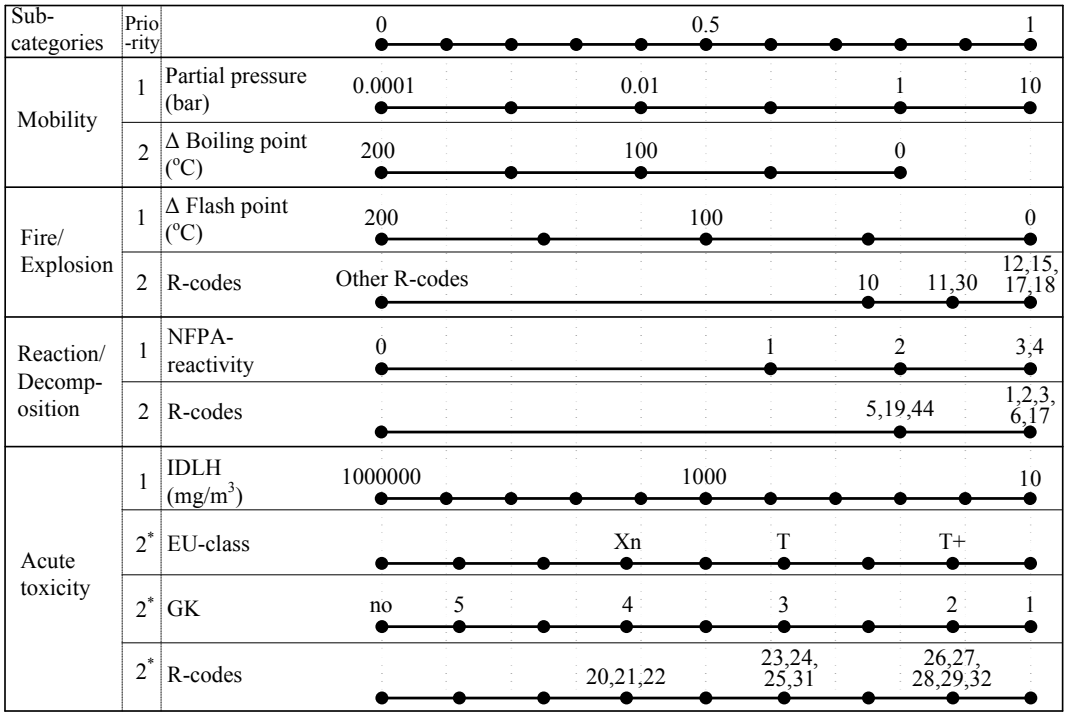
Figure S2: Hazard index values for sub-categories in health index (*H*)

The estimation of safety index (*S*) is based on four sub-categories (*cS*) that include mobility, fire/explosion, reaction/decomposition and acute toxicity. In

equation S6, m_k^F is the specific mass flow of the k^{th} chemical and I_k^{cS} is the hazard index value of the k^{th} chemical in the relevant sub-category.

$$S = \sum_{cS} \max_{F} \left[\max_{k} (m_k^F \times I_k^{cS}) \right] \qquad (S6)$$

The hazard index value in different health sub-categories is calculated based on the scales shown in figure S3.



Partial pressure: Partial pressure of pure component at 25°C
Δ Boiling point: Temperature difference between standard boiling point and 25°C
Δ Flash point: Temperature difference between flash point and 25°C
IDLH: Immediately Dangerous to Life and Health (National Institute for Occupational Safety and Health)
GK: Giftklasse (Swiss poison class)
*take maximum index value when more than one parameter has same priority

Figure S3: Hazard index values for sub-categories in safety index (*S*)

The values of *E, H* and *S* calculated using the equations S4, S5 and S6, respectively, are substituted in equation 4, in the article to calculate the EHS index for the process.

Process description

The case study presented in the article involves production of but-1,3-diene via biobased and petrochemical processes. In the biobased process, ethanol is converted to but-1,3-diene over heterogeneous catalyst in a gas phase reaction at around 400 ^{o}C. The table S1 shows the relevant inputs and outputs along with the stream mass fractions for this reaction that are considered in the preliminary assessment. The chemicals with zero fractions (e.g. ethoxyethane mass fraction in table S1) do not play a direct role in the presented results for the case study. However, the physiochemical properties of these chemicals are included in the model to be used when the process information indicates their presence in the reaction. Some other studies for this conversion report the presence of these compounds.

Table S1: Ethanol to but-1,3-diene conversion reaction

Inputs		Outputs	
Chemical name	**Mass fraction (wt%)**	**Chemical name**	**Mass fraction (wt%)**
Ethanol	100	But-1,3-diene	41.2
Water	0	Ethene	6.6
		Ethanal	8.6
		Hydrogen	1.9
		Ethoxyethane	0
		But-1-ene	0
		Ethanol	10
		Water	31.7

In the reference petrochemical process, but-1,3-diene is produced as a co-product in steam cracking of naphtha at around 800 ^{o}C to produce ethene. The table S2 shows the relevant inputs and outputs for this conversion that are considered in the preliminary assessment.

Table S2: Steam cracking of naphtha

Inputs		Outputs	
Chemical name	**Mass fraction (wt%)**	**Chemical name**	**Mass fraction (wt%)**
Naphtha	100	Ethene	32.4
		Propene	16.8
		But-1,3-diene	5.0
		Benzene	10.4
		Hydrogen	1.1
		Methane	13.9
		Other C4 (Butane, But-1-ene, 2-Methylpropene)	6.2
		Other aromatics (Methylbenzene, dimethylbenzene)	0
		Pentane, Hexane	4.0
		C7+ non aromatics (Heptane)	1.2
		Fuel oil	9.0

PCEI inputs

Based on the mass balances reported in table S1 and S2, the subsequent values for PCEI calculation are reported in table S3.

Table S3: Source and index values of the PCEI parameter for the but-1,3-diene production case study

Indicators	Bioethanol process		Naphtha process	
	Process value	Index value	Process value	Index value
Presence of water	Yes (distill)	1	No	0
Product concentration	18.47	0.047	3.94	0.6
Minimum boiling point difference	25.2 K	0	1.9 K	1
Reaction mass loss	0.71	0.38	0	0
Reaction enthalpy	47.75 kJ/mol	0	384 kJ/mol (avg)*	1
Number of co-products	3	0.5	9	1
Pre-treatment of feedstock	0	0	0	0
Total		1.93		3.60

Raw material environmental impacts

Bio-Ethanol

Considering the context of the but-1,3-diene case study, the bioethanol being used for this assessment is assumed to be produced in the European Union (EU). Hence, a general European feedstock mix for bioethanol is used for this assessment. This feedstock mix is based on the process 'Ethanol (at distillation, RER/U, biomass)' in the ecoinvent database[12].

In the case of greenhouse gas (GHG) emissions associated with bioethanol a range of different values can be found in literature. Considering this variability, the European Union Directive 2009/28/EC represents a good benchmark for GHG emissions associated with bioethanol in the EU. This directive stipulates a 35% GHG savings per unit energy content, from a biofuel in comparison to its fossil counterpart. These GHG savings are the minimum requirement for a fuel to be classified as 'biofuel' for a variety of compliance purposes. Since, all bioethanol producers in EU are expected to comply with this directive, this was used as a reference for bioethanol GHG emissions in this study. The calculation procedure is as follows:

GHG emissions associated with reference fossil fuel (including both production and use of fossil fuel): 83.8 gCO_2/MJ

GHG emissions associated with bioethanol based on 35% reduction: 54.1 gCO_2/MJ

* T. Ren, M. Patel and K. Blok, *Energy,* 2006, 31, 425-451

Energy content of bioethanol: 26.9 MJ/kg

Based on the above values, associated GHG emission value of 1.46 kg CO_2/kg bioethanol is used for the case study. It should be noted that this value represents only the fossil CO_2 emissions from the bioethanol production process. The biogenic CO_2 emissions are not considered since the biogenic CO_2 is recycled into biomass in a rather short time frame.

The cumulative energy demand (CED) associated with bioethanol is derived from the mean value associated with the above mentioned 'Ethanol (at distillation, RER/U, biomass)' process in the ecoinvent database[12]. Based on this reference a value of 71.4 MJ/kg is used for the case study.

Naphtha
Considering the EU context, the GHG emissions and CED associated with naphtha production are based on the process 'Naphtha (at refinery, RER/U)' in the ecoinvent database[12]. This represents an average for naphtha production in the EU. The corresponding mean values for GHG emissions and CED are 0.42 kg CO_2/kg naphtha and 53.1 MJ/kg naphtha respectively.

As evident, the GHG and CED values for a feedstock are based on benchmarked or average data. Hence, the inherent uncertainty has been considered in the uncertainty analysis.

Uncertainty parameters

The values presented in tables S4 and S5 are used for uncertainty analysis.

Table S4: Uncertainty analysis data

	Units	Distribution	Mean	Std. Dev.	Max	Min
$CED_{ethanol}$	MJ/kg	Normal	71.4	8.92		
$CED_{naphtha}$	MJ/kg	Normal	53.1	1.66		
$GHG_{ethanol}$	$kgCO_2$/kg	Lognormal	1.46	0.52		
$GHG_{naphtha}$	$kgCO_2$/kg	Normal	0.42	0.04		
$Selectivity_{EtOH2butadiene}$		Triangular	0.78		0	1
Prices						
Ethylene	Euro/MT	Normal	951	182		
Butadiene	Euro/MT	Normal	1292	498		0(trunc)
Naphtha	Euro/MT	Normal	679	208		0(trunc)
Propylene	Euro/MT	Normal	767	213		
Benzene	Euro/MT	Normal	927	288		
Ethanol	Euro/MT	Normal	666	71.6		

Table S5: Price correlations for uncertainty analysis

	Ethylene	Butadiene	Naphtha	Propylene	Benzene	Ethanol
Ethylene	1.0					
Butadiene	0.6	1.0				
Naphtha	0.8	0.5	1.0			
Propylene	0.8	0.7	0.6	1.0		
Benzene	0.9	0.5	0.9	0.7	1.0	
Ethanol	0.3	0.2	0.3	0.4	0.2	1.0

System boundary discussion

Table S6 shows the raw scores for the glucose-based process case, which lead to figure 14 in the article. Table 4 in the article shows the raw scores for the ethanol-based process; these raw scores form the basis for index ratios presented in figure 9 in the article. In both these cases (figure 14 and figure 9) the system boundary for the naphtha-based process is the same and thus parameter scores for naphtha-based process are identical. A comparison of these two cases with different system boundaries for the biobased process illustrates the interdependence and interaction between the different parameters which have been considered in the assessment model.

Table S6: Glucose- and naphtha-based but-1,3-diene process scores for each parameter

Parameters[+]	**Glucose-based**	**Naphtha-based**
Economic constraint (index)	0.88	0.83
Environmental impact of raw materials (normalized index)[#]	0.64	0.93
Process cost and environmental impact (index)	4.05	3.60
EHS hazard potential (index)	1.38	2.67
Risk aspects (index)	0.14	0.15

+ Lower values are better for the respective processes.
# Cumulative energy demand (MJ/kg but-1,3-diene): 70.43 (glucose); 61.17 (naphtha).
# GHG emissions (kg CO_2 eq./ kg but-1,3-diene): 1.10 (glucose); 3.98 (naphtha).

The economic constraint of glucose-based process is lower as compared to the ethanol-based process because glucose as a raw material is located earlier in the value chain as compared to ethanol. Nevertheless, the end product is same (but-1,3-diene) in both the cases. Hence, this difference in economic constraint is reflected in the PCEI and EHSI parameters which respectively are a proxy for the process costs and represent process hazards. The PCEI value for the glucose-based process is relatively higher as compared to that for the ethanol-based process, since it accounts for the extra processing requirements. Thus, by itself the economic constraint does not give a good idea about the process economics. However, in combination with the PCEI it can give an indication, albeit preliminary, of the process economics.

In the case of EHSI, as expected, the score before allocation is higher for the glucose-based process (2.50) as compared to that for the bioethanol-based process (2.05). However, the extended system yields more co-products (2-hydroxypropanoic acid, butanedioic acid). Hence, the allocated hazards indicated in table S4 are lower. However, the additional co-products also result in an increase in the PCEI parameter which compensates for the lower allocated EHSI score.

The glucose-based process shows a lower environmental impact of raw material as compared to the ethanol-based process. However, this results in a comparatively higher PCEI parameter which acts as a proxy for the environmental impacts associated with the process. These aspects explain the significantly higher PCEI score for the glucose-based process as compared to the ethanol-based process. Thus the interaction between the system boundary and different parameters plays an important role in the outcome of this assessment.