Developing and testing a tool for sustainability assessment in an early process design phase – Case study of formic acid production by conventional and carbon dioxide-based routes

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ABSTRACT

This paper suggests a 'Sustainability Assessment Tool' that can be used in early design phases of production processes. "Green Chemistry" principles were considered as a baseline when proposing the sustainability indicators. European chemicals regulations and databases were also applied and used as a baseline in chemicals hazards assessment. The tool is an excel based checklist, with multiple choice answers that are scored based on their severity of impact. This Sustainability Assessment Tool was tested by comparing two formic acid production routes. It is proposed that using the tool as a guideline in the early stages of a chemical process design can provide competitive advantages in research as it provides guidance on the critical target areas of the process that should be further developed. This can further guide researchers and engineers through the piloting and manufacturing stages. In addition it is also expected that the suggested sustainability assessment tool can be used as an educating purpose to foster sustainability in process design work during all the design stages.

KEYWORDS

Sustainability assessment, sustainability indicators, Green Chemistry, REACH, CLP, Carbon dioxide utilization, environmental sustainability, social sustainability, economic sustainability formic acid

HIGHLIGHTS

- Research evaluates how sustainability can be evaluated in conceptual design phase
- Sustainability indicators were selected based on Green Chemistry principles
- A sustainability assessment tool (SAT) is proposed for chemical process design
- REACH and CLP regulation used as a baseline in chemicals hazards assessment
- The SAT tool provides readiness to drive sustainability through the R&D process

1 Introduction

Sustainability assessment has gained popularity as a decision-making tool for process development and intent to predict the sustainability implications of anticipated actions. Sustainability assessment can be described as the process by which decision making is directed towards sustainability. It is usually linked with derivation of indicators which are useful in determining the current level of social, economic and environmental factors and to state which of these sustainability related factors development are needed (1).

Green Chemistry can be described as a design tool that seeks to re-create materials required and used by the society in order to reduce their adverse impact on human health and the environment (2). Green Chemistry has made a significant impact on improving chemical industry practices; however, it provides mainly a qualitative guideline in designing chemical processes. Green Chemistry and later Green Engineering has attempted to provide tools for chemical engineers, however, these tools are providing largely qualitative guidelines. In order to reach the goal of sustainable production, it is not enough of adding some qualitative environmental or social priorities to do merely better than the previous design. Doing less bad is not good enough and will not lead to sustainable practices. (3) There is need to quantify and compare the complex impacts of different reaction routes, as well there is need to define indicators to measure the complex set of potential impacts are already in the process design and laboratory testing/piloting phase.This article proposed the DfE (Design for Environment) type of checklist tool based on the principles of green chemistry to help to compare several design possibilities and select the most sustainable one, based on the principles from green chemistry, REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) and CLP (classification, labelling and packaging of substances and mixtures) by changing them to practical questions with scoring values. The sustainability assessment tool will be tested on the assessment of two production route of formic acid; a commercial route involving methyl formate hydrolysis and the second one is laboratory scaled carbon dioxide route.

2 Sustainability assessment in early design phase

Traditionally, sustainability and environmental considerations are made in the process design in the phase when already equipment design and plant wide control are completed. (4) This research evaluates the problem, how the design for sustainability can be performed in very early conceptual design phase or rather already on phase, where still basic research is done to investigate new reaction routes for syntheses of chemicals. The essence of the problem is, how can the wide range of impacts that are generated during upstream and downstream processes be assessed at an early design stage to take measures towards the impact abatement? The hypothesis is that it is easier to steer towards sustainability at the early stages in a product's life-cycle. The majority of these principles are ethical guidelines which are considered invaluable in educational considerations for training engineers and scientists to foster sustainable development. (5-7)

Sustainable design is very challenging, and there are several existing tools to create the awareness on potential environmental impacts, such as sustainability principles, checklists, guidelines etc. and to score some limited number of environmental aspects with toolboxes or to create full lifecycle assessment (LCA). (8-10) Design tool that are also raising awareness are eco-design (11), design for the environment (DfE), and green design (12, 13). There are some reports to integrate LCA to process design (14-17) , which are very time consuming and needs lots of resources. LCA with cradle to cradle (C2C) thinking is very good and appreciated way to assess sustainability, however, the indicators proposed in LCA are not very practical to steer the process development in a practical way. There are also several computer-aided tools available (18), but those can be applied is already designed in detail. So the time and selection of tool is very essential, should be done in conceptual design stages, when it is by no means comprehensive or conduct environmental sustainability through engineering design once a detailed design is already created. (8)

Figure 1 is a modified figure from Dimian (2008), where a new proposal is shown to conduct the sustainability assessment in the early phase, where the alternatives for the reaction routes and possible raw material selection is still in review (circulated in red color). The advantage with assessing the sustainability is that, it highlights the major issues which in many cases cannot be changed later during the process design. Also, it can be used while designing a new benign process and to ensure that the new process is sustainable. It is just not an estimation (in worst case based on wrong facts), in many cases it has been seen that new material or process method is more environmental friendly. It can be concluded that in fact the new process can have negative impact to sustainability, if all the aspects are not considered. There is need for a tool to address this, where different alternatives of process synthesis are evaluated.

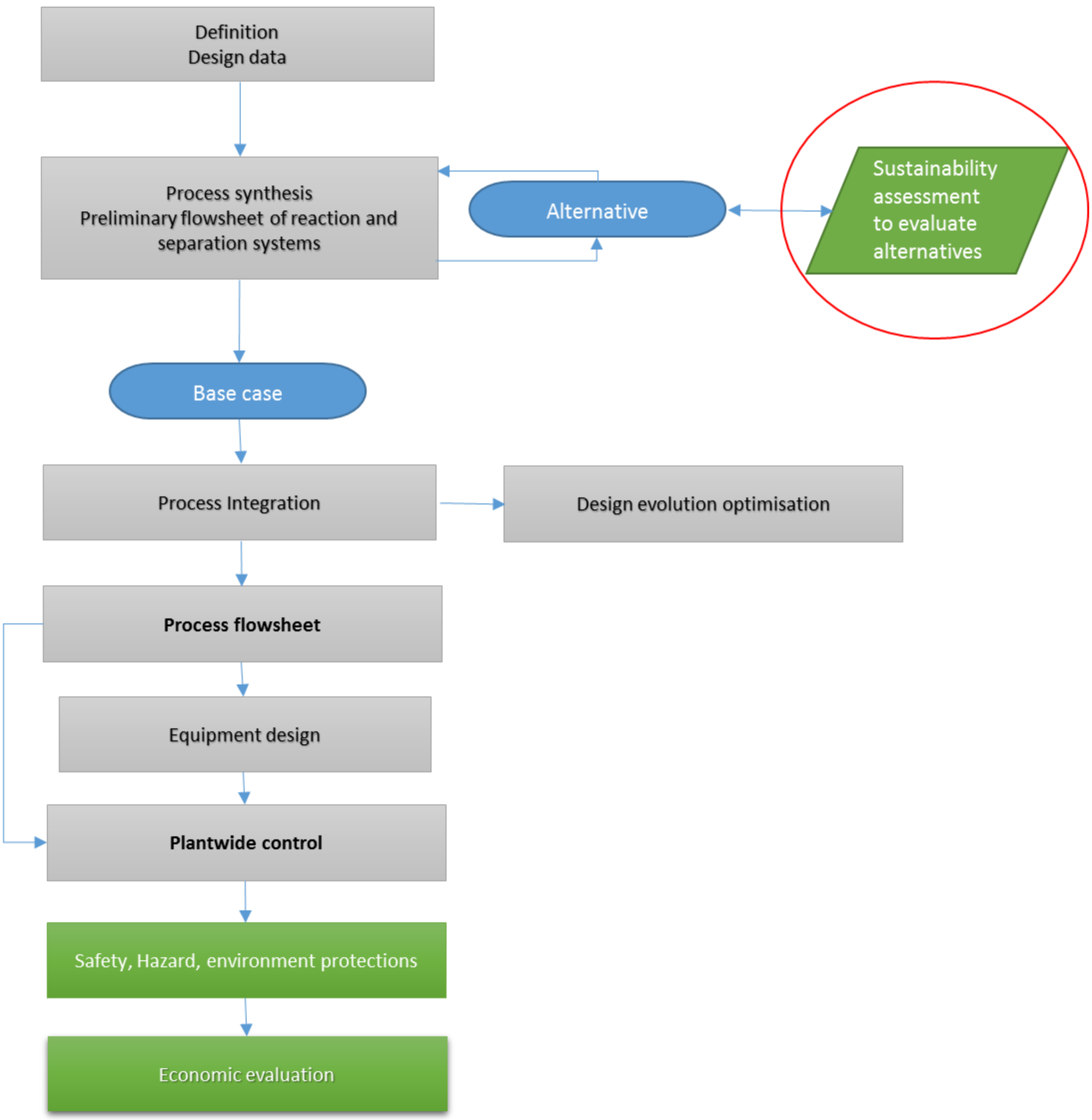


Figure 1. Phases of process design, sustainability assessment part added.

2.1 Sustainable design indicators

Environmental considerations have been a part of chemical process design and everyday operation for more than a decade. However, in process planning, the end-of-pipe thinking of environmental issues prevails. As well, the social and economic aspects of sustainability, the so-called triple bottom line thinking is missing. There is a need for metrics and tools, to translate the complex concept of sustainability into practical and measurable results. However, there are no methodologies available to assess new processes and products at the early design phase.

Green chemistry is the design of chemical products and processes that reduce or eliminate the use and/or generation of hazardous substances, a well concept emerged as a solution to avoiding altogether waste and emissions by preventing pollution at the root of the source. Green Chemistry was first introduced as an answer to the Pollution Prevention Act of 1990. The act established end-of-pipe solution inclosing pollution should be stopped and pollution prevention should be embraced by improved design (19). Green chemistry can be described as “the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture, and application of chemical products”. It can be described as a form of pollution prevention. It entails discovering various ways to find solutions to environmental problems by the continuous process of designing chemical syntheses and products. It achieves pollution prevention by the application and utilization of chemical engineering principles and methods for reduction of pollution at the source. As an assessment tool related to sustainability, the Green Chemistry cannot itself be used as a design tool (20), it is only a list of principles that could not be without any practical guidance.

As discussed earlier most of the available tools concentrate on environmental assessment only, So engineers are well versed to consider environmental aspects, but economic and especially social implications are more challenging to evaluate at the design phase of a new product or process. Social sustainability evaluation should be more crucial in the early process development. In chemical process design, safety and health issues are especially important to consider. It is expected that this strong visualization of weak points would provide incentives for improvement strategies. This would also provide a well-defined evaluation of progress towards meeting the Green chemistry principles.

In the table 1, the sustainability indicators proposed based on the twelve GC principles.

Table 11. Sustainability indicators proposed for design phase comparison with the 12 Principles of Green Chemistry.

Sustainability design indicators	Green Chemistry principle
WASTE PREVENTION Affect the overall costs and profit acquired with the process. The question about the amounts of waste produced in the supply chain of the raw materials/chemicals needed for the process in development might be hard to answer but is important to be considered. The social sustainability of the process is closely related to the nature of the waste produced. In C2C-thinking one can say that it is fine to produce waste if it all becomes utilized, especially if it is a valuable side-product.	Prevent waste It is better to prevent waste than to treat or clean up waste after it is formed.
MATERIALS EFFICIENCY To consider how not to waste any raw materials. This will probably also affect the profit gained with the process. Here it is also necessary to consider the side products produced, and whether they are valuable and saleable. By the Industrial Ecology Principles all the materials entering the process should come out as a part of a saleable product. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once. The reactor type and number of process units and also the amount of waste produced might be diminished when using a catalyst. Lower temperature and pressure could also be utilised. If noble metals are used as catalysts this could lead to social and economic pressures.	Maximise atom economy Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product. Use catalysts, not stoichiometric reagents Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
RAW MATERIALS SELECTION	Design less hazardous chemical syntheses

To consider also the materials used for the process and the supply chain of the materials since if the product of a process is environmentally benign but is made using hazardous or non-renewable substances, the impacts have just been shifted to another part of the products life cycle. The health and safety considerations in this point are of major importance in the Chemical risk assessment process since the overall chemical supply and production chain should possess little or no toxicity to human health and the environment for the process to be totally sustainable. To consider in the early stages of the process development also where the materials come from and whether they are renewable or depleting. Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined. Usage of renewable materials will probably have a positive effect on the overall profit gained by the process. The social question in this point is vital since the extraction of the raw materials needed in the process might be questionable. This is also related to the cultivation of the renewable materials used. The DFE and LCA principles emphasize the nature of raw materials.	Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment. Use renewable feedstocks Raw material of feedstock should be renewable rather than depleting whenever technically and economically practicable.
PRODUCTS BENIGN BY DESIGN The health and safety of the product produced have to be considered already in the beginning of the process development since this affects the usability and marketability of the product and the overall social sustainability of the process. This is also a very important matter when considering the possible profit gained with the process in the future. REACH regulating the chemical use is vital to take into consideration as well as other legislation. The material safety data sheets can be used to check what kind of concerns are related to the products produced. But now with the most updated data for material classification can be found trough CPL database. The product safety is vital also in the chemical risk assessment to be considered already in the design phase. One should also consider how hazardous are the chemicals used in the supply chain. The persistency of the chemical product might induce its accumulation into nature and biological organisms. The non-persistency of the products produced is a very important matter to consider already from the very beginning of the new process development. Also the nature of the degradation products is important to take into account, as these might be really hazardous. The social sustainability is related to the health and safety of the degradation products. DFE concentrates on the lifetime of a product as well on serviceability.	Design safer chemicals and products Chemical products should be designed to preserve efficacy of function while reducing toxicity. Design chemicals and products to degrade after use Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
FEWER ANCILLARIES The use of solvents and other auxiliary chemicals and the type of them is crucial when considering the safety of the reaction. Especially the toxicity and volatility of these chemicals will affect the worker and the overall process safety and are also estimated in the chemical risk assessment process. This might also have a big effect on the production cost and profit gained, based on eco-efficiency calculations. Also the chemicals used in the supply chain should once more be considered. Derivatives use additional reagents and generate waste. In addition to generating waste, temporary modifications might also increase the production cost. The considerations about social sustainability do also in this point concentrate on the health and safety of the workers.	Use safer solvents and reaction conditions The use auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used. Avoid chemical derivatives Unnecessary derivatization (blocking group, protection/ deprotection, temporary modification of physical /chemical processes) should be avoided whenever possible.
ENERGY EFFICIENCY Large deviation from ambient temperature and pressure, as well high energy demand separation method might cause excessive use of energy also increasing the cost and causing possible explosion hazards. By the Industrial Ecology Principles one should also consider where the	Increase energy efficiency Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods

process energy goes and whether it is all used for the desired material transformation. If the process produces waste heat it should be considered if there is a chance of utilizing it somewhere else. LCA usually measures energy consumption through the whole lifecycle.	should be conducted at ambient temperature and pressure.
RISK AND HAZARD MANAGEMENT The real-time monitoring could also minimize the formation of by-products and enhance safety. Especially work safety can be enhanced by real time monitoring of the process. Should be considered at the design phase of the process since it will largely affect the scalability of the process. Chemical risk assessment also takes into account the worker and general safety of the planned process. Processes used in the supply chain should be considered to enhance the overall sustainability.	Analyse in real time to prevent pollution Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
	Minimise the potential for accidents Substances and the form of a substance used in a chemical process should be chose so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

These sustainable design indicators are provided to follow weather sustainability requirements are met in design process. This review of green chemistry principles to be in line with the proposed sustainability indicators are consolidates that the view of selected indicators are sufficient and these are used in the SAT presented later in this paper.

2.2 Chemicals hazard assessment based on REACH and CLP

Protection of human health and the environment from chemicals and associated risks is the goal of the European REACH (21) and CLP regulations (22). They have renewed and upgraded the previous chemicals regulatory framework of the European Union (EU) in order to ensure that there is free circulation of substances on the internal/international market and to enhance competitiveness and innovation. REACH confirms that industries are responsible for both assessing and managing the risks associated with chemicals, giving suitable safety information of chemicals to users, and promoting alternative testing methods (23).

Chemicals marketed in the EU have to be registered. Registration document of chemicals contains general information, safety data sheets (SDS), chemical safety report (CSR), and chemical safety assessment (CSA). Testing for health hazards under REACH includes acute toxicity, skin corrosion and irritation, serious eye damage and irritation, skin or respiratory sensitizer effect, mutagenic or carcinogenic impacts, toxicity for reproduction, specific target organ toxin in single exposure, specific target organ toxin in repeated exposure, and aspiration hazard. This data is used to classify all chemicals. This classification data can be found from the C&L inventory database (24) provided by European chemical agency (ECHA). This classification is based on CLP directive (New Regulation of The European Parliament and of The Council on Classification, Labelling And Packaging of Substances and Mixtures, Amending and Repealing Directives 67/548/EEC and 1999/45/EC, and Amending Regulation (EC) No 1907/2006). The latest and most accurate data is used in SAT assessing environmental, health and physical hazards classification of all feedstock, auxiliary chemical, solvents, separation agents, waste, emission, products and by products used in the processes assessed in this research. All data used with SAT is presented later.

3 Sustainability assessment procedure

The sustainability assessment tool (SAT) proposed in this research provides set of questions for process designers to consider, in order to incorporate all aspects of sustainability into their designs. The SAT provides easy education and knowledge to design and understand what are the important issues during design of chemical process? The SAT follows the principles of green chemistry as well as accounts hazard of chemicals as described by REACH and CLP.This DfE type of checklist tool is based on these main indicators combination with the principles from green chemistry. These are converted to practical questions with several answer options. List of questions is shown in Appendix 1. Total number of questions are 209. There is choice of selection from options for each question given. Answers are valuated, so that the worst answer option gets the highest number. The options are provides in such way that the comparison with two or more cases is easier to conduct. If there is possibility to select several options the idea is to select the worst one. All points weighed that the total value of each sustainability aspect with in the indicator has the same maximum point value (max 10 points). This weighing in SAT ensures that all questions are not equal, to avoid for example safety issues to grow as a highest impact in the assessment due to fact that in Green Chemistry safety issues are highlighted in serval principles.

Sustainability assessment process is as described in figure 2. In order to answer all these questions in the SAT, it requires evaluator to collect a set of information, which is called “facts and assumption” in the SAT sections. It is a challenging task to find all the basic data for the cases that are to be compared in the SAT. Fact and assumptions table contains the most relevant data. Used literature to find out the data, used thermodynamic calculations to find the energy consumption, planned laboratory tests to get most relevant data to be used in the assessment, such as yield, selectivity, catalyst stability etc. Engaged engineers to have the best knowledge that agrees the basic data. If the data is incorrect then the result can mislead, and that becomes the weakest point of the SAT.

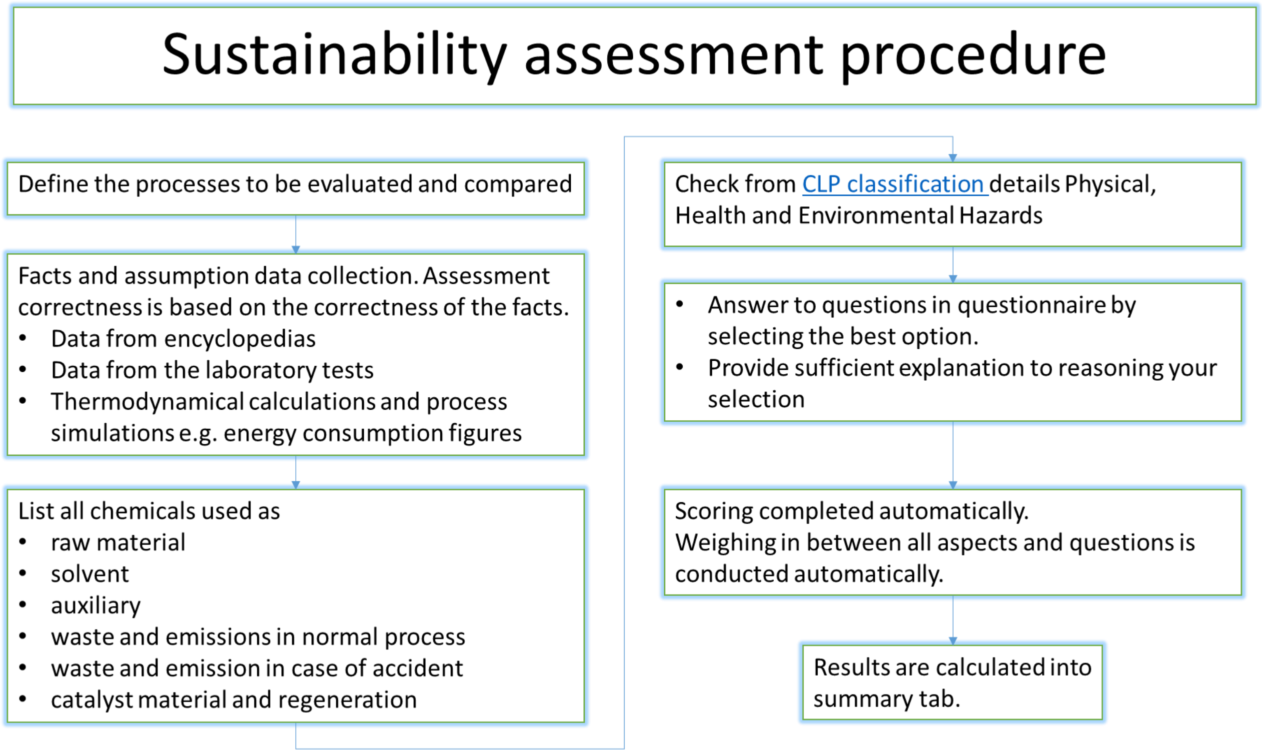


Figure 2. Description of sustainability assessment procedure.

Avoid assessing the same substances and materials in several parts of the assessment. For example if the by-product produced in the process can be recycled back to the process and if the same as raw material, assess it only in raw material part. In safety assessment if there are several substances with same hazard code use the worst one in the assessment. Idea with the SAT is to only highlight the issues of concern, but not to do any risk assessment evaluation on those. SAT is provided help to compare the several design possibilities and select the most sustainable. Further, this article demonstrates the working of this tool on the case study of assessing formic acid production routes.

4 Formic Acid Production Routes assessed

Formic acid (HCOOH), the simplest carboxylic acid, is a valuable chemical product with a world annual production of over 500 thousand tons in 2013 (25). Formic acid is widely used in many fields like in the textile and leather industries, in rubber production, and as an intermediate in the chemical and pharmaceutical industries. (26) There are several reaction routes in which formic acid can be manufactured at commercial and laboratory scale including, direct hydrolysis of methyl formate, liquid-phase oxidation of butane and light naphthas, acidolysis of formate salts (25), oxidation of hydrocarbons, hydrolysis of formamide, direct synthesis from carbon monoxide and water (27), and hydrogenation of CO_2 (26). The most commonly used process is hydrolysis of methyl formate from its salt (27).

In the assessment, production of formic acid via one commercial route and one laboratory scaled route are considered. The commercial route is methyl formate hydrolysis, and the laboratory scaled process route is direct synthesis from carbon dioxide. The reaction equations are as follows:

Route A: Production of formic acid by formate synthesis (1) and hydrolysis of methyl formate (2)

$$CH_3OH + CO \rightarrow HCOOCH_3 \quad (1)$$

$$CH_3OOCH + H_2O \rightarrow CH_3OH + HCOOH \quad (2)$$

Route B: Direct synthesis of formic acid from carbon dioxide and hydrogen

$$CO_2 + H_2 \rightarrow HCOOCH \quad (3)$$

4.1 Production of formic acid by formate synthesis (Route A)

Methyl formate hydrolysis basically involves the synthesis of formic acid via a two stage process. The first stage entails methanol (CH_3OH) being carbonylated with carbon monoxide (CO) [7]. In the second stage formic acid (HCOOH) and methanol (CH_3OH) is derived from hydrolyzed methyl formate (CH_3OOCH) and water (27). In this process, methanol obtained as a side product was recycled back to the first stage (25, 27).

Compressed carbon monoxide and methanol are converted into methyl formate reactor in which carbonylation reaction was carried out at about 4 MPa and a temperature of approximately 80 °C. Catalyst (sodium methoxide, CH_3NaO) was fed into the reactor in a methanol solution. Unreacted methanol and the dissolved catalyst were returned to the reactor; deactivated catalyst (primarily sodium formate) was crystallized and discharged. Waste gas from the reactor was burned. In the second stage, the methyl formate obtained reacts with water. This hydrolysis takes place at around 120 °C and 9 bar. The hydrolysis was catalyzed by the formic acid (autocatalysis). Due to unfavorable equilibrium auxiliary chemical e.g. terniary amine was added to the reactor. In the final stage of the process formic acid obtained from this reactor was dehydrated via distillation to achieve high concentration end product (26).

Figure 3 shows the assumed process flowsheet that was used to make all assumptions. Please note this is not a totally correct flow as some simplifications has been made to be able to conduct full assessment.

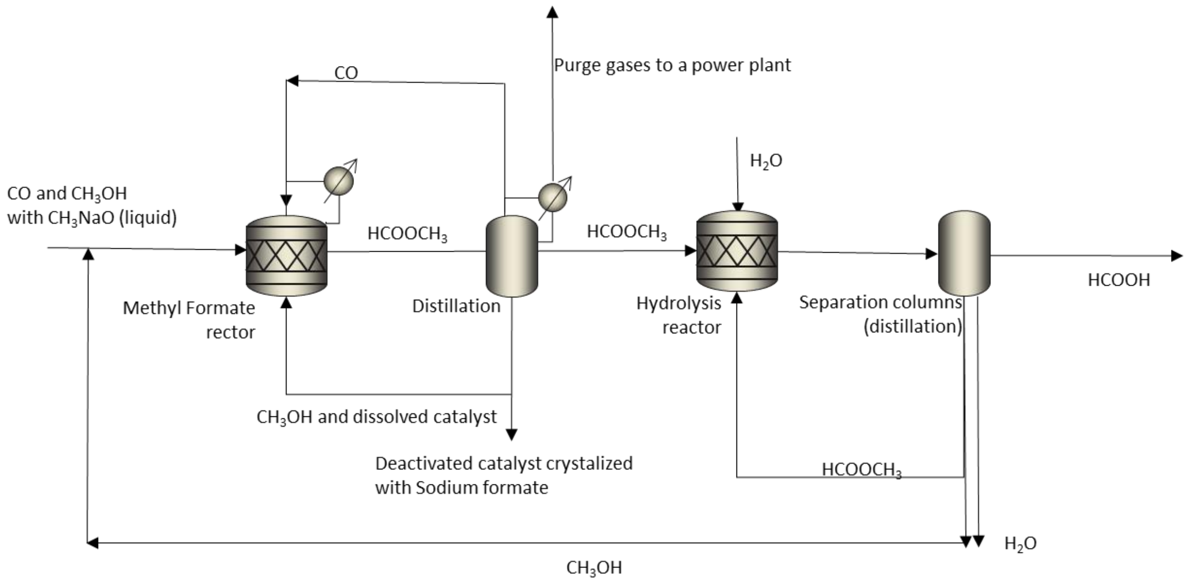
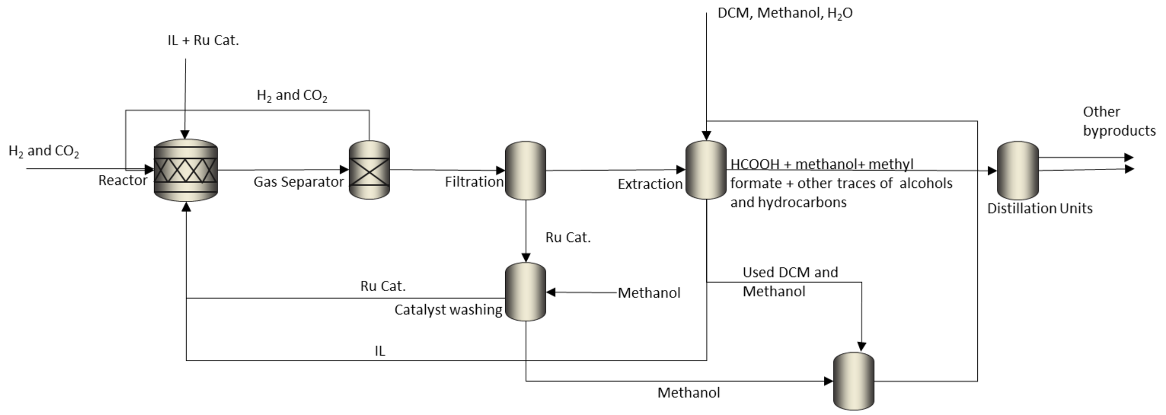


Figure 3. Process flow diagram for production of formic acid by formate synthesis (Route A)

4.2 Direct synthesis of formic acid from carbon dioxide and hydrogen (Route B)

Direct hydrogenation of CO_2 to formic acid is a method of producing formic acid that encourages CO_2 reduction but it is still in the laboratory scale, mainly due to unfavorable thermodynamics (28).
In this experimental reaction route starting materials were H_2 and CO_2. The synthesis of formic acid occurred at a temperature and pressure of 50 ^oC and 150 bar, respectively. A supercritical phase of CO_2 was maintained throughout the experiment. A heterogeneous encapsulated ruthenium catalyst was employed in the reaction and a phosphonium ionic liquid promoter was used along with the catalyst to boost the yield of HCOOH. The ionic liquid is also of high viscosity which made its separation easy. (12)
Figure 4 shows the assumed process flowsheet (including planned separation phases for catalyst, ionic liquid and formic acid) that was used to make all assumptions. Please note this is not a totally correct flow as some simplifications has been made, to be able to conduct full assessment.



4.3 Figure 4. Process flow diagram for direct synthesis of formic acid from carbon dioxide and hydrogen (Route B)

5 Process Simulations

The purpose of the simulations was to determine the energy composition and the purpose of the energy balance was to determine the total amount of energy used in the reaction process. Simulations were conducted by using AspenPlus software. The formate hydrolysis process (route A) consisted of two reactors (formate and hydrolysis reactors), a gas separation unit and two separation columns. The CO_2 based process (route B) was comprised of a reactor, a gas separation unit and separation columns. Units on the flowsheet are described in Tables 3 and 4.

Table 2. Description of units for Methyl formate hydrolysis process (route A).

Process Unit and Type	Notes
Stoichiometric reactor	Formate reactor. Reaction conditions T= 80ºC, P = 40bar
Stoichiometric reactor	Hydrolysis reactor, Reaction ConditionsT=120 °C, P= 9 bar
Component separator	Separation of CO
RadFrac column	Separation of CH_4O, $HCOOCH_3$ and
RadFrac column	Purification of HCOOH

Table 3. Description of units for CO_2 based formic acid synthesis (route B).

Process unit and Type	Notes
Stoichiometric reactor	Reactor conditions. T= 50ºC, P = 150 bar
Component separator	Separation of H_2 and CO_2
RadFrac column	Separation of CH4O, HCOOCH3
RadFrac column	Purification of HCOOH

5.1 Simulation results

Simulation results for material balances are gathered in Table 5.

Table 4. Calculated material balances for studied formic acid routes.

Commercial route A:	Input [kmol/h]	Product stream [kmol/h]	Side streams [kmol/h]
CH_3OH	1	Trace	0.314
CO	1		0.02
H_2O	0.98	0.012	0.673
$HCOOCH_3$		Trace	0.636
HCOOH		0.244	0.050
CO_2 based route B:	**Input [kmol/h]**	**Product stream [kmol/h]**	**Side streams [kmol/h]**
CO2	1		0.9835
H2	1		0.9687
H_2O		0.0002	0.011
$HCOOCH_3$		Trace	0.0038
HCOOH		0.005	0.0002
CH_3OH		Trace	0.0036

6 Sustainability Assessment of Formic Acid Routes

The data related to process efficiency are based on the simulations made in Aspen and also some figures are from literature. For example energy demand for commercial route A is 5.114 kwh and for CO_2 based route B 0.355 kwh are calculated by using Aspen, as well the sensitivity changes (T and P), that were measured with the slope of the sensitivity curve. All features and assumptions used in sustainability assessment for synthesis of formic acid by hydrolysis of methyl formate and the direct synthesis from carbon dioxide and hydrogen for the production of formic acid are shown in Tables 6 and 7. (25, 27, 29, 30) All chemical classification data are found in appendix 2 tables 9 and 10.

Table 5. Most important features and assumptions for two selected processes used based on literature and Aspen calculations.

Features	Commercial Methyl formate route	Lab scale CO_2 based route
Raw material costs (kwh/kmol)	CH_3OH = 257.9 CO = 134.6	H_2= 98.6 CO_2= 32.21
Selectivity of HCOOH (%)	100	14.43 (experimental results) 32.1 (used in Aspen calculations)
Energy Consumption (kwh)	5.114	0.355
Thermodynamic yield of HCOOH (kmol/h)	0.013	$2.95 \cdot 10^{-6}$
Yield of HCOOH (kmol/h)	0.244	0.005
Energy Consumption (kwh/1kmol HCOOH produced)	18.6	71
Energy Consumption of separation units (kW)	7.037	0.096
Conversion (%)	reaction 1: 98 (CH_3OH) reaction 2: 30 (CH_3OOCH)	1.65
Total energy (raw material and process) [kwh/kmol HCOOH]	411.1	210.8
Purity of HCOOH (%)	95	95
Actual yield (measured or found from the literature)	24.43%	0.545%
Atom economy (%)	59	100
m (slope) Sensitivity calculated for T change[1]	Reaction 1: -0.0054 Reaction 2: 0.0001	0.049
m (slope) Sensitivity calculated for P change[1]	Reaction 1: 0.0034 Reaction 2: 0	0.0197

[1] based on thermodynamic calculations

Table 6. General information of the two selected processes.

Features	Commercial Methyl formate route	Lab scale CO_2 based route
Process description	Synthesis of formic acid by formation and hydrolysis of methyl formate	Direct synthesis from carbon dioxide and hydrogen
Raw materials	CH_3OH, CO and H_2O	CO_2 and H_2
Raw material sources	Syngas from fossil fuel to produce CO by reforming. Fossil fuel is from natural gas.	H_2 from H_2O splitting. CO_2 separated from flue gas.
Reaction Route	$CH_3OH+CO \rightarrow HCOOCH_3$ $CH_3OOCH+H_2O \rightarrow CH_3OH+HCOOH$	$CO_2+H_2 \rightarrow HCOOH$
Intermediate	$HCOOCH_3$	none
Side-products	CH_3OH (Main portion recycled back to the process and the rest (vent gases) burned for energy.	Acetic acid, methanol, $HCOOCH_3$, hydrocarbons. CO_2 and H_2 can be recycled back to process
Waste/ Emissions/ Waste water	Inactivated catalyst CH_3NaO (after treatment as a feedstock for deicing product). Small amounts of unreacted CH_3OH and CO, most of them is recycled or burnt for energy.	No
Higher risk case of accident	CO creates risks in case of accident	H_2 creates higher risks in case of accident
Process Conditions	reaction 1. T= 80 ºC, P = 40 bar reaction 2. T= 120 ºC, P = 9 bar	T= 50 ºC, P = 150 bar,
Solvents and Auxiliary Chemicals	Sodium formatete to crystalize inactivate catalyst	Dichloromethane (DCM), methanol and water, Phosphonium ionic liquid is promoter
Catalyst	1. reaction: CH_3NaO (homogenous) 2. reaction: $HCOOCH_3$ (autocatalyst)	Encapsulated Ru catalyst (heterogenious)
Catalyst reusability	No regeration needed	Washing with methanol
Separation processes	Distillation of HCOOH and Catalyst for recycling	Filtration and extractive distillation and gas separation for H_2 and CO_2

7 Discussion of the results of formic acid production route A and B

In table 8 and figure 5 below shows the summary of sustainability scores for both cases A and B. The highest impact in case A is raw materials selection, while in case B, the highest impact is in risk and hazard management for health issues. In case B, this risk and hazard indicator is relatively high, due to safety issues.

Table 7. Sustainability scores of case A and B.

Case A Commercial Formate route	Environmental	Social	Economic	Health	Total
WASTE PREVENTION	1.11	0.59	0.00	1.11	2.81
MATERIALS EFFICIENCY	1.88	0.59	2.67	1.11	6.24
RAW MATERIALS SELECTION	4.29	1.72	10.00	3.89	19.89
PRODUCT BENIGN BY DESIGN	1.67	0.59	0.00	2.22	4.48
FEWER ANCILLARIES	2.50	0.00	3.13	1.94	7.57
ENERGY EFFICIENCY	5.63		3.33		8.96
RISK AND HAZARD MANAGEMENT	3.50	10.00	3.33	2.50	19.33
TOTAL SCORE					**69.29**

Case B CO_2 based route	Environmental	Social	Economic	Health	Total
WASTE PREVENTION	1.39	0.00	2.50	0.00	3.89
MATERIALS EFFICIENCY	5.63	0.59	4.17	2.50	12.88
RAW MATERIALS SELECTION	2.86	1.25	1.25	0.83	6.19
PRODUCT BENIGN BY DESIGN	2.08	0.59	0.00	2.22	4.89
FEWER ANCILLARIES	1.67	1.03	4.38	3.33	10.40
ENERGY EFFICIENCY	6.88		5.00		11.88
RISK AND HAZARD MANAGEMENT	2.50	6.67	6.67	10.00	25.83
TOTAL SCORE					**75.96**

Regarding waste prevention, even though route B does not produce waste as such, due to small conversion it produces a lot of CO_2 emissions. The CO_2 can be recycled back to the process, but it requires an additional process to be built into the production process and tested before having this process as a commercial scale. In route A, Sodium methoxide (CH_3NaO) has some health and safety aspects according CLP and those needs to be taken care of in process safety plan.

Materials efficiency in route B have more negative impacts in environmental point of view due to the fact that the catalyst used on the process have more impact to environment due to fact that noble metal is used, as well the regeneration of encapsulated Ru catalyst require additional washing chemicals and processes. Ruthenium trichloride used as reference chemical in CLP assessment and with that result catalyst has some health and safety aspects that needs to be taken care of. In Route B, the highest impacts raw material selection for economic issues due the fact that yields are very low for this reaction route.

When assessing raw materials selection the amount of raw materials needed in route B is much higher in order to achieve same capacity. But route B uses more renewable feedstock which provides more advantage. Carbon monoxide and methanol as a feedstock are also more harmful than carbon dioxide and hydrogen. In safety point of view raw material do not have a lot of difference, but in the health of point of view route A uses more harmful material for human health. Raw material costs (energy amount kwh/kmol) are higher in route A than in route B, also route B can have economic advantage of using renewables.

Benign product by design part, the main product in both processes is naturally the same, but route B produces a lot more by products than route A. For the health and safety point of view these by-products do not have any additional affects, compared to the route A. Hydrocarbons that are not in very detailed level known have some hazardous effects and for that reason have a bit higher environmental impact.

While reviewing fewer ancillaries indictor route A have a bit higher environmental impact due to two stage reaction route, even the route B have more hazardous auxiliary chemicals used (ionic liquid and dichloromethane). These chemicals have also higher safety and health impact. This necessitates the use of personal protection equipment, which also affects the costs. Another economic point of view is amount of process units that are higher in route B.

In terms of energy efficiency, the routes have also some differences. Route B energy need for separation is less per produced mole of formic acid, but other energy issues are worse in route B, and therefore it have more negative impacts to both environment and economic issues.

Route A has higher impacts in environmental and safety point of view in risk and hazard management, while route B has the higher health impacts due to fact that it uses carcinogenic auxiliary substance. Both reaction routes require well-educated personnel working with these chemicals. Route B is also more sensitive to changes in process conditions (both temperature and pressure).

Some of the questions of the SAT are not possible to answer due to the lack of facts and data to be able to answer correctly. This means there are some uncertainties with the SAT results. In our research 96.0% of the questions are answered in route A, while the number for route B is a bit lower, 94.4%.

When all indicators are calculated together, route A have total score of 69.28, and route B 75.97. In that sense we could argue that route A is more sustainable at the moment and route B needs to develop some of its vague points. Route B is very competitive with the raw material selection, but with all other indicators it has worse points. In many of them the difference in not very high, but in materials efficiency and use of ancillaries, route B has a lot development to be conducted. Route A is commercial production route that has been developed several decades ago, but the advantage of comparing a route in design with a commercial one is to highlight the sustainability indicators that need to be developed further to be able to be competitive current commercial routes. Even though the raw material are renewable and more environmental friendly in route B, it needs to improve its process, especially in terms of yield and the used ancillaries need to be more sustainable.

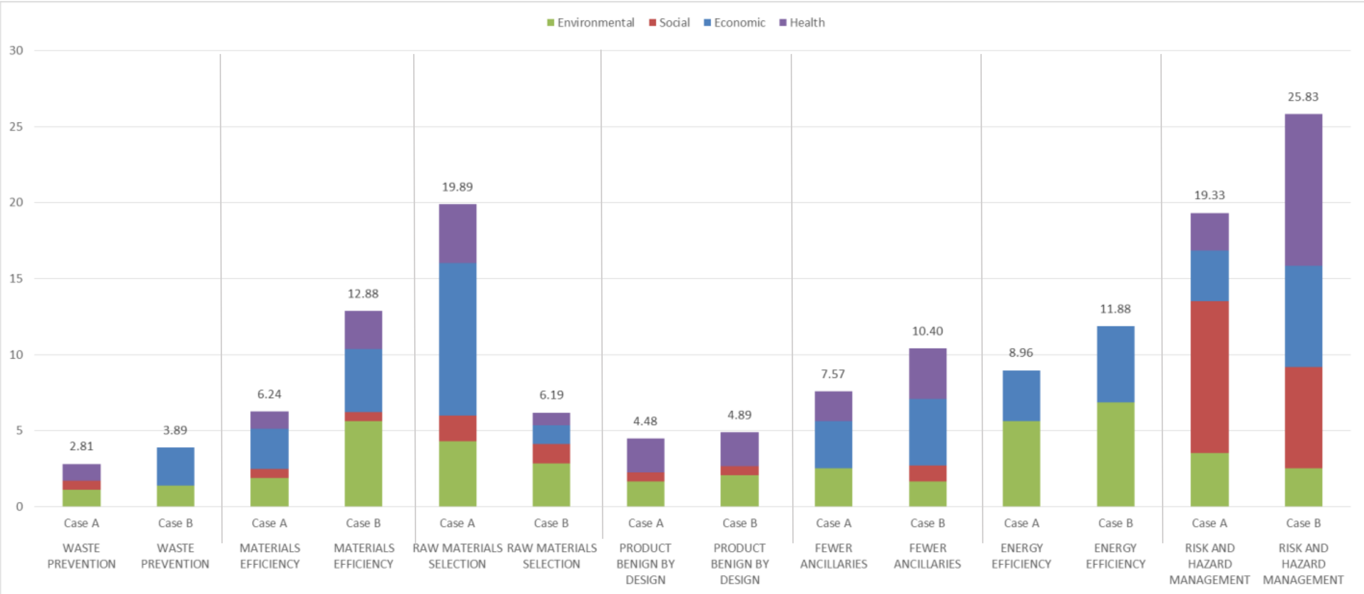


Figure 5 Sustainability impact scores for formic acid commercial route A and CO_2 route B.

8 Conclusion

In this research the set of sustainability indicators were selected as a base to develop a tool for sustainable process design. These sustainability indicators were selected using the principles of green chemistry, which is well-established among chemical professionals. However, the Sustainability indicators were extended to include wider considerations of sustainability aspects, including health and safety issues according latest EU chemical legislation (REACH and CLP) and following indicators to assess sustainability in early design phase were selected; 1) Waste prevention, 2) Materials efficiency, 3) Raw materials selection, 4) Product benign by design, 5) Fewer ancillaries, 6) Energy efficiency and 7) Risk and hazard management.

The sustainability assessment tool (SAT) presented in this paper was tested on formic acid production routes. We did not include any field testing on the usability of the SAT. That would be a next research step to test how easily this tool could be used for any chemical engineer or chemist.

Using the questions list as a guide in the early stages of a chemical process design, one can provide competitive advantages for the company when marketing the process. As well, research groups could use the tool as guidance what are the main point in the process that should be developed to progress sustainability. It is also proposed that researchers and engineers should be educated to use sustainability concepts and consider the questions listed in our SAT tool, to provide them with the readiness to drive sustainability through chemical process R&D.

ACKNOWLEDGEMENTS

This work was performed within the collaborative project “Sustainable Catalytic Syntheses of Chemicals using Carbon Dioxide as Feedstock (GreenCatCO2)” supported by Department of Science and Technology, Government of India (DSTGOI), and The Academy of Finland. The authors would like to thank the Academy of Finland (Project nos. 129173 (SUSE) and 140122 (GreenCatCO2)) and the Finnish Funding Agency for Technology and Innovation, Tekes (Project no. 40313/09 (Fermet)) for financial support. Ganapati D. Yadav also thanks DST for J.C. Bose National Fellowship and received support from R.T. Mody Distinguished Professor Endowment.

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APPENDIX 1.

Table 8. Questions in SAT.

1. Waste Prevention
1.1. Environmental
1.1.1 Does the process produce solid waste?
1.1.2 Is there any possibility to prevent or re-use the waste?
1.1.3 Is the waste hazardous? See the link
1.1.4 Does the process produce emissions (gaseous waste)?
1.1.5 Are there any substances or compounds in the emission hazardous for the ozone layer (according to the CLP)?
1.1.6 Does your process produce wastewater?
1.1.7 Are there any hazardous substances or compounds to the aquatic environment according CLP in waste water?
1.1.8 Does your process produce by-products?
1.1.9 Are there in the supply chain of the raw materials significant amounts of waste produced?
1.2. Social and safety
1.2.1 Are there any ethical issues related to generation or utilization of waste, emission or waste water?
1.2.2 Are there any substances or compounds in waste, emissions or waste water, which are explosive?
1.2.3 Are there substances or compounds in waste, emissions or waste water, which are flammable gases?
1.2.4 Are there substances or compounds in waste, emissions or waste water, which flammable aerosols?
1.2.5 Are there substances or compounds in waste, emissions or waste water, which are oxidizing gases?
1.2.6 Are there substances or compounds in waste, emissions or waste water, which are gases under pressure, dissolved gas, liquid gas or refrigerated liquid gas?
1.2.7 Are there substances or compounds in waste, emissions or waste water, which are flammable liquids?
1.2.8 Are there substances or compounds in waste, emissions or waste water, which are flammable solids?
1.2.9 Are there substances or compounds or mixtures in waste, emissions or waste water, which are any self-reactive?
1.2.10 Are there substances or compounds in waste, emissions or waste water, which are pyrophoric liquids?
1.2.11 Are there substances or compounds in waste, emissions or waste water, which are pyrophoric solids?
1.2.12 Are there substances or compounds in waste, emissions or waste water, which are self-heating?
1.2.13 Are there any substances or mixtures which in contact with water emit flammable gases in waste, emissions or waste water?
1.2.14 Are there substances or compounds in waste, emissions or waste water, which are oxidizing liquids?
1.2.15 Are there substances or compounds in waste, emissions or waste water, which are oxidizing solids?
1.2.16 Are there substances or compounds in waste, emissions or waste water, which are organic peroxides?
1.2.17 Are there substances or compounds or mixtures in waste, emissions or waste water, which are corrosive to metals?
1.3. Economic
1.3.1 Is there any cost related to the treatment and disposal of the waste?
1.3.2 Can you derive profit from waste or by-products?
1.4. Health
1.4.1 Are waste, emission or waste water acutely toxic?
1.4.2 May waste, emission or waste water cause skin corrosion, irritation or sensitization?
1.4.3 May waste, emission or waste water cause serious eye damage or irritation?
1.4.4 Are waste, emission or waste water mutagenic?
1.4.5 Are waste, emission or waste water carcinogenic?
1.4.6 Are waste, emission or waste water toxic for reproduction?
1.4.7 Are waste, emission or waste water specific target organ toxin in single exposure?
1.4.8 Are waste, emission or waste water specific target organ toxin in repeated exposure?
1.4.9 Are waste, emission or waste water aspiration hazard or cause respiratory sensitization?

2. Materials efficiency
2.1. Environmental
2.1.1 Does the separation operations consume lot of material? (if the same capacity compare with different cases)
2.1.2 Does your process use catalysts?
2.1.3 Does your process make use of noble/rare earth metal catalyst?
2.1.4 Does the use of catalyst create waste due to catalyst deactivation (sintering, poisoning, and fouling)?
2.1.5 Is there additional catalyst regeneration needed?
2.1.6 How often the catalyst must be regenerated/replaced?
2.1.7. Are the catalytic materials hazardous to the aquatic environment according REACH?
2.1.8. Are the catalytic materials hazardous for the ozone layer (Ozone) according REACH?
2.2. Social
2.2.1 Does the use of catalysts make the reaction conditions safer by e.g. lowering the temperature and pressure needed?
2.2.2 Are there any catalytic materials, which are explosive?
2.2.3 Are there any catalytic materials, which are flammable gases?
2.2.4 Are there any catalytic materials, which are flammable aerosols?
2.2.5 Are there any catalytic materials, which are oxidizing gases?
2.2.6 Are there any catalytic materials, which are gases under pressure, dissolved gas, liquid gas or refrigerated liquid gas?
2.2.7 Are there any catalytic materials, which are flammable liquids?
2.2.8 Are there any catalytic materials, which are flammable solids?
2.2.9 Are there any catalytic materials, which are self-reactive substances or mixtures?
2.2.10 Are there any catalytic materials, which are pyrophoric liquids?
2.2.11 Are there any catalytic materials, which are pyrophoric solids?
2.2.12 Are there any catalytic materials, which are self-heating substances or mixtures?
2.2.13 Are there any catalytic materials, which in contact with water emit flammable gases?
2.2.14 Are there any catalytic materials, which are oxidizing liquids?
2.2.15 Are there any catalytic materials, which are oxidizing solids?
2.2.16 Are there any catalytic materials, which are organic peroxides?
2.2.17 Are there any catalytic materials corrosive to metals?
2.3. Economic
2.3.1 Cost of catalyst?
2.3.2 Does the use of catalyst reduce the process temperature and pressure and diminish the cost?
2.3.3 Does the use of catalyst provide savings in raw material costs?
2.3.4 Does the use of catalyst provide savings in energy costs?
2.3.5 Does the use of catalysts reduce the production cost e.g. by chancing the type of reactors used, the number of process units and the construction materials?
2.3.6 Does the catalyst regeneration or change of the catalyst affect to the costs?
2.3.7 What is theoretical yield (Atom economy) based predicted by a stoichiometric calculation based on the number of moles of all reactants present?
2.3.8 What is actual yield (measured or found from the literature)?
2.3.9 What is the conversion?
2.3.10 What is the selectivity?
2.3.11 What is thermodynamic yield, calculated at process conditions?
2.3.12 Does the process have high separation capability?
2.3.13 Is the processing time long?
2.3.14 Does the process require maintenance?
2.3.15 Do all the materials entering the process come out as part of a saleable product?

2.4. Health
2.4.1 Are catalytic material acutely toxic?
2.4.2 May catalytic material cause skin corrosion or skin irritation or skin sensitization?
2.4.3 May catalytic material cause serious eye damage or eye irritation?
2.4.4 Are catalytic material mutagenic?
2.4.5 Are catalytic material carcinogenic?
2.4.6 Are catalytic material toxic for reproduction?
2.4.7 Are catalytic material specific target organ toxin in single exposure?
2.4.8 Are catalytic material specific target organ toxin in repeated exposure?
2.4.9 Are catalytic material aspiration hazard or cause respiratory sensitizer?
3. Raw Materials Selection
3.1. Environmental
3.1.1 Does your process use raw materials that are potentially harmful? (Use here all necessary data depending on type of the materials used. NOTE that all health and safety issues are asked later, concentrate only to environmental hazards.)
3.1.2 Does your process use (raw) materials, which are hazardous to the aquatic environment according REACH)?
3.1.3 Does your process use (raw) materials, which are hazardous for the ozone layer (Ozone) according REACH?
3.1.4 Are the raw materials used renewable or non-renewable?
3.1.5 Amount of raw materials needed, if the same capacity would be the same?
3.1.6 Are these materials readily available?
3.1.7 Could/are these materials be derived from waste streams?
3.2. Safety
3.2.1 Are there any raw materials used in process, which are explosive?
3.2.2 Are there any raw materials used in process, which are flammable gases?
3.2.3 Are there any raw materials used in process, which are flammable aerosols?
3.2.4 Are there any raw materials used in process, which are oxidizing gases?
3.2.5 Are there any raw materials used in process, which are gases under pressure, dissolved gas, liquid gas or refrigerated liquid gas?
3.2.6 Are there any raw materials used in process, which are flammable liquids?
3.2.7 Are there any raw materials used in process, which are flammable solids?
3.2.8 Are there any raw materials used in process, which are self-reactive substances or mixtures?
3.2.9 Are there any raw materials used in process, which are pyrophoric liquids?
3.2.10 Are there any raw materials used in process, which are pyrophoric solids?
3.2.11 Are there any raw materials used in process, which are self-heating substances or mixtures?
3.2.12 Are there any substances or mixtures in raw materials used in process, which in contact with water emit flammable gases?
3.2.13 Are there any raw materials used in process, which are oxidizing liquids?
3.2.14 Are there any raw materials used in process, which are oxidizing solids?
3.2.15 Are there any raw materials used in process, which are organic peroxides?
3.2.16 Are there any substances or mixtures in raw materials used in process, which corrosive to metals?
3.3. Economic
3.3.1 What is the cost of raw material? (compare cases)
3.3.2 Does the use of renewables increase cost?
3.4. Health
3.4.1 Are chemicals used in the process (raw materials) acutely toxic?
3.4.2 May chemicals used in the process (raw materials) cause skin corrosion or skin irritation or sensitization?
3.4.3 May chemicals used in the process (raw materials) cause serious eye damage or eye irritation?
3.4.4 Are chemicals used in the process (raw materials) mutagenic?

3.4.5 Are chemicals used in the process (raw materials) carcinogenic?
3.4.6 Are chemicals used in the process (raw materials) toxic for reproduction?
3.4.7 Are chemicals used in the process (raw materials) used in process specific target organ toxin in single exposure?
3.4.8 Are chemicals used in the process (raw materials) used in process specific target organ toxin in repeated exposure?
3.4.9 Are chemicals used in the process (raw materials) used in process aspiration hazard or cause respiratory sensitization?
4. Product Benign by design
4.1. Environmental
4.1.1 Is the product and by products defined as Persistent Bio accumulative Toxic (PBT) Chemicals? PBT and vPvB criteria according to Annex XIII to REACH
4.1.2 Does the product have a high harmful environmental impact at the-end-of life (**take into notice also the side products)**?
4.1.3 Do the products produced contain harmful or hazardous materials (take into notice also the side products)?
4.1.4 Does the use of product lead to harmful emissions?
4.1.5 Are the products or chemicals produced hazardous to the aquatic environment according REACH?
4.1.6 Are the products or chemicals produced hazardous for the ozone layer (Ozone) according REACH?
4.2. Social
4.2.1 Are there any ethical conflicts regarding the product?
4.2.2 Are there any products or by products produced in process (take into notice also the new side products, if differ from raw materials), which are explosive?
4.2.3 Are there any products or by products produced in process (take into notice also the new side products, if differ from raw materials), which are flammable gases?
4.2.4 Are there any products or by products produced in process (take into notice also the new side products, if differ from raw materials), which are flammable aerosols?
4.2.5 Are there any products or by products produced in process (take into notice also the new side products, if differ from raw materials), which are oxidizing gases?
4.2.6 Are there any products or by products produced in process (take into notice also the new side products, if differ from raw materials), which are gases under pressure, dissolved gas, liquid gas or refrigerated liquid gas?
4.2.7 Are there any products or by products produced in process (take into notice also the new side products, if differ from raw materials), which are flammable liquids? Select the most hazard one, if many compounds
4.2.8 Are there any products or by products produced in process (take into notice also the new side products, if differ from raw materials), which are flammable solids?
4.2.9 Are there any products or by products produced in process (take into notice also the new side products, if differ from raw materials), which are self-reactive substances or mixtures?
4.2.10 Are there any products or by products produced in process (take into notice also the new side products, if differ from raw materials), which are pyrophoric liquids?
4.2.11 Are there any products or by products produced in process (take into notice also the new side products, if differ from raw materials), which are pyrophoric solids?
4.2.12 Are there any products or by products produced in process (take into notice also the new side products, if differ from raw materials), which are self-heating substances or mixtures?
4.2.13 Are there any products or by products produced in process (take into notice also the new side products, if differ from raw materials), which in contact with water emit flammable gases?
4.2.14 Are there any products or by products produced in process (take into notice also the new side products, if differ from raw materials), which are oxidizing liquids?
4.2.15 Are there any products or by products produced in process (take into notice also the new side products, if differ from raw materials), which are oxidizing solids?
4.2.16 Are there any products or by products produced in process (take into notice also the new side products, if differ from raw materials), which are organic peroxides?
4.2.17 Are there any products or by products produced in process (take into notice also the new side products, if differ from raw materials), which are corrosive to metals?
4.3. Economic
4.3.1 Is there any significant cost related to the harmful nature of the chemicals in the product?
4.3.2 Is there an indication that end-users would not accept the product?
4.4. Health
4.4.1 Is produced chemical or product (take into notice also the new side products, if differ from raw materials) acutely toxic?

4.4.2. May produced chemical or product (take into notice also the new side products, if differ from raw materials) cause skin corrosion or skin irritation or skin sensitization?
4.4.3 May produced chemical or product (take into notice also the new side products, if differ from raw materials) cause serious eye damage or eye irritation?
4.4.4 Is produced chemical or product (take into notice also the new side products, if differ from raw materials) mutagenic?
4.4.5 Is produced chemical or product (take into notice also the new side products, if differ from raw materials) carcinogenic?
4.4.6 Is produced chemical or product (take into notice also the new side products, if differ from raw materials) toxic for reproduction?
4.4.7 Is produced chemical or product (take into notice also the new side products, if differ from raw materials) specific target organ toxin in single exposure?
4.4.8 Is produced chemical or product (take into notice also the new side products, if differ from raw materials) specific target organ toxin in repeated exposure?
4.4.9 Is produced chemical or product (take into notice also the new side products, if differ from raw materials) aspiration hazard or respiratory sensitizer?
5. Fewer Ancillaries
5.1. Environmental
5.1.1 Are the auxiliary chemicals, solvents, or separations agents that are used in processes considered hazardous?
5.1.2 Are the used auxiliary chemicals, solvents, or separations agents hazardous to the aquatic environment according REACH (Aquatic Acute 1, 2, 3 or Aquatic Chronic 1, 2, 3, 4)?
5.1.3 Are the used auxiliary chemicals, solvents, or separations agents hazardous for the ozone layer (Ozone) according REACH?
5.1.4 Are there multistage synthetic routes in the process?
5.1.5 Are there blocking or protection groups used in the process?
5.1.6 Do these stages lead to the generation of additional quantities of unwanted by-products and waste?
5.2. Social
5.2.1 Are there any auxiliary chemicals, solvents, or separations agents, which are explosive?
5.2.2 Are there any auxiliary chemicals, solvents, or separations agents, which are flammable gases?
5.2.3 Are there any auxiliary chemicals, solvents, or separations agents, which are flammable aerosols?
5.2.4 Are there any auxiliary chemicals, solvents, or separations agents, which are oxidizing gases?
5.2.5 Are there any auxiliary chemicals, solvents, or separations agents, which are gases under pressure, dissolved gas, liquid gas or refrigerated liquid gas?
5.2.6 Are there any auxiliary chemicals, solvents, or separations agents, which are flammable liquids?
5.2.7 Are there any auxiliary chemicals, solvents, or separations agents, which are flammable solids?
5.2.8 Are there any auxiliary chemicals, solvents, or separations agents, which are self-reactive substances or mixtures?
5.2.9 Are there any auxiliary chemicals, solvents, or separations agents, which are pyrophoric liquids?
5.2.10 Are there any auxiliary chemicals, solvents, or separations agents, which are pyrophoric solids?
5.2.11 Are there any auxiliary chemicals, solvents, or separations agents, which are self-heating substances or mixtures?
5.2.12 Are there any auxiliary chemicals, solvents, or separations agents, which in contact with water emit flammable gases?
5.2.13 Are there any auxiliary chemicals, solvents, or separations agents, which are oxidizing liquids?
5.2.14 Are there any auxiliary chemicals, solvents, or separations agents, which are oxidizing solids?
5.2.15 Are there any auxiliary chemicals, solvents, or separations agents, which are organic peroxides?
5.2.16 Are there any auxiliary chemicals, solvents, or separations agents corrosive to metals?
5.2.17 Does the quality of auxiliary chemicals solvents, or separations agents, necessitate the use of protective gear?
5.3. Economic
5.3.1 Is there need for extensive personal protective equipment e.g. gas mask, protective clothing or alarm systems?
5.3.2 Amount of process units?
5.3.3 Cost of process units?
5.3.4 Is there additional consumption of materials and energy is associated with additional stages in the process?
5.4. Health

5.4.1 Are auxiliary chemicals solvents, or separations agent acutely toxic?
5.4.2 May auxiliary chemicals solvents, or separations agent cause skin corrosion or skin irritation or skin sensitization?
5.4.3 May auxiliary chemicals solvents, or separations agent cause serious eye damage or eye irritation?
5.4.4 Are auxiliary chemicals solvents, or separations agent mutagenic?
5.4.5 Are auxiliary chemicals solvents, or separations agents carcinogenic?
5.4.6 Are auxiliary chemicals solvents, or separations agent toxic for reproduction?
5.4.7 Are auxiliary chemicals solvents, or separations agent specific target organ toxin in single exposure?
5.4.8 Are auxiliary chemicals solvents, or separations agent specific target organ toxin in repeated exposure?
5.4.9 Are auxiliary chemicals solvents, or separations agent aspiration hazard or cause respiratory sensitizer?
6. Energy efficiency of the process
6.1. Environmental
6.1.1 Does the separation operations consume lot of energy?
6.1.2 Do the processes require large deviation from ambient temperature?
6.1.3 Is there room for optimization?
6.1.4 Do the processes require large deviation from ambient pressure?
6.3 Economic
6.3.1 Total cost estimate of energy? Compare the cases.
6.3.2 Is it possible to recover heat generated in process?
6.3.3 Savings possible for changing temperature and pressure?
7. Risk and hazard management
7.1. Environmental
7.1.1 Is your process especially sensitive to changes in process condition in terms formation of by-products?
7.1.2 Are there any substances or compounds hazardous to the aquatic environment according REACH if process conditions change?
7.1.3 Are there any substances or compounds hazardous for the ozone layer (Ozone) according REACH if process conditions change?
7.1.4 Are there hazards related to the designed process (synthetic and formulation activities, involved operations or reaction conditions)?
7.1.5 What type of precautions are needed to take to minimize the potential for accidents?
7.2. Social
7.2.1 Overall, how dangerous is the process. How many safety issues totally? If in all safety questions only amount are calculated and then compared with this question.
7.2.2 Do the safety procedures lead to improved quality of working conditions?
7.2.3 Is there a need for advanced training related to the health and safety issues on used chemicals/ raw materials?
7.3 Economic
7.3.1 Is your process sensitive to changes in process condition (temperature change) in terms of yields?
7.3.2 Is your process sensitive to changes in process condition (pressure change) in terms of yields?
7.3.3 Is there significant cost variations associated with changes in process conditions?
7.4. Health
7.4.1 Overall, how many health issues are the process. How many safety issues totally?

Table 9. Chemicals used and produced in Case A. (see the CLP data from the substance name link and general substance data from CAS number link)

Substance name	**CAS number**	**CPL Information**		
Waste				
Sodium methoxide **(CH_3NaO)**	124-41-4	Self-heat. 1	H251	Self-heating: may catch fire
		Skin Corr. 1B	H314	Causes severe skin burns and eye damage
Raw materials				
Carbon monoxide (CO)	630-08-0	Press.Gas		
		Flam. Gas 1	H220	Extremely flammable gas
		Acute Tox. 3	H331	Toxic if inhaled
		Repr. 1A	H360 D	May damage unborn child
		STOT RE 1	H372	Causes damage to organs through prolonged or repeated exposure
Methanol (CH_3OH)	67-56-1	Flam. Liq. 2	H225	Highly flammable liquid and vapour
		Acute Tox. 3	H301	Toxic if swallowed
		Acute Tox. 3	H311	Toxic in contact with skin
		Acute Tox. 3	H331	Toxic if inhaled
		STOT SE 1	H370	Causes damage to organs
By-products				
Methyl Formate **(CH_3OOCH)** **Intermediate product and catalyst**	107-31-3	Flam. Liq. 1	H224	Extremely flammable liquid and vapour
		Acute Tox. 4	H302	Harmful if swallowed
		Eye Irrit. 2	H319	Causes serious eye irritation
		Acute Tox. 4	H332	Harmful if inhaled
		STOT SE 3	H335	May cause respiratory irritation
Product				
Formic acid (HCOOH)	64-18-6	Skin Corr. 1A	H314	Causes severe burns and eye damage
Auxiliary chemicals				
Sodium formate	141-53-7	Skin Irrit. 2	H315	Causes skin irritation
		Eye Irrit. 2	H319	Causes serious eye irritation
		STOT SE 3	H335	May cause respiratory irritation
		Acute Tox. 4	H302	Harmful if swallowed
Catalyst				
Sodium methoxide **(CH_3NaO)**	124-41-4	Self-heat. 1	H251	Self-heating: may catch fire
		Skin Corr. 1B	H314	Causes severe skin burns and eye damage

Table 10. Chemicals used and produced in Case B. (see the CLP data from the substance name link and general substance data from CAS number link)

Substance name	CAS number	CLP information		
Waste and Raw Materials				
Carbon dioxide (CO_2)	124-38-9	Press.Gas./ Liq.Gas	H280	Contains gas under pressure, may explode if heated
According to the classification in CLP notifications: gas under pressure and may explode if heated and contains refrigerated gas and may cause cryogenic burns or injury.		Ref.Liq.Gas	H281	Contains refrigerated gas, may cause cryogenic burns or injury
		Acute Tox.4	H332	Harmful if inhaled
		STOT SE 3	H335	May cause respiratory irritation
Hydrogen (H_2)	1333-74-0	Flam. Gas 1	H220	Extremely flammable gas
		Press.Gas.		
Product				
Formic acid (HCOOH)	64-18-6	Skin Corr. 1A	H314	Causes severe burns and eye damage
By-products				
Methyl Formate (CH_3OOCH)	107-31-3	Flam. Liq. 1	H224	Extremely flammable liquid and vapour
		Acute Tox. 4	H302	Harmful if swallowed
		Acute Tox. 4	H332	Harmful if inhaled
		Eye Irrit. 2	H319	Causes serious eye irritation
		STOT SE 3	H335	May cause respiratory irritation
Acetic Acid ($C_2H_4O_2$)	64-19-7	Flam. Liq. 3	H226	Flammable liquid and vapour
		Skin Corr. 1A	H314	Causes severe burns and eye damage
Auxiliary chemicals				
Dichloromethane (CH_2Cl_2)	75-09-2	Carc. 2	H351	Suspected of causing cancer
Methanol (CH_3OH)	67-56-1	Flam. Liq. 2	H225	Highly flammable liquid and vapour
		Acute Tox. 3	H311	Toxic in contact with skin
		Acute Tox. 3	H301	Toxic if swallowed
		Acute Tox. 3	H331	Toxic if inhaled
		STOT SE 1	H370	Causes damage to organs
Phosphonium based ionic liquid,Trihexyltetradecylphosphonium bromide	654057-97-3	Skin Irrit. 2	H315	Causes skin irritation
According CLP notifications: causes serious eye irritation, causes skin irritation and may cause respiratory irritation.		Eye Irrit. 2	H319	Causes serious eye irritation
		STOT SE 3	H335	May cause respiratory irritation
Catalyst				
Encapsulated Ru catalyst, Ruthenium trichloride	10049-08-8	Aquatic Chronic 2	H411	Toxic to aquatic life with long-lasting effects
According CLP notifications: causes severe skin burns and eye damage, is toxic to aquatic life with long lasting effects, is harmful if swallowed, causes serious eye damage and may be corrosive to metals.		Skin Corr. 1B	H314	Causes severe skin burns and eye damage
		Eye Dam. 1	H318	Causes serious eye damage
		Acute Tox. 4	H302	Harmful if swallowed
		Met. Corr. 1	H290	May be corrosive to metal