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Bridging sustainability and intensified flow processing within process design for sustainable future factories

Abstract: A holistic, life cycle based evaluation approach was followed within the European collaborative project CoPIRIDE, in order to provide multi-criteria decision support for environmentally benign and cost efficient process design strategies in front of a scale-up of newly developed concepts. The approach is presented by means of three case studies, dealing on the one hand with different catalyst plate reuse options, and on the other hand with two process concepts for intensified processing of natural feedstocks by means of epoxidation and transesterification reactions. Key criteria for future sustainable production processes could be identified prior to the transfer of the experimental flow chemistry results to pilot scale processing.

Keywords: decision support; eco-efficiency; life cycle assessment; life cycle costing; process intensification.

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1 Introduction

During the last decades, Europe has developed into a global leader in sustainable development [1]. The European chemical industry has contributed greatly to this success. On the one hand, this was realized by the implementation of improved cleaning technologies and on the other hand, by the development of more material and energy efficient process strategies. The latter can be gained, e.g., by optimized or novel synthetic pathways, devices, and process conditions. The current status of fine chemical, pharmaceutical, and related industries approaching green chemistry and sustainability was summarized by Watson [2]. Where step change improvements can be gained by means of these measures, the term “process intensification” is used [3]. Besides environmental savings, cheaper processes, smaller equipment and plants, safer processes and shorter time-to-market are expected from this. Thus, process intensification is established today as one encouraging concept to further improve the sustainability of chemical processes [4]. A recent overview of its impact on industry is given by Harmsen [5].

The collaborative project CoPIRIDE (EU Seventh Framework Program for Research and Technological Development: CP-IP 228853) took up the idea of process intensification for a holistic, comprehensive, and integrated process and plant development, focusing on key issues such as, e.g., the chemical process itself, the reactor design and fabrication, catalyst development and a novel container plant concept [6]. Chemical core processes, such as the epoxidation and transesterification of vegetable oils, ammonia production, polymer chemistry reactions and sugar hydrogenation, were redesigned using flow chemistry processing often in combination with intensified synthesis conditions (also called Novel Process Windows) [7, 8]. In order to ensure the future sustainability of the processes under development, the design was supported by appropriate environmental and cost analyses and evaluation activities starting at an early stage of process development, since costing structures and environmental impacts become mostly predefined during this stage.

Although flow chemistry, especially microreaction technology, has already turned out to be a suitable tool to improve conventional engineering in a plethora of chemical reactions, it has provide significant benefits in, e.g., yield, selectivity, heat management, safety and/or production costs, to become a sustainable alternative. This is why a methodology of accompanying sustainability assessment and holistic decision making was followed within CoPIRIDE. Hot-spot up to holistic life cycle assessment (LCA) and life cycle costing (LCC) analyses were utilized in order to provide decision support [9–11]. Information about the inputs and outputs of the process, including the flow rates, compositions, pressure, temperature, and physical state of all material streams, the energy consumption rate from various sources and resulting costs served as database. During an evaluation step, the information was summarized using different process intensification indicators in order to assess whether the requirements specified during the objective formulation step are met. The screening step ended with a ranking of alternatives according to their overall level of attractiveness, applying multi-criteria decision making tools. The key criteria for process improvement determined by that, were then taken into account within the next iterative step of process design. The sustainability evaluation approach is summarized in Figure 1.

Here, the application of multi-criteria decision making tools in parallel to process design activities and the decision support gained from this for a knowledge-based eco-efficient process design in front of a scale-up of novel concepts, will be presented. The results of LCA and LCC analyses can be indifferent or even contradictory. Then, outranking approaches are helpful in making an unbiased search for the best performing candidates meeting several criteria.

2 Methodological approach

The potential ecological impacts of alternative production pathways can be assessed and compared by means of a comparative LCA. LCA is an internationally standardized methodology for "compilation and evaluation of the inputs, outputs and environmental impacts of a product system throughout its life cycle" normed by the International Organization for Standardization (ISO) [12, 13]. This holistic approach includes the whole life cycle of a product, process or service: extraction of resources, the production of all materials, energies used in the product system, the usage through to products recycling, reuse and disposal (also called "cradle-to-grave"). During the third step of LCA, the life cycle impact assessment (LCIA), the calculated mass and energy flows are assigned to different environmental impact categories, e.g., according to mid-point indicators like global warming potential (GWP) [14] (for more categories see Table 1).

If LCA is used as a decision making tool during process design, the analysis is typically related to a product unit, which is similar for all alternatives under consideration. Then, the analysis mostly comprises only the life cycle stages up to the production of the purified product (called "cradle-to-gate").

In early stages of process design, further strategies for simplification are often necessary [15]. This is, on the one hand, due to the limited data base and process knowledge gained so far, and on the other hand, due to the required quickness in response to the development team. The evaluation task can be also associated with a different level of knowledge about the alternative systems, e.g., the comparison of a newly developed laboratory-scaled process with an industrially established production process. These challenges can be met by simplified LCA (SLCA) [16], based, e.g., on process simulation or calculation of

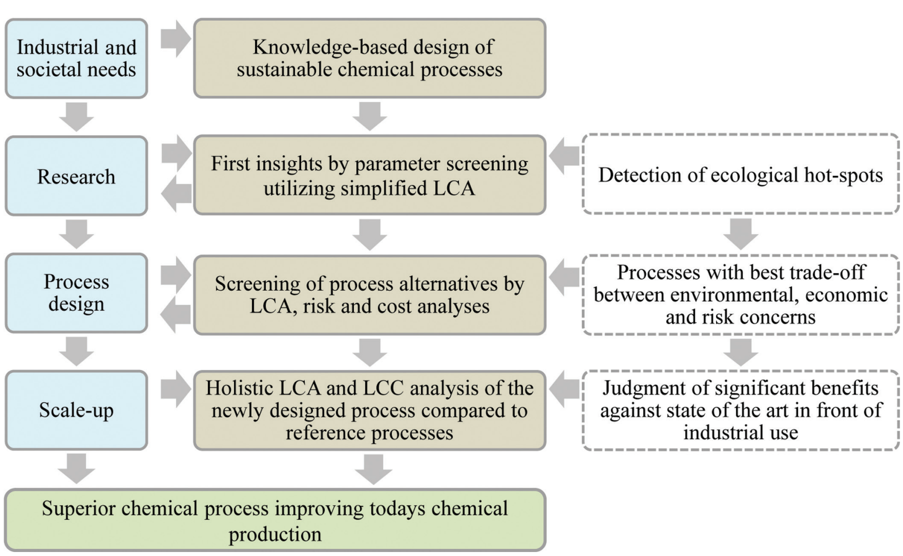


Figure 1 Evaluation approach within CoPIRIDE according to Kralisch and colleagues [11].

Table 1 Life cycle impact assessment (LCIA) categories [7] used for (S)LCA investigation in case studies A–C.

LCIA category	Abbreviation
Global warming potential	GWP
Abiotic resource depletion potential	ADP
Ozone depletion potential	ODP
Photochemical ozone creation potential concerning low NO_x	POCP
Acidification potential	AP
Eutrophication potential	EP
Land use	
Human toxicity potential	HTP
Terrestrial eco-toxicity potential	TETP

hypothetical case scenarios first. It is lower in time and effort and allows, e.g., the exclusion of certain life cycle stages, impact categories and the use of generic data modules to fill data gaps. Although the methodological rules defined in the ISO norms for life cycle management [12, 13] are not fully met, SLCA is a very helpful approach to start with an iterative screening and detection of ecological hot-spots from a holistic point of view already in early design stages. Thus, environmental fail decisions can be avoided right from the start [16]. It has already been used for screening purposes by several working groups [17–22]. However, within the further design progress and with an enhanced data base, the SLCA outcome should be refined and extended, resulting in a detailed LCA (Figure 1).

For process modeling during life cycle inventory (LCI) and LCIA in SLCA, as well as detailed LCA, e.g., the software Umberto can be used [23]. By this, material and energy flows of experimental or production processes and up-stream and down-stream processes can be modeled. Such software is often used in combination with Ecoinvent, a broad database for (mostly) European LCI data [24]. Then, the environmental burden resulting from process alternatives can be assessed using common LCIA categories (see Table 1).

By means of a combination of LCA with LCC [25, 26] analyses as a second evaluation method, a detailed insight into the impact of, e.g., single reagents, process modules or process parameter variations on the resulting eco-efficiency of the overall process becomes possible. The LCC analysis has been developed according to the principles of LCA and summarizes all costs connected with the life cycle of a product, process or service, again in a cradle-to-gate or cradle-to-grave approach. Similar to LCA, decisions taken at an early stage of process development possess a higher impact on LCC than those taken at a later stage of the product life cycle.

The results of LCA and LCC can be summarized in an eco-portfolio (see Figure 2). The eco-portfolio offers the possibility of graphical representation of environmental impacts in relation to costs of individual scenarios and to derive recommendations for action from this [27].

As a consequence of the fact that usually more than one objective is incorporated in a process design and evaluation progress, typically, a multi-objective decision making problem occurs in the case of contradictory or indifferent results within the eco-portfolio. The problem of comparing several alternatives with respect to several objectives can be solved using standardized algorithms for identifying Pareto-optimal [28] solution candidates constituting the basis for, e.g., partial ranking (outranking) procedures. For this objective, fast acting purpose, the software D-Sight [29] was used within our work. The concept has been already successfully used for the development of eco-efficient synthesis and application strategies for ionic liquids (see Kralisch et al. [19] and Reinhardt et al. [30]). As a result of the outranking, preferences for specific, Pareto-optimal options can be quantified. The results are transferable to an eco-portfolio depiction referred to environmental and cost efficiency. At this, environmental efficiency is determined based on the relative saving potentials in different LCIA categories (see Table 1), referring to the worst as well as best case candidates (highest or lowest environmental impact potential, respectively), calculated in each of these categories. It can be summarized in one environmental efficiency value by means of weighting factors. Cost efficiency is calculated likewise, taking into account relevant variable and fixed production cost criteria, e.g., investment, material, energy, personnel, and waste treatment costs. In both

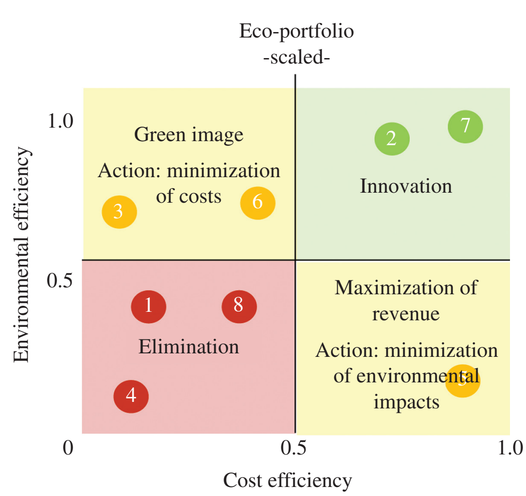


Figure 2 Eco-portfolio related to cost and environmental efficiency of alternative scenarios.

cases, higher values (scaled from 0 to 1) point to more preferential options.

The following environmental and cost-oriented strategies can be obtained, depending on the quadrant of the eco-portfolio figure, where the scenario is included (see Figure 2):

- Elimination: The alternative is considered as not efficient regarding environmental and economic criteria and should be discarded or fundamentally rethought.
- Green image: The considered alternative leads to essentially environmental, but not economic, efficiency. The objective of cost minimization should be focused.
- Innovation: Environmental and economic benefits can both be drawn from the considered alternative.
- Maximization of revenue: The alternative considered leads to higher economic (profit-increase), but not environmental, efficiency. There should be focus on improvement of the environmental efficiency.

In the work presented here, the results of outranking are valid under the following regulations: linear minimization of all LCIA criteria (or costs), relative values ranging from percentage equal weight of all criteria, and were determined using the software D-Sight. We decided for an equal weighting of all LCIA criteria, due to the fact that all of the more specific weighting methods suggested so far were found to be internally inconsistent in terms of treatment of place and time, and incomplete, lacking environmental interventions and effect routes [31].

Besides eco-efficiency considerations, the potential hazards for humans and ecosystems of substances are important criteria when justifying novel synthesis pathways. For this purpose, the environmental, health and safety (EHS) method developed by Hungerbühler and colleagues was found to be a suitable, user-friendly approach to assess risks resulting from the handling of chemicals [32, 33]. It facilitates the estimation of the risks at an early stage of process design and was used within CoPIRIDE to critically judge the environmental risks connected with the transfer of conventional to supercritical biodiesel process conditions applying the same concept of outranking the best suited process alternatives. This aspect will not be discussed here (for more information see Kralisch and colleagues, 2013 [11]).

3 Results

At the beginning of process design within the CoPIRIDE project, R&D activities especially were supported by environmental and cost efficiency evaluation. The knowledge gained by means of these early stage investigations will be demonstrated in an example, dealing with different catalyst plate reuse options (case study A).

Later, the evaluation procedure was refined and narrowed down in parallel to the ongoing process development in several optimization-evaluation-loops. At the end, the environmental impacts and costs of the newly designed chemical processes were quantified and compared with the state of the art. This holistic design approach will be discussed by means of two case examples, focusing on, on the one hand, the evaluation of the epoxidation reaction of soybean oil (SBO) from laboratory scale investigations to pilot plant engineering (case study B), and on the other hand, the comparative evaluation of different concepts for biodiesel generation via transesterification (case study C). In both cases, the key criteria for a future sustainable production process could be defined prior to the transfer of the experimental flow chemistry results to pilot scale processing.

3.1 Case study A: analysis of catalyst plate reuse options

Due to the process design activities within CoPIRIDE focusing on flow conditions, reactor and especially catalyst development activities aiming for, e.g., long-life time and reusability, play an important role in the context of sustainability. In particular, within the project consortium, catalyst plates consisting of Ru/alumina catalytic coatings on stainless steel microstructured substrates were of interest. In order to identify the most eco-efficient option of catalyst plate treatment after use, a simplified cost analysis and LCA for the catalytic coating of microchannels, including the removal of the coating, and the recycling of the plates as well as of the catalytic compounds, was done (more detailed information can be found in Kressirer et al. [10]).

Here, the results of an eco-efficiency analysis based on experimental scale investigations are briefly summarized for catalytic plates with a size of 150×225×2 mm and with channel depth of 400 µm and diameter of 600 µm. After thermal pretreatment of fresh stainless steel plates, the catalyst was coated on the walls of the microchannels. Prior to use, the coated plates were dried and calcined. After use, there were several possibilities of treatment:

- Disposal of the plates and preparation of new ones.
- Removal of the coating and use of a new coating slurry on the recycled stainless steel plates.
- Removal of coating and recycling of stainless steel plates as well as of the catalytic components.

The analysis is based on the full capacity and under consideration of the life time of each device used within this process. The removal of the coating was done in four different ways, of which two were suited to recycle the catalytic components (Table 2). The term "base case" was used for the disposal of plates after use without removal of the coating or the recycling of the plates.

Figure 3 shows an outranking of the environmental efficiency of the base case scenario *versus* Methods 1–4, taking into account typical environmental impact categories evaluated within the LCIA step (see Table 1 for explanation of the abbreviations). As an example, the base case was found to be preferential in the case of GWP and abiotic resource depletion potential, whereas Method 2 should be preferred concerning eutrophication potential, acidification potential, photochemical ozone creation potential concerning low NO_x, ozone depletion potential and terrestrial eco toxicity potential. These outranking results of environmental efficiency provided the basis for the eco-efficiency analysis depicted in Figure 4.

Considering both, environmental aspects and costs, Methods 2 and 3 for catalyst plate treatment after use were found to be the most sustainable options. This outcome influenced further catalyst and reactor design activities within the CoPIRIDE project in a substantial manner.

3.2 Case study B: reaction under harsh conditions from batch to flow – epoxidation of SBO

Case study B deals with process intensification of the epoxidation of SBO. Epoxidized SBO (ESBO) is bio-based, non-toxic, non-corrosive and biodegradable and can substitute phthalates, legally prohibited in some applications [34]. Thus, it is the most common oleochemical used for PVC compounding. Due to its excellent market and green product expectations, the improvement of its current production process has been chosen as one development case within the CoPIRIDE project.

In industry, the reaction is usually performed in pulse-fed-batch or fed-batch reactors at a reaction temperature between 60°C and 70°C, gradually adding the oxidant reagents to the oil. ESBO is produced by reacting hydrogen peroxide with the double bonds contained in the SBO oil molecules under the presence of formic acid (Scheme 1) and a mineral acid, such as sulfuric or phosphoric acid. Due to its highly exothermic nature, the reaction requires a sufficient control addressing corresponding safety issues. To overcome the limitations of the time and energy consuming batch process, the synthesis of ESBO was planned to be transferred to a flow process within the project [6, 35] in order to increase the productivity as well as its eco-efficiency [9].

Within the initial development stage, process simulation was found to be a powerful tool for screening of different alternatives [6]. It was apparent that due to the interfacial mass transfer and heat management, the reaction can be speeded up by utilizing microreaction technology and possibly also by Novel Process Windows (e.g., high temperatures).

As a first step, the influence of different parameter variations was screened by a set-up of 13 partly theoretical scenarios. They were based on information of the existing production process under batch conditions, results from process simulation, pilot plant engineering and expert knowledge of the partners involved in the process development (more detailed information can be found in Kralisch et al. [9]). Based on these early investigations, the following key criteria for the development of a sustainable epoxidation process were defined: i) maximizing the yield of the epoxidized product, ii) minimizing the amount of H_2O_2 and HCOOH, and iii) best suited reaction temperature range: 100°C–120°C (in cases where digestion times of 1 h and more are foreseen in the process) or synthesis at high temperatures (150°C–180°C) and residence times within seconds, if technically feasible. The conjoint implementation of all optimization ideas in the pilot process can lead, for example, to a reduction of environmental impacts up to 12% in terms of the LCIA category GWP, or 11% in terms

Table 2 Options of treatment of catalytically coated microstructured plates [10] considered for eco-efficiency analysis.

Method	Description	Removal time (h)
Base case	Coating with γ-alumina+$RuCl_3$, disposal of plates after use	
Method 1	Coating with γ-alumina+$RuCl_3$, removal of coating with 37 wt% nitric acid, reuse of plates	1.5
Method 2	Coating with γ-alumina+$RuCl_3$, removal of coating with citric acid, tartaric acid, Na gluconate, recycling of coating, reuse of plates	0.25
Method 3	Coating with γ-alumina+$RuCl_3$, removal of coating with NaOH, ethanolamine, Na gluconate, recycling of coating, reuse of plates	1
Method 4	Coating with γ-alumina+$RuCl_3$, removal of coating with 20 wt% nitric acid, reuse of plates	1.5

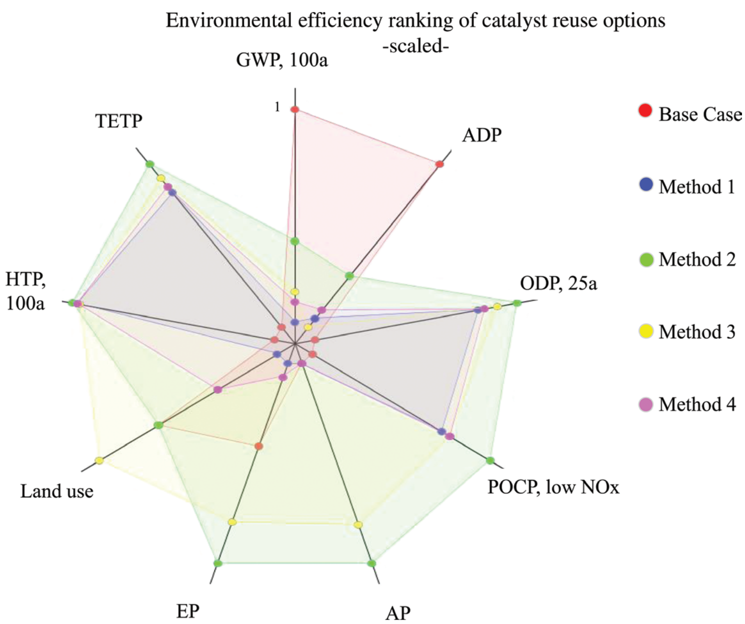


Figure 3 Multi-criteria outranking of base case *versus* Methods 1–4 concerning environmental efficiency, taking into account several life cycle impact assessment (LCIA) categories.

of human toxicity potential. The results also showed that the environmental benefits of the synthesis under Novel Process Windows and short residence times will strongly depend on the resulting ESBO yield and on the hydrogen peroxide decomposition rate [6]. In a case where the amount of hydrogen peroxide would have to be increased due to a significant decomposition at high temperatures, the human toxicity potential would escalate, resulting in a worse environmental balance compared to process alternatives at lower reaction temperatures [9]. An optimum between temperature, reaction time, yield, decomposition rate and technical feasibility had to be found here.

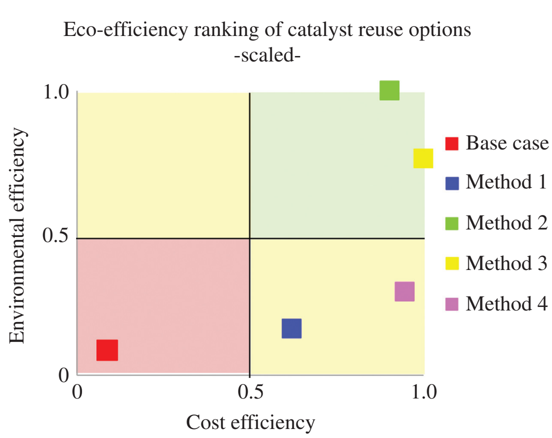
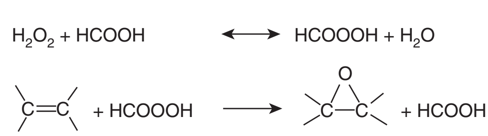


Figure 4 Multi-criteria outranking of different methods for catalyst plate treatment after use according to their environmental and cost efficiency.

In the next step, the existing industrial fed-batch process for SBO epoxidation at Mythen S.p.a., Italy, covering an annual production volume of 18,500 t, was taken as benchmark for a sustainability evaluation of the new process under development at pilot scale (planned annual production capacity: 2,500 t). For this, detailed information about the production and post-processing steps, including hydrogen peroxide decomposition, neutralization, and separation, were provided by the company. Two pilot scale process alternatives (pilot process, base case: continuous flow at elevated temperature and short residence time; pilot process, best case: pilot process, base case and reduced material and energy demand) were taken into account including again, the environmental burden related to all educts, solvents and auxiliaries, energy supply, synthesis, work-up and treatment of wastes. The process parameters of these SBO processing alternatives are summarized in Table 3. A more detailed insight into the optimization task and support for process design decisions could be gained from this. Figure 5 shows an outranking of the environmental efficiency of the process alternatives under consideration for pilot scale, compared



Scheme 1 Soybean oil epoxidation: sequence of the occurring reactions placed at the double bounds of oil compounds.

Table 3 Scenarios considered for environmental and cost efficiency evaluation of soybean oil (SBO) processing [9].

Epoxidized SBO process scenario	Industrial fed-batch	Pilot process, base case[a]	Pilot process, best case[a]
Operation	Fed-batch	2-step continuous flow+discontinuous digestion	2-step continuous flow+discontinuous digestion
Reaction temperature (°C)	60–70	150	150
Reaction time (min)	420	0.5+60 (digestion)	0.5+60 (digestion)
Annual capacity (t/a)	18,500	2,500	2,500
Yield (%)	90	90	90
$Mole_{H2O2}$ per DB	1.3	1.3	1.1
$Mole_{HCOOH}$ per DB	0.3	0.3	0.2
Heat recovery	No	No	Yes
Work-up	Yes	Yes	Yes

[a]Hypothetical process based on experimental investigations, process simulation and process engineering.

to the industrial fed-batch process against different LCIA criteria. A clear preference for an intensified flow process operating at elevated temperatures with reduced H_2O_2 and HCOOH excess and heat recovery (pilot process, best case) was found among the three candidates considered.

In addition to the comparative environmental assessment, an evaluation of the future production costs of utilizing the new flow chemistry concept as alternative to the established fed-batch production plant was also performed (see Figures 6–9). The ESBO production costs are composed of variable and fixed cost components. Investment costs, calculatory depreciation and imputed interests considered as fixed costs were estimated from average values of typical equipment costs, in the case of the established production process. In Figure 6, the composition of typical investment costs taken into account for the hypothetical installation of a new fed-batch process is illustrated. They sum up to overall investment costs of €1.5 million.

The composition of the overall production costs for the ESBO fed-batch production plant is shown in Figure 7. The considered cost categories for the variable costs are those for materials, energy, personnel and disposal. These cost figures are obtained, e.g., by assessing the quantitative consumption of raw materials, auxiliaries and supplies with a corresponding price. Energy costs (in the form of supply costs for electrical current and natural gas) are those costs that are incurred in the production of the

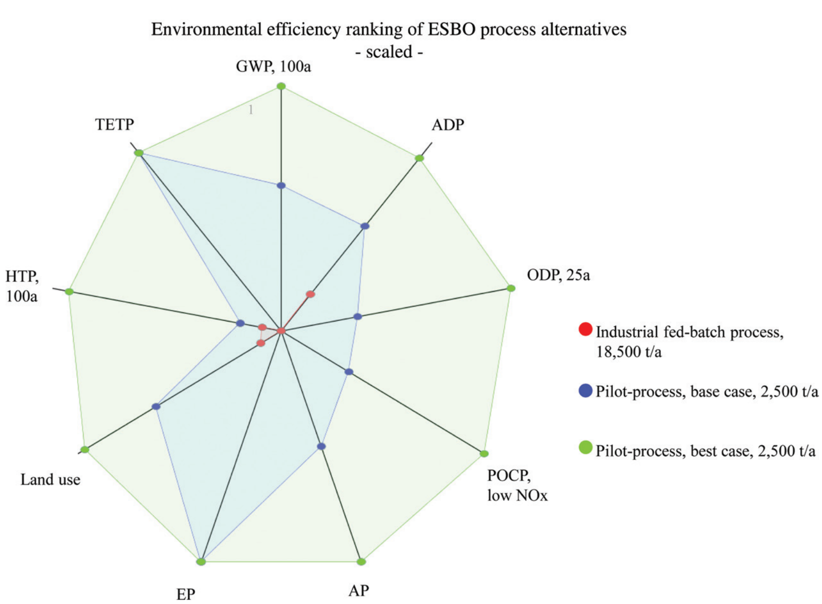


Figure 5 Multi-criteria ranking of epoxidized soybean oil (ESBO) process alternatives (industrial fed-batch, 18,500 t/a; pilot process, base case, 2,500 t/a; pilot process, best case, 2,500 t/a) concerning environmental efficiency (saving potential) taking into account several LCIA categories.

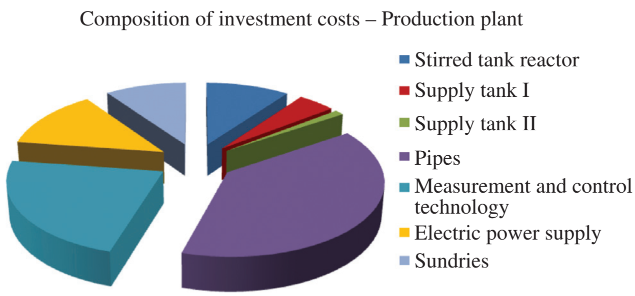


Figure 6 Composition of theoretical investment costs for an epoxidized soybean oil (ESBO) fed-batch production plant.

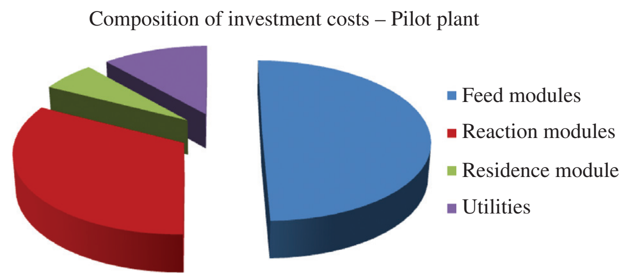


Figure 8 Composition of investment costs for the epoxidized soybean oil (ESBO) pilot plant, best case scenario.

product and are required for the operation of the plant. Personnel costs consist of salaries, wages and social costs. Also, waste arises during the production of the product. It was disposed of separately, for which additional costs incurred. The variable costs were dominated by the costs of the feedstock SBO (€0.45/l) followed by the costs for hydrogen peroxide and formic acid.

Based on the production costs of the existing production process, a prognosis for the impact on potential cost savings of a scale-up of the new processing concept to pilot scale was done. In Figures 8 and 9, the composition of the costs estimated for installing and operating is shown. Here, an annual outcome of 2,500 t per year is assumed. The calculation is based on the same market prices for materials, energy, natural gas and disposal as well as typical personnel costs for a production in Italy; in this case, it is also based on a detailed plan of investment costs.

As shown in Figure 9, the share of personnel costs on the overall production costs is higher for the pilot process, due to the significantly lower annual production capacity. However, in the case of increasing production capacities, the personnel costs can be expected to significantly fall below the personnel costs of the reference fed-batch process [9]. In combination with further cost savings gained by an increase of the annual production capacity of the microreaction plant concept, advantages of the overall production costs against the fed-batch process are likely. In summary, the results of this comparative evaluation pointed out that the overall ESBO production costs are dominated by variable costs independent from batch or continuous processing. In the case of the new pilot plant, the estimated share of variable costs is 97%.

Combining the results of the economic and the environmental assessments of the three case scenarios discussed, an eco-efficiency ranking of the alternative process options was created (see Figure 10). The overall cost efficiencies were interrelated to the environmental efficiencies (see Figure 5). In all cases, the same yield of 90% high-quality ESBO (oxirane number>6) was assumed. From the current state of knowledge, the most favorable scenario would be a continuously operating production process with a reduced amount of required substances and heat recovery (pilot process, best case scenario). Figure 10 reveals that this result was found due to improvements in environmental efficiency. Thus, further process intensification activities should mainly concentrate on a minimization of the production costs, in order to come out with an innovation (scenarios located in the up-right part of the eco-portfolio). As stated before, this can be supported by further capacity increase. But the main key criteria will be the most efficient use of the materials, demanding for: i) maximized yield and ii) minimized

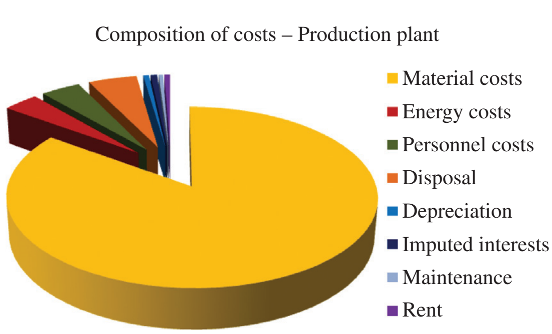


Figure 7 Composition of production costs for the epoxidized soybean oil (ESBO) fed-batch production plant.

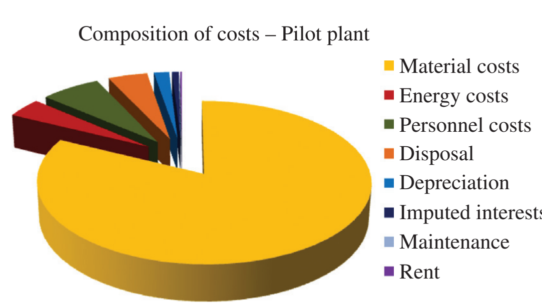


Figure 9 Composition of future production costs for the epoxidized soybean oil (ESBO) pilot plant, best case scenario.

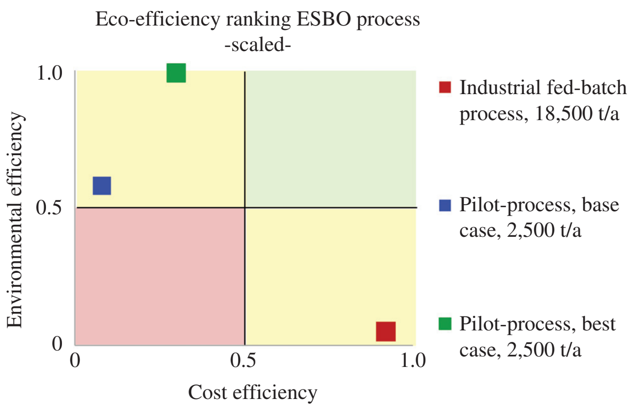


Figure 10 Eco-efficiency ranking of three discontinuously or continuously running epoxidized soybean oil (ESBO) process scenarios.

oxidative media excess. In order to meet these critical targets, recently promising progress has been made in the development of a highly active, selective heterogeneous catalyst, suited for continuous processing [36].

3.3 Case study C: reaction under harsh conditions from batch to flow – process design for intensified biodiesel production

The third case study deals with the development of a novel, intensified biodiesel production alternative [11, 37–40]. Biodiesel, a biodegradable, nontoxic diesel fuel substitute, has shown a significant added value compared to petrodiesel, because of its higher lubricity, lack of sulfur and aromatics and its carbon footprint benefits. However, in current comparative environmental studies between biodiesel and petroleum-based diesel, some significant drawbacks, such as direct and indirect land use changes, nitrous oxide emissions, the decrease of biodiversity and the competition to food, are also mentioned [41]. The CoPIRIDE project rose to the challenge of an intensified and more sustainable biodiesel production process (Scheme 2):

Economic and ecological screening analyses of 18 process parameter variations at an early stage of process design revealed:

- A clear advantage for waste vegetable oil as biodiesel feedstock.
- The advantages of methanol over ethanol or methyl acetate as a reactant as well as solvent [11].

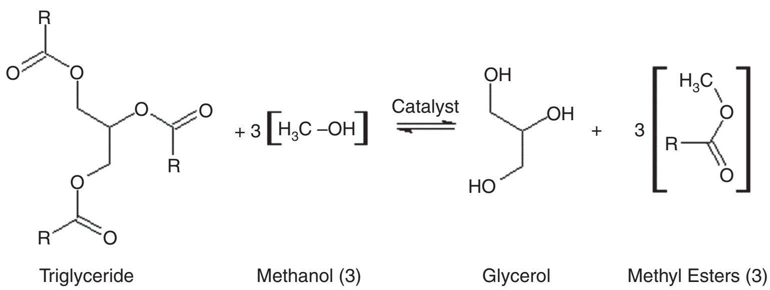
In the next step, detailed LCA and cost analyses comparing five alternative process routes (pretreated alkali-catalyzed, acid-catalyzed, heterogeneous acid-catalyzed, and two supercritical alternatives) utilizing waste vegetable oil and methanol, were carried out for industrial scale processing (production capacity 8,000 t/a). Four of these routes were based on the work of West et al. published in 2008 [42]. The fifth was based on a simulation of an improved supercritical process alternative developed within the project, based on the results of the initial screening procedure applying ASPEN Tech 11.1 as software tool (see Table 4). The analysis included pretreatment, product separation and purification, and the recovery of methanol.

The outranking of the resulting environmental efficiency of these process alternatives is shown in Figure 11 as the basis for eco-efficiency determination. The supercritical processes D and E are characterized by more or less the same environmental impacts (overlaying yellow and pink points and areas). More importantly, conventional process alternatives have benefits in none of the LCIA criteria considered. All in all, a reduction of the GWP (as a representative and relevant environmental impact) by nearly 70% can be gained utilizing the new CoPIRIDE process concept, compared to traditional heterogeneously or homogeneously catalyzed transesterification processes at moderate process conditions. Emission savings of approximately 6,900 t/CO_2-equivalents per year can

Table 4 Summary of operation conditions modeled in ASPEN Tech for five biodiesel process alternatives utilizing waste oil and methanol in all cases; processes A–D in accordance to West et al. [42]; scenario E taken from Kralisch and colleagues [11].

	Process A[a]	Process B	Process C	Process D	Process E
Catalyst	H_2SO_4/NaOH	H_2SO_4	SnO	N/A	N/A
Reactor type	CSTR/CSTR	CSTR	Multi-phase	CSTR	TR/μR
Pressure (kPa)	400/400	400	101.3	20,000	20,000
Temperature (°C)	70/60	80	60	350	380
Alcohol/oil ratio	6:1/6:1	50:1	4.5:1	42:1	42:1
Residence time (h)	1/4	4	3	0.333	0.083
Conversion (%)	100/95	97	94	98	98
Work-up and methanol recovery	Yes	Yes	Yes	Yes	Yes

[a]Including pretreatment.
CSTR, continuous stirred tank reactor; TR, tubular reactor; μR, micro reactor.



Scheme 2 Transesterification reaction of vegetable oil and methanol.

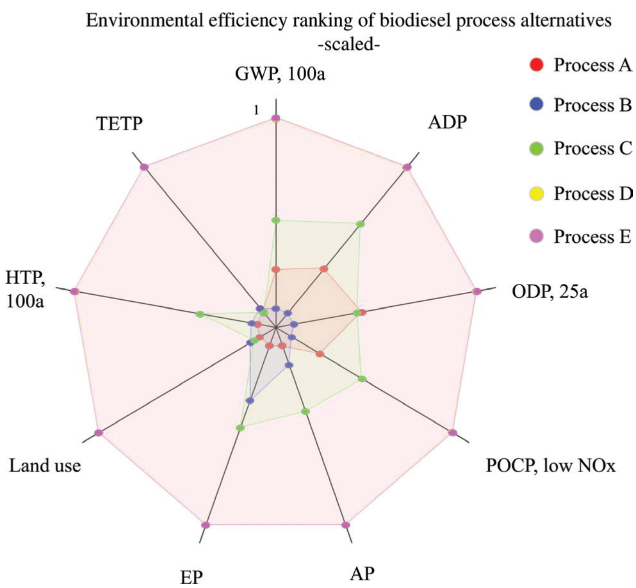


Figure 11 Multi-criteria outranking of different biodiesel process alternatives utilizing waste vegetable oil (Process A: pretreated alkali-catalyzed; Process B: acid-catalyzed; Process C: heterogeneous acid-catalyzed; Process D: supercritical process, mass and energy flows considered according to West et al. [42] and Process E: supercritical process developed within CoPIRIDE) concerning environmental efficiency, taking into account several life cycle impact assessment (LCIA) categories.

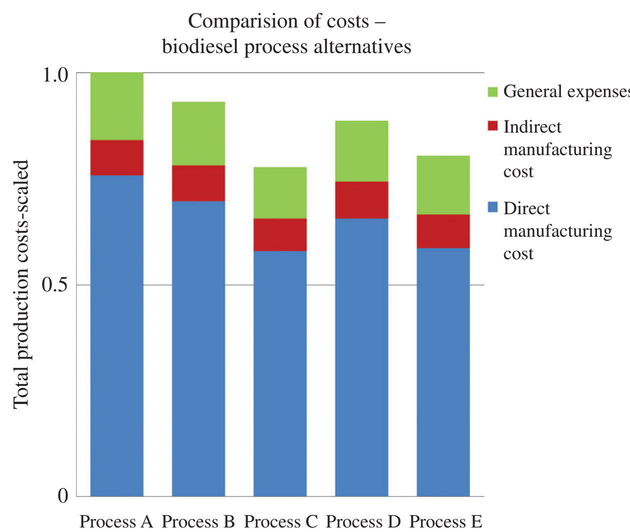


Figure 12 Comparison of production costs for different biodiesel production alternatives (Process A: pretreated alkali-catalyzed; Process B: acid-catalyzed; Process C: heterogeneous acid-catalyzed; Process D: supercritical process, all published by West et al. [42] and Process E: supercritical process developed within CoPIRIDE) feedstock in all cases: waste vegetable oil.

be expected from the technology transfer at a production capacity of 8,000 t biodiesel/a.

Further, a cost analysis of the new developed process E in comparison to the results published by West et al. [42] (A–D) was performed. This cost analysis included pretreatment, product separation and purification, and the recovery of methanol. The resulting general expenses, direct (required for the production) as well as indirect manufacturing costs (overhead costs) are shown in Figure 12. More detailed information cannot be published due to confidentiality reasons. The conventional, heterogeneously catalyzed process C was found to be the cheapest. However, the total manufacturing costs of process E were between 12% and 20% less than the total manufacturing costs of the processes A and B, mostly applied in industry (see Figure 12).

In Figure 13, the results of the LCA investigation and the cost analysis were used as basis for an eco-efficiency portfolio, pointing out the outranking results under consideration of both key criteria for sustainability. It can clearly be seen that, although process C was found to be more cost efficient than the supercritical processes D and E (CoPIRIDE process), the latter is more environmentally benign and more eco-efficient (Pareto-optimal).

The following general lessons were learned from case study C for biodiesel production: i) supercritical is beneficial against conventional processing in the case of waste vegetable oil utilization, but not preferred for fresh oil, ii) the ratio between oil and alcohol or acetate should be kept as low as possible, and iii) heterogeneous should be preferred against homogeneous catalysis, both due to decreased efforts for downstream processing.

An explanation of the background of the results shown in Figure 13 is given in Figure 14. Whereas the good eco-efficiency of process C is mainly reasoned by its cost efficiency, environmental issues were mainly addressed in the cases of process D and E.

Based on the outcome of the eco-efficiency analysis, a mini-plant for a supercritical production process of biodiesel, through a transesterification of waste vegetable oil using methanol in intensifying continuous flow reactors, was designed by Chemtex Italia, Politecnico di Torino and further partners. Here, a supercritical environment enhances the contact among the above-mentioned reagents and intensifies the process. Clear safety benefits can be gained, due to the processing in continuous micro-flow compared to a continuous stirred tank reactor (CSTR) [11]. The mini-plant will allow for a continuous production of about 6 l/h biodiesel.

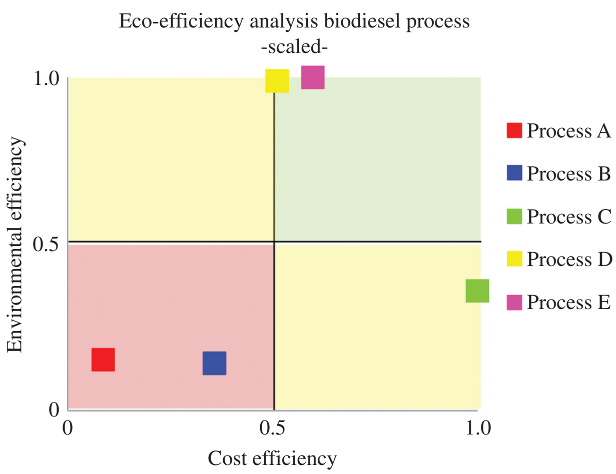


Figure 13 Eco-efficiency ranking of different biodiesel process alternatives utilizing waste oil (Process A: pretreated alkali-catalyzed; Process B: acid-catalyzed; Process C: heterogeneous acid-catalyzed; Process D: supercritical process, all published by West et al. [42] and Process E: supercritical process developed within CoPIRIDE) ranked according to their environmental and cost efficiency.

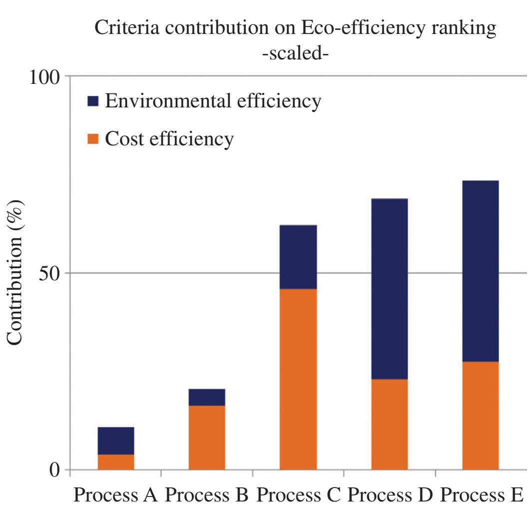


Figure 14 Criteria contribution on overall eco-efficiency ranking of different biodiesel process alternatives utilizing waste oil (Process A: pretreated alkali-catalyzed; Process B: acid-catalyzed; Process C: heterogeneous acid-catalyzed; Process D: supercritical process, all published by West et al. [42] and Process E: supercritical process developed within CoPIRIDE).

4 Conclusions

The results presented here allow an insight into the efforts needed for and the chances of intensified flow chemistry process design under consequent consideration of environmental and cost criteria.

By means of a broad screening of environmental impacts of established production alternatives, as well as of novel design concepts, valuable information about drawbacks and advantages of these alternatives as well as of specific parameter combinations could be gained in an early stage of process design. The suggestions for improvement of sustainability aspects against state of the art concepts were followed within the next steps of process design, whereas the evaluation procedure was refined and intensified during the whole process development. Finally, a comparison of the development outcome with state of the art reference processes, by means of detailed LCA and LCC analyses, allowed for a profound comparison of alternative approaches.

Indeed, the process design accompanying results pointed out that a continuously running microreaction process has the potential to be superior against an established (fed-) batch process. But it is not *a priori* “sustainable”. Significant efforts for process intensification by means of flow chemistry, e.g., in combination with a Novel Process Windows regime, can be necessary to reach this goal. For this, first of all, the underlying chemistry has to be understood, especially in novel process regimes [9].

The outcome in case study B could be mainly reasoned by the strong share of the raw material costs of SBO on the overall production costs. Thus, maximization of yield of high quality ESBO utilizing a minimum of oxidative media was found to be the key figure for material cost savings. In combination with savings in personnel costs, due to a reduced time for operating and supervising compared to the batch process, a further reduction of the overall production costs can be expected for a future industrial plant based on the pilot plant concept.

In case study C, clear benefits concerning environmental sustainability of biodiesel generation could be shown for the combination of supercritical processing, waste oil and methanol. First results regarding enhanced safety properties in the context of microstructured devices during biodiesel production by supercritical processing were also found [11]. In spite of harsh reaction conditions connected with higher safety risks, it might become a suitable alternative, due to benefits arising from significantly shortened residence times and reduced EHS risks within small scale reactor hold-up.

Last, but not least, answering case study overlapping questions, such as catalyst treatment after use (see case study A), can provide valuable support to meet the needs of sustainable future factory design from the beginning.

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