



**NTNU – Trondheim**  
Norwegian University of  
Science and Technology

# Life Cycle Assessment on the Conversion of CO<sub>2</sub> to Formic Acid

**Alvaro Robledo-Diez**

Master in Industrial Ecology

Submission date: June 2012

Supervisor: Edgar Hertwich, EPT

Co-supervisor: Xiangping Zhang, EPT

Norwegian University of Science and Technology  
Department of Energy and Process Engineering



## Preface

This project is a master thesis for the department of Energy and Process Engineering at NTNU spring 2012.

The project consists on the study of a process involving the electrochemical reduction of CO<sub>2</sub> in order to get formic acid. This process is on experimental phase and is being researched by DNV research & Development, that also provides most data used on this study.

I would like to thank DNV, especially Edward Rode for his help, also Bhwana Singh, Guillaume Majeau-Bettez, my CO-Supervisor Xiangping Zhang and my supervisor Edgar Hertwich for their help.

Trondheim 15<sup>th</sup> of June 2012

Alvaro Robledo Díez

## Summary

The objective of this work is to provide an environmental assessment of the impacts that the electrochemical conversion of CO<sub>2</sub> to formic acid produces. In order to do this, Life Cycle Assessment has been used.

This is a process that is being currently studied at DNV Research & development, and has been based on data provided by them. Because of the process being yet at experimental phase, there have been some uncertainties regarding lack of data, but the results obtained are believed not to differ too much from reality.

The analysis consists on the evaluation of the requirements and outputs for the production of 100 tons of formic acid 85wt%. There are some byproducts related to this process that have been studied in the following chapters.

The results show that electricity is the main source of impacts, and therefore changing the electricity source has a very big importance on the system final environmental impacts.

The comparison between this process and the most relevant route for producing formic acid nowadays, the methyl formate route, has been used during the whole report due to its usefulness.

## Table of contents

Preface.....	1
Summary .....	2
Table of contents .....	3
Table of figures.....	5
List of tables .....	6
1 Introduction .....	7
2 Formic Acid.....	8
2.1 Properties and use .....	8
2.2 Production routes.....	8
2.2.1 Methyl formate hydrolysis.....	9
2.2.2 Oxidation of hydrocarbons .....	10
2.2.3 Hydrolysis of formamide.....	10
2.2.4 Preparation of free formic acid from formates.....	10
3 Methodology.....	11
3.1 Life Cycle Assessment.....	11
3.2 Impact Assessment Method .....	12
3.3 System Boundary .....	12
3.4 Allocation.....	13
4 Process description.....	14
4.1 Electrochemical reactor.....	14
4.2 Additional processes .....	15
4.2.1 Separator 1.....	15
4.2.2 Compressor 2 and membrane.....	15
4.2.3 Separator 2 and compressor 1 .....	16
4.2.4 Distillator.....	16
5 Life Cycle Inventory .....	17
5.1 Inputs.....	17
5.2 Energy requirements.....	17

5.3 Infrastructure .....	18
5.4 Hydrolysis of methyl formate .....	19
5.5 Outputs .....	19
6 Results & Discussion .....	20
6.1 Environmental impacts for the base case.....	20
6.2 Comparison of environmental impacts between the different paths.....	20
6.3 Greenhouse gas emissions .....	22
6.3.1 Factors that contribute to the GWP .....	23
6.3.2 Emitted Greenhouse gasses.....	24
6.4 Advanced study on GWP of the methyl formate route.....	25
6.5 Sensitivity Analysis .....	27
6.5.1 Electricity Source .....	27
6.5.2 Allocation .....	27
6.6 Boundary discussion and CO2 tracking .....	28
6.7 Data sources, uncertainties and full scale development.....	28
7 Conclusion.....	30
Sources .....	31
Appendix and Formulas .....	32

## List of figures

Figure 1 Boundary of the process .....	12
Figure 2 Process drawing .....	14
Figure 3 Total impacts from each path for a production of 100 ton formic acid 85 wt% .....	21
Figure 4 Relative impacts for each path.....	22
Figure 5 Total GWP impacts for different technologies.....	23
Figure 6 GHG contribution to GWP with US electricity mix .....	24
Figure 7 GHG contribution to GWP with US electricity from coal plant with CC .....	24
Figure 8 GHG contribution to GWP with electricity from PV.....	25
Figure 9 GHG contribution to GWP with methyl formate route .....	25

## List of tables

Table 1 Formic Acid basic properties .....	8
Table 2 Formic Acid uses .....	8
Table 3 Prices and allocation for the different outputs .....	13
Table 4 Shows material inputs for a production of 100 ton of 85 wt% formic acid .....	17
Table 5 Energy requirements of the different components for the production of 1 ton formic acid 85 wt%.....	18
Table 6 Total impacts for the production of 100 ton of formic acid 85 wt% .....	20
Table 7 Impacts on GWP for 100 ton formic acid 85 wt% production. Divided into background and foreground .....	24
Table 8 Relative contribution to GWP in the methyl formate route by the different processes .....	25



## 1 Introduction

Nowadays, the implementation of environmental friendly processes is gaining importance. One of the most relevant factors in the whole picture is global warming. The contribution of one process to global warming is determined by the amount of certain gasses that are emitted to the atmosphere, being usually CO<sub>2</sub> the most important.

This is a big problem for all the power plants based on fossil fuels, since the amount of these gasses that are emitted is very high. Because of this, carbon capture plants are starting to gain importance, this is, power plants where the KWh of electricity is more expensive than in a traditional power plant but that can capture most of the CO<sub>2</sub> that otherwise would be emitted to the atmosphere.

The question now is what to do with that CO<sub>2</sub>. There are two options, CO<sub>2</sub> can be stored or utilized. In this study we are going to focus on a particular way of utilizing the CO<sub>2</sub>, that is transforming it into formic acid by an electrochemical process.

The approach will be a Life cycle assessment (LCA) on the whole process, considering different types of energy sources for the energy used in the process and using as input CO<sub>2</sub> coming from a carbon capture plant.

In order to get a clear picture, we will compare this LCA with the one for the production of formic acid using methyl-formate, which is the most common process for manufacturing formic acid nowadays, so we can get an idea on whether or not this process is feasible at large scale, since it is only at experimental phase right now.

The study is based on data provided by DNV Research & Development, who are the ones researching the process.

## 2 Formic Acid

Here I will make a short introduction of formic acid properties, use and ways of production, in order to get a general idea of the reasons for the study of this new process. No personal research has been made in this chapter and the information comes from the reliable sources listed.

### 2.1 Properties and use

Formic acid, of chemical formula  $\text{HCOOH}$ , is a colorless liquid with a penetrating odor at room temperature. It is miscible in water and is considered a corrosive chemical, which properties are: (PubChem 284)

Table 1 Formic Acid basic properties

Molar Mass	46.03g/mol
Density	1.22g/ml
Melting point	8.4°C
Boiling Point	100.8°C

Formic acid is mostly used as a preservative and antibacterial agent in livestock feed. It is used as preservative for silage and animal feed, in the production of leather and as a coagulant in the production of rubber. (Chemical) & (Ullmann's encyclopedia of industrial chemistry - Formic Acid)

Table 2 Formic Acid uses

Silage/animal feed	35%
Leather	25%
Rubber	10%
Pharmaceuticals, crop protection agents	10%
Other	20%

### 2.2 Production routes

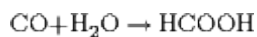
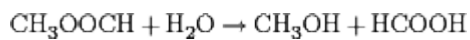
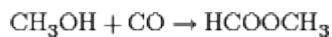
Currently, there are four ways of producing formic acid commercially: (Ullmann's encyclopedia of industrial chemistry - Formic Acid)

1. Methyl formate hydrolysis
2. Oxidation of hydrocarbons
3. Hydrolysis of formamide
4. Preparation of free formic acid from formates

While years ago the most popular technique was the production of formic acid as a byproduct of acetic acid, the economical disadvantages linked to this process have led to an increase of production by dedicated processes.

### 2.2.1 Methyl formate hydrolysis

The production of formic acid by hydrolysis of methyl formate is a two stage process, first, methanol is carbonylated with carbon monoxide, then, methyl formate is hydrolyzed to formic acid and methanol. The methanol obtained as a product in the second stage is returned to the first stage: (Ullmann's encyclopedia of industrial chemistry - Formic Acid)



Although the carbonylation of methanol is relatively problem-free and has been carried out industrially for a long time, only in the last few years the hydrolysis of methyl formate has been developed into an economically feasible process. The main problems in the process are associated with work-up of the hydrolysis mixture. Because of the unfavorable position of the equilibrium, reesterification of methanol and formic acid to methyl formate occurs rapidly during the separation of unreacted methyl formate. Problems also arise in the selection of sufficiently corrosion-resistant materials. (Ullmann's encyclopedia of industrial chemistry - Formic Acid)

This process is the most efficient way of industrially producing formic acid nowadays, and because of that we are going to compare the results of our LCA with those of the LCA on the production of formic acid from this route.

### 2.2.2 Oxidation of hydrocarbons

Formic acid is produced as a byproduct in the liquid-phase oxidation of hydrocarbons to acetic acid. In one of the possible processes, butane is used as the hydrocarbon, and ca. 50 kg of formic acid is produced per ton of acetic acid.

Unreacted hydrocarbons, volatile neutral constituents, and water are separated first from the oxidation product. Formic acid is separated in the next column; azeotropic distillation is generally used for this purpose. The entrainers preferred in this process are benzene or chlorinated hydrocarbons. The formic acid obtained is around 90% wt, and is possible to get up to 98% wt in further distillations. (Ullmann's encyclopedia of industrial chemistry - Formic Acid)

### 2.2.3 Hydrolysis of formamide

Formic acid is produced this way in a three-stage process. In the first stage, methanol is carbonylated to methyl formate, in the second stage, formamide is produced by ammonolysis of ethyl formate, and in the third stage, sulfuric acid is used to hydrolyze formamide to formic acid and ammonium sulfate.

Forty years ago, around one third of formic acid production was obtained this way, but due to the upgrade of the methyl formate route it has lost most of his share. (Ullmann's encyclopedia of industrial chemistry - Formic Acid)

### 2.2.4 Preparation of free formic acid from formates

Formates are obtained as byproducts in the production of polyhydric alcohols. The reaction of formates with strong mineral acids is the oldest known process for producing formic acid commercially. If formates or sodium hydroxide are available cheaply or occur as byproducts in other processes, formic acid can still be produced economically in this manner. (Ullmann's encyclopedia of industrial chemistry - Formic Acid)

## 3 Methodology

### 3.1 Life Cycle Assessment

Life cycle assessment is a systematic set of procedures for evaluating the environmental impacts attributable to the functioning of a product or service system throughout its life cycle. (Agency, 2010)

Life Cycle Assessment can be divided into three steps:

- Compiling an inventory of relevant inputs and outputs
- Evaluating the potential environmental impacts associated with those inputs and outputs.
- Interpreting the results of the inventory and impact phases in relation to the objectives of the study.

For doing all this, the boundary of the system must be clearly defined and understood, since otherwise the results will lack meaning.

Life cycle assessment relates production with inputs and outputs in the following way:

$$x = Ax + y$$

Where  $x$  is a vector accounting for the total outputs of the system,  $A$  is the requirement matrix, which interrelates the different processes in the foreground of our system and  $y$  is a vector accounting for the final production desired from one process.

The previous equation can be rewritten as:

$$x = (I-A)^{-1} * y = L * y$$

Where  $L$  is the Leontief inverse matrix, which provides information regarding the outputs needed for a certain given final demand.

Now, for a given stressor matrix  $S$ , which indicates the emissions caused by one unit output of the different processes, we can define  $E = S * x = S * L * y$  that tells us how much stressors are emitted for our process outputs.

Finally, if we relate those stressors to environmental impacts using a characterization matrix  $C$ , we can get the total impacts of the system as:  $d = C * S * L * y$

### 3.2 Impact Assessment Method

The LCA software Arda version 13\_3 will be used to model the system.

This program is directly linked to the Ecoinvent database, which has standardized information about thousands of processes and stressors that will be used in the background of our system.

Different simulations will be run, depending on the energy source we choose for our process.

### 3.3 System Boundary

As mentioned before, it is essential to have very clear the boundary of the system, in order to be able to get meaningful results.

In our system, the boundary will go from the final products of our process all the way down to the inputs and the processes needed for treating these inputs. The only thing that is left outside the boundary is the final use of our outputs.

In the real process, energy would be provided in the form of heat and electricity, but for this approximation we have assumed it is only electricity. Also, some other minor inputs like the catholyte and anolyte flows and the KCL added to the deionized water will be neglected, since they have a minimum importance in the process final impacts and some much bigger approximations will have to be done because of the process being at an experimental phase. All this will be explained in the following chapters. The following of the CO<sub>2</sub> will be explained in the discussion chapter.

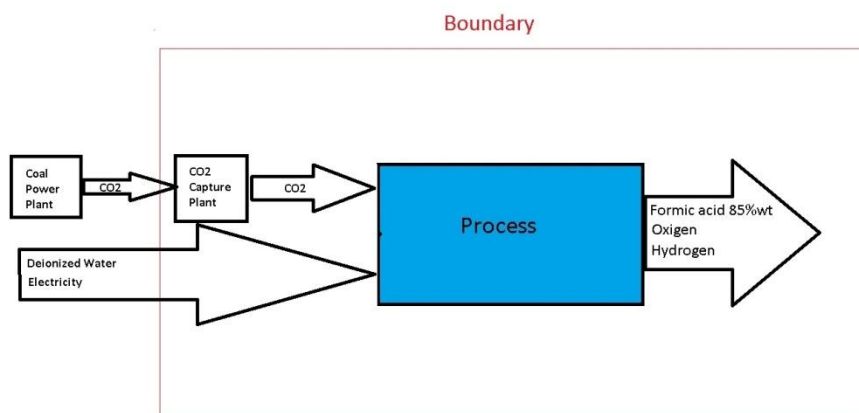


Figure 1 Boundary of the process

### 3.4 Allocation

Many processes generate more than one product, so in order to solve how many impacts should be associated with each product, we use allocation.

There are several types of allocation; the main ones are allocation based on mass, energy or price.

In a mass based allocation, for example, if you have 2 outputs that weight 9 and 1 kg respectively, 90% of the impacts will be related to the first output and 10% to the second one.

Of course this is only an approximation, and we must be very careful with the kind of allocation we choose, since results can vary a lot.

In our process, since we want our outputs in order to sell them, price based allocation seems to be the most appropriate, nevertheless, I will also show how mass based allocation would be in order to see the differences.

Table 3 Prices and allocation for the different outputs

Product	Kg/kg formic acid	Price (\$/kg)	Price based allocation (%)	Mass based allocation (%)
<b>HCOOH 85% (l)</b>	1	0.700	94.8	73.4
<b>O<sub>2</sub> (g)</b>	0.357	0.0166	0.8	26.2
<b>H<sub>2</sub> (g)</b>	0.00471	6.82	4.4	0.4

Prices are based in (J. Beck, Spring 2010)

This indicates that if the process we consider is “production of formic acid” we should only account for 94.8% of the emissions the software will show in the results.

This results clash a little with the preliminary consideration from DNV assuming O<sub>2</sub> to be the main byproduct, since this shows that H<sub>2</sub> would give more than 5 times more money than O<sub>2</sub>. In the appendix we find the flows that lead to the numbers in the “kg/kg formic acid” column.

## 4 Process description

This is a general flow diagram on how the process would look like:

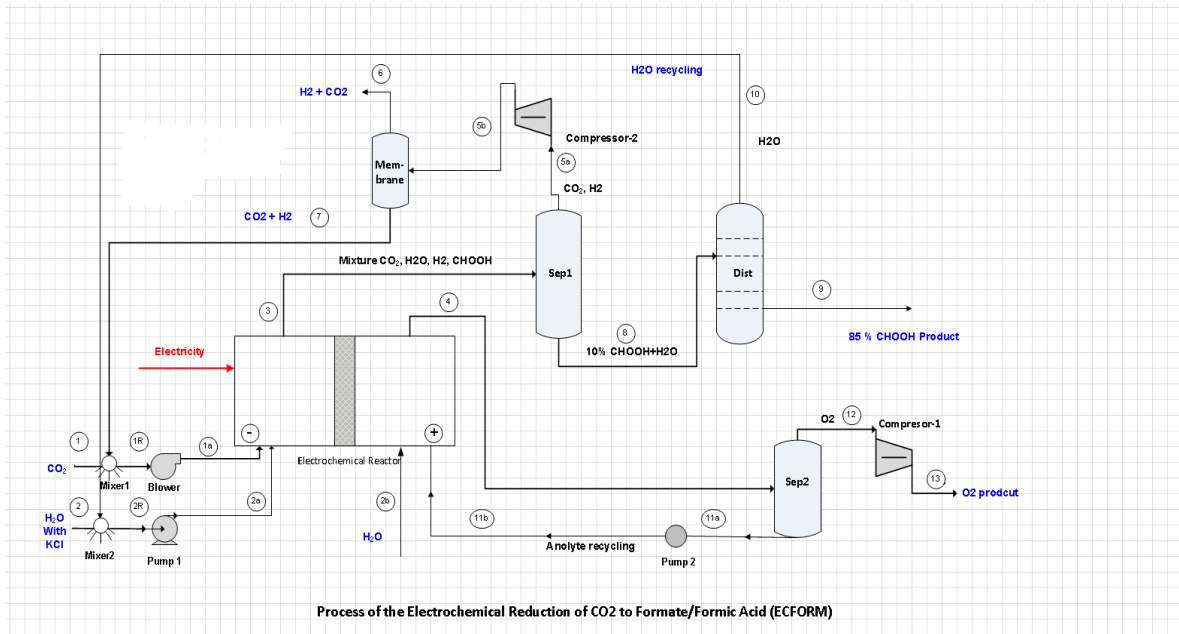


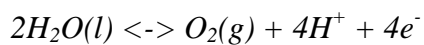
Figure 2 Process drawing

As we can see, there are two inputs, CO<sub>2</sub> and H<sub>2</sub>O, and three outputs, HCOOH, O<sub>2</sub> and H<sub>2</sub>. There are big flows of CO<sub>2</sub> and H<sub>2</sub>O that are continuously recycled in the process.

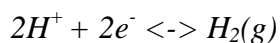
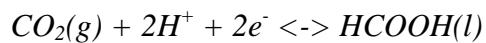
### 4.1 Electrochemical reactor

The reactions that take place in the electrochemical reactor are:

#### Anode:

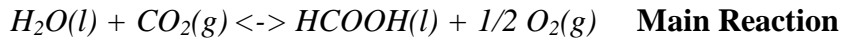


#### Cathode:





**Total:**



We have a mixture of CO<sub>2</sub>, H<sub>2</sub>O, HCOOH and H<sub>2</sub> coming out of the cathode and O<sub>2</sub> mixed with anolyte flow coming out of the anode.

In order to increase the conductivity on both sides of the reactor, an electrolyte is used. 1M H<sub>2</sub>SO<sub>4</sub> is used in the anode and 2M NaCl in the cathode. Also, in order to favor the main reaction, KCl is mixed with the deionized water that goes into the cathode. For the purpose of this LCA these flows will be neglected, but of course they should be taken into account when making an economic viability study.

For estimating the flows, we have used the following data provided from DNV:

- Electrochemical reactor efficiency: 15%. This means that out of 100 moles of CO<sub>2</sub> that enter the reactor, only 15 react to form formic acid. The rest is recycled.
- Selectivity H<sub>2</sub>/HCOOH = 0.15. This means that for each 100 moles of HCOOH forming in the main reaction, there will be 15 moles of H<sub>2</sub> forming in the secondary one.
- Functional unit: 100ton 85%wt HCOOH/day.<sup>1</sup>
- Composition of formic acid-water out of the reactor: 10%wt HCOOH

## 4.2 Additional processes

### 4.2.1 Separator 1

Consists on a simple separator that divides the stream out of the cathode into one gaseous stream (CO<sub>2</sub> and H<sub>2</sub>) and a liquid one (H<sub>2</sub>O and HCOOH).

### 4.2.2 Compressor 2 and membrane

The compressor compresses the mixture up to 50bar, and the membrane separates the H<sub>2</sub> of the CO<sub>2</sub> with an efficiency of 85%, which means that stream 6 in the flow diagram is composed by 85% H<sub>2</sub> and 15% CO<sub>2</sub> (molar based). The ratio between fresh CO<sub>2</sub> entering the reactor and recycled one is around 1/6.

---

<sup>1</sup>85%wt means that 100 tons of product is composed by 85 tons of HCOOH and 15 tons of water.

#### **4.2.3 Separator 2 and compressor 1**

A simple separator separates the gas from the liquid so that the anolyte is recirculated back to the reactor. The compressor compresses the oxygen up to 4 bar in order to be able to transport it.

#### **4.2.4 Distillator**

The distillator makes the HCOOH flow go from 10% wt to 85% wt by evaporating most of the water and sending it back to the electrochemical reactor. The ratio between new water and recycled one is around 1/15.

## 5 Life Cycle Inventory

### 5.1 Inputs

#### CO<sub>2</sub>

The CO<sub>2</sub> consumed by the electrochemical reactor is considered to come from a carbon capture plant, and the impacts implied in capturing the CO<sub>2</sub> are inside the system boundary. Since this process of capturing CO<sub>2</sub> is not implemented in the ecoinvent database, I will take the data from Bhwana Singh's doctoral thesis "Environmental evaluation of carbon capture and storage technology and large scale deployment scenarios". (Singh, 2011)

#### Deionized water with KCl

The water that goes into the reactor has to be deionized and with some KCl. We will take the standardized process "water, deionized, at plant/ CH/ kg" from the eco-invent database, neglecting the KCl for the reasons explained before.

Table 4 Shows material inputs for a production of 100 ton of 85 wt% formic acid

Material input	Value	Unit	Process
CO <sub>2</sub>	81.30	Ton	Customized
H <sub>2</sub> O	48.26	Ton	water, deionized, at plant/ CH/ kg

### 5.2 Energy requirements

In this process, energy will be needed for all the components showed in the flow diagram, and also some for capturing the CO<sub>2</sub> and for the auxiliaries and minor components that have not been drawn. Some in the form of heat and some in the form of electricity.

The aim of this study is not to get into details about the energy consumption from every component but to assess the impacts caused by them, in order to do this, some approximations are needed. Taking DNV's advice, we have approximated the consumption of the whole installation to that of the main four energy consuming elements; that are the electrochemical reactor, the distillator, and the two compressors. For simplicity we will consider they only use electricity, although the distillator will most likely use mostly heat. The energy required for capturing the CO<sub>2</sub> is also taken into account separately. Here is a table where we can see the energy inputs required **per ton of formic acid produced:**

Table 5 Energy requirements of the different components for the production of 1 ton formic acid 85 wt%

Process	Value	Unit
Elec. Reactor	6	MWh
Distillator	1	MWh
Compressor 1	0.01	MWh
Compressor 2	0.43	MWh

All the values in this table were provided by DNV.

This gives us an idea on the energy consumption required per ton of formic acid produced; it should be around 7.5MWh/ton.

Regarding the energy source, three different approximations will be studied: US electricity mix; US photovoltaic mix; and electricity coming from a power plant with carbon capture, in which case the CO<sub>2</sub> captured will be used in our system too. For this last approximation, data from the study mentioned before (Singh, 2011) will be used, and some more complex calculations must be used, because the power plant will have two outputs, electricity and CO<sub>2</sub>. You can find this explained in the calculations chapter.

### 5.3 Infrastructure

When assessing the impacts of a process, it is important to take into account the share of these that are produced by the process infrastructure, which includes materials, manufacturing and end-life of the components.

Due to the process being yet at an experimental phase, there is not good enough data for the infrastructure at the moment, so we have decided not to include it and leave the chapter opened in case this data is available in the future.

To compensate for the impacts that would have been caused by the infrastructure, the maximum values of energy provided from DNV have been chosen, in order to compensate one thing for the other. Of course this is a rough approximation, but we believe that the results obtained will be reliable enough to get to some useful conclusions.

#### 5.4 Hydrolysis of methyl formate

As it has been mentioned in previous chapters, in order to get a meaning out of the results from the LCA, we need to compare them with those you get from the LCA of formic acid produced from conventional sources. We will compare it to the production of formic acid from methyl formate, since this is the most efficient route nowadays and there is a standardized process in the ecoinvent database for this route.

This process has the advantage of being less energy intensive, using around 3.5 MWh/ton of formic acid produced, but that does not mean that it will have fewer impacts.

For making a perfect comparison, a very good knowledge of this process would be needed, because factors like the energy source or the boundary of the system are a little bit unclear in the ecoinvent process “formic acid from methyl formate, at plant” which is what we are going to use for the comparison. Hopefully in the future this can be done with more detail if formic acid starts to be produced from CO<sub>2</sub> at large scale.

#### 5.5 Outputs

Since all the outputs have commercial value, we cannot consider any stressors to be emitted.

## 6 Results & Discussion

### 6.1 Environmental impacts for the base case

This table shows the impacts caused by the production of 100 tons of formic acid with electricity taken from a power plant with carbon capture, which is our base case.

Table 6 Total impacts for the production of 100 ton of formic acid 85 wt%

Impact Category	Unit	Impacts
agricultural land occupation	m2a	12356,7424
climate change	kg CO2-Eq	83344,767
fossil depletion	kg oil-Eq	246669,039
freshwater ecotoxicity	kg 1,4-DCB-Eq	0,80853964
freshwater eutrophication	kg P-Eq	3,183E-05
human toxicity	kg 1,4-DCB-Eq	98424,6488
ionizing radiation	kg U235-Eq	7974,37336
marine ecotoxicity	kg 1,4-DCB-Eq	53,4367355
marine eutrophication	kg N-Eq	180,638346
metal depletion	kg Fe-Eq	0,00298845
natural land transformation	m2	9,0935E-06
ozone depletion	kg CFC-11-Eq	0,01198082
particulate matter formation	kg PM10-Eq	161,387508
photochemical oxidant formation	kg NMVOC	1180,52412
terrestrial acidification	kg SO2-Eq	806,937405
terrestrial ecotoxicity	kg 1,4-DCB-Eq	15,1312274
urban land occupation	m2a	8265,60819
water depletion	m3	2546,97018

### 6.2 Comparison of environmental impacts between the different paths

As it has been mentioned before, we are considering three different energy sources for our process, and also a parallel process where the formic acid is produced from methyl formate. In the following two graphs, we are going to make a comparison between them.

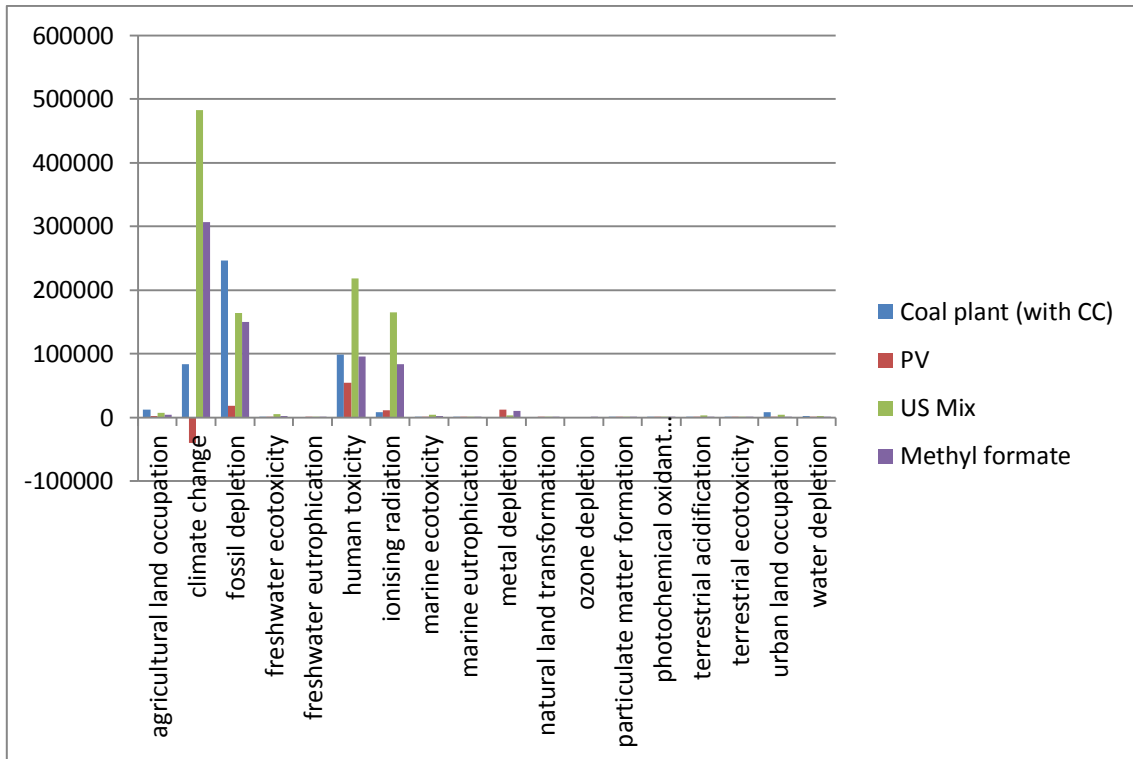


Figure 3 Total impacts from each path for a production of 100 ton formic acid 85 wt%

We can observe that climate change is the most relevant impact category for most paths, but fossil depletion, human toxicity and ionizing radiation should also be taken into account.

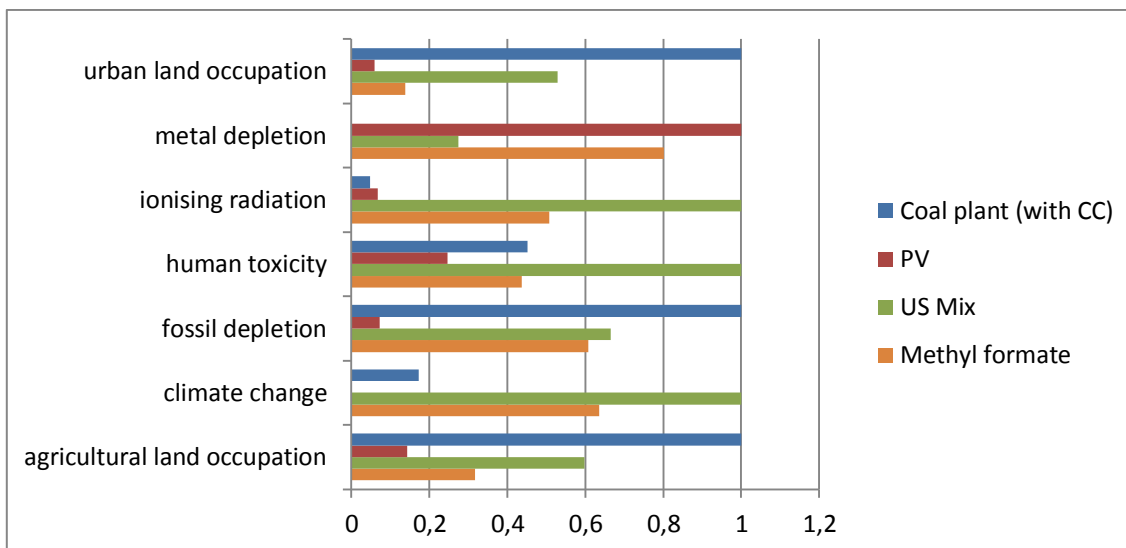


Figure 4 Relative impacts for each path

In this graph a value of 1 means that the path has the most impacts in that category and the other paths have a value related to that. We have only chosen the most important ones in order to get a clearer graph.

From this results, we can see the huge importance that the origin of the energy used in the process has in the final impacts and, as expected, we observe that if we use as energy source the electricity mix from the US, the impacts are bigger than those from the methyl formate route while using electricity from photovoltaics or from a carbon plant with carbon capture have less impacts than the existing methyl formate route.

Of course these results have to be taken carefully, because in addition to the limitations linked to the experimental nature of the formic acid production from CO<sub>2</sub> process, we are comparing it to a standardized methyl formate route, which impacts can also vary depending on the energy source used.

### 6.3 Greenhouse gas emissions

Climate change is one of the most important impact categories in our process. In fact, the production of formic acid from CO<sub>2</sub> was from the beginning addressed as a way to reduce CO<sub>2</sub> emissions by utilizing the output of CO<sub>2</sub> from a power station rather than emitting the CO<sub>2</sub> to the atmosphere.



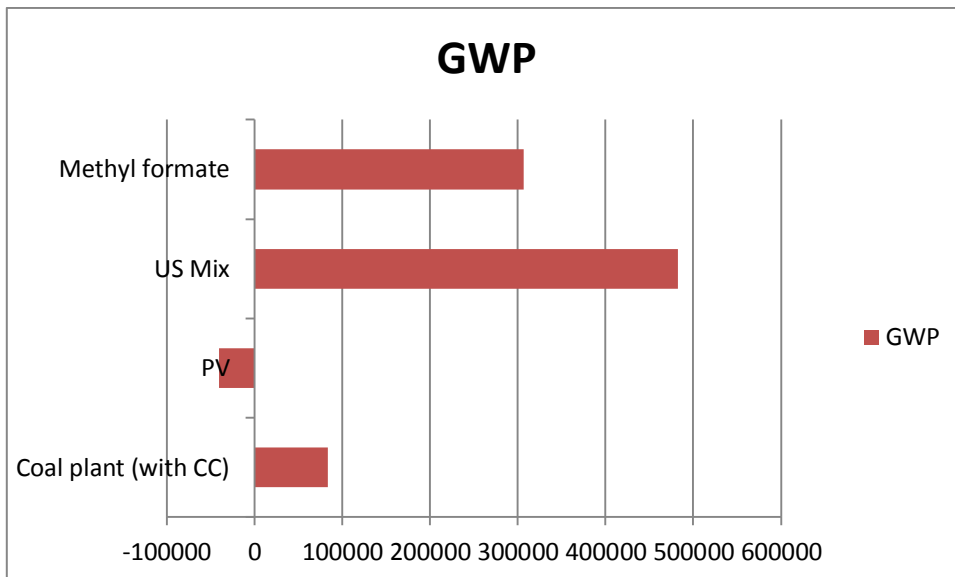


Figure 5 Total GWP impacts for different technologies

In this table we can see the global warming potential of the different technologies for getting formic acid.

We can observe that the most pollutant route would be our process using US electricity mix. Then the methyl formate route follows closely, then using electricity from a coal plant with carbon capture and finally using electricity from photovoltaics.

### 6.3.1 Factors that contribute to the GWP

Because of the simplifications we have applied to the system, the only processes that emit stressors are:

- The production of electricity in the background for the different system components to work and,
- The electricity used in the capture of CO<sub>2</sub> for the input of the system in the foreground.

The first process always has a positive GWP effect, this is, emits CO<sub>2</sub> (or equivalents). But the second process, despite it also consumes energy, since it avoids CO<sub>2</sub> from going into the atmosphere, it will have a negative value of CO<sub>2</sub> emissions.

Table 7 Impacts on GWP for 100 ton formic acid 85 wt% production. Divided into background and foreground

Energy source	Background GWP impacts	Foreground GWP impacts	Total GWP impacts
US Mix	558627	-75769	482857
PV	159113	-75769	83344
Coal plant (CC)	35242	-75769	-40527

This explains why we can get a negative value of GWP, as long as the emissions of our electricity source are very low, like in the PV case.

From this results, I think it is reasonable to disregard the US Mix electricity option, since it does not make too much sense to be studying a technology in where reduction of CO<sub>2</sub> emissions are given importance at the expense of a higher energy demand, and then use a very pollutant electricity mix that emits 8 times more CO<sub>2</sub> than what you are able to “avoid” in the capture process.

### 6.3.2 Emitted Greenhouse gasses

Although when we are accounting for greenhouse gasses we speak in terms of kg of CO<sub>2</sub> equivalents, there are other gasses apart from CO<sub>2</sub> that are being emitted; this will be shown in the following figures:

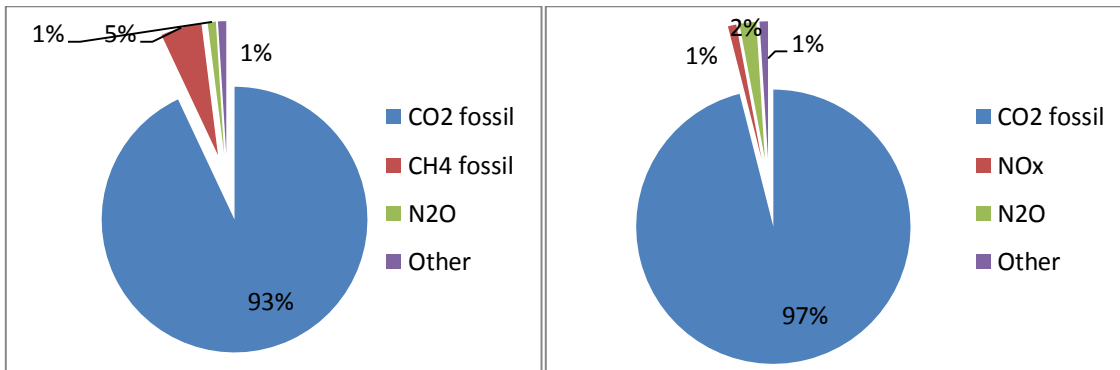


Figure 6 GHG contribution to GWP with US electricity mix

Figure 7 GHG contribution to GWP with US electricity from coal plant with CC

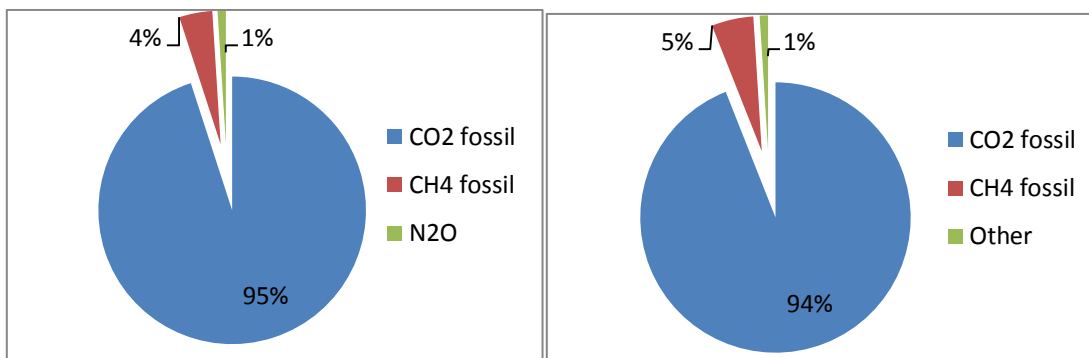


Figure 8 GHG contribution to GWP with electricity from PV

Figure 9 GHG contribution to GWP with methyl formate route

We can see that the main contributor for GWP is always CO<sub>2</sub>. Also, the relevance of each process for the total GHG emissions is directly proportional to the share of electricity it consumes. This happens because we have assumed all energy consumption to be electricity and from the same procedence.

Because of all said, this last four figures shouldn't be given too much importance.

#### 6.4 Advanced study on GWP of the methyl formate route

Like we mentioned before, there is some uncertainty regarding the procedence of the energy used on the methyl formate standarized process. In order to get a general idea, here is a table that shows the processes that contribute the most to GWP:

Table 8 Relative contribution to GWP in the methyl formate route by the different processes

Process name	Relative contribution to GWP (%)
Natural gas, burned in industrial furnace	29%
Light fuel oil, burned in industrial furnace	14%
Hard coal, burned in industrial furnace	12%
Lignite, burned in power plant	5%

We can see that the most pollutant processes are based in fossil fuel combustion, which explains why this route has more GWP impacts than our “clean” processes, those based on PV and in Power plant with carbon capture.

If we want to get more detail on the processes that produce the impacts, a structural path analysis should be done. With this, you can see the whole chain of processes that is responsible for the impacts, instead of only the raw process. Here I will only show the two process chains that contribute the most to GWP.

*natural gas, burned in industrial furnace -> heat, unspecific, in chemical plant -> formic acid from methyl formate, at plant -> Formic acid from methyl-formate* **29% Emissions**

*light fuel oil, burned in industrial furnace -> heat, unspecific, in chemical plant -> formic acid from methyl formate, at plant -> Formic acid from methyl-formate* **14% Emissions**

This shows that the two most pollutant processes for GWP are used to produce heat in a chemical plant that uses that heat for making the formic acid. So the methyl formate route is based on heat, while the CO<sub>2</sub> one is based on electricity.

This here is something very important to take into account when comparing the two routes: heat energy is cheaper than electricity, but also heat based processes are less likely to be carried out with renewable energy sources, because most renewable sources, except from biomass, give as output electricity, which is higher quality energy than heat, so using it for heat purposes is a waste of money.

So it is most likely that the process “formic acid from methyl formate” cannot get its emissions drastically reduced just by changing its energy source, at least not without paying a big price, so this is a motivation for continuing the research on the electrochemical reduction of CO<sub>2</sub> to get formic acid, and even more if the global demand for formic acid increases and the emissions produced by the methyl route become no longer affordable.

Nevertheless, I would like to remark once more that the research on the methyl formate route has not been a priority in this study, no there could be some looseness in this analysis.

## 6.5 Sensitivity Analysis

In order to see the influence that the choices we have made can have on the final results, a sensitivity analysis is made.

### 6.5.1 Electricity Source

Due to the process being experimental, we have had to make a lot of approximations, considering no infrastructure by now and considering all the energy requirements to be electricity are some of them. Due to this, and to the clean nature of the process, where all outputs are used and there is no waste, more than 90% of the impacts are directly related to the primary energy source, so changing the energy source means changing the process itself, at least in environmental terms.

Also, even if we were able to get all the data required to simulate a suitable infrastructure and its impacts and changed electricity for heat where it was needed, the electricity source would continue having a main role in environmental impacts, so this is definitely one of the key factors of this process.

### 6.5.2 Allocation

In the methodology chapter we explained allocation and how to apply it to our case. It is important to notice that in this case the difference between allocating by price and allocating by mass is quite big, because while in the first one we would account for 95% of the process' impacts, using mass allocation we would only account for less than 75% of them, which would lead to an important decrease in the impacts of the process.

Like we mentioned in the methodology chapter we will use price allocation, which means that we would only account for 95% of the impacts that have been shown in all the tables and figures. Those numbers have not been changed because I wanted to show the exact results from the study, and since the difference between allocated numbers and non-allocated ones is small, the conclusions the reader will get from the tables and figures is not going to be different.

Finally, just wanted to point out that it does not even exist a real sensitivity analysis on allocation, because allocating on mass does not make any sense and would be just a mistake.

## 6.6 Boundary discussion and CO<sub>2</sub> tracking

Like we mentioned in previous chapters, the boundary of the system goes from the final products to the initial inputs, this is, deionized water, electricity and CO<sub>2</sub>.

While deionized water and electricity are processes that are taken directly from the database, the CO<sub>2</sub> provenance can cause some controversy.

In our process, we only take into account the capture of the CO<sub>2</sub> once it is an output of a coal power plant. We do not take into account any of the processes that take place in the power plant, we work like if the CO<sub>2</sub> was there and we just have to capture it.

But, does this make sense? It does, as long as there are power plants that emit CO<sub>2</sub> and that CO<sub>2</sub> is being emitted to the atmosphere, we can consider the process “capturing CO<sub>2</sub>” accounting for the energy required for capturing the CO<sub>2</sub> but also for the environmental benefits of preventing the CO<sub>2</sub> from going into the atmosphere.

Regarding the outputs, one can think: “Ok, I account for the benefits of capturing CO<sub>2</sub> in the inputs, but then, in the outputs I don’t take into account the final use of the formic acid, and it is very likely to produce CO<sub>2</sub> in its end life, depending of which use you give to it.” How does this stand?

This is an issue of double counting, you cannot take into account the emissions that the formic acid will emit, because when somebody else uses that formic acid, if he does an LCA or any similar analysis, he will take into account the CO<sub>2</sub> emissions that his process produces, so if you have already counted them, you are doing it twice.

## 6.7 Data sources, uncertainties and full scale development

The data used in this report has been provided mainly by DNV, the energy requirements and the behavior of the electrochemical reactor and rest of the components of the facility has been addressed by them. There can be some inaccuracies but the data is solid in general.

In the parts where the biggest uncertainties where, we have done big approximations, but always looking for solutions that influenced the environmental results as little as possible.

Because of these approximations, the analysis made has not been deep, but tried to keep it simple and solid. The results make sense and not big deviations from reality are expected.

Regarding full scale development, this facility is targeting a production of 100 tons of formic acid per day, which means 36500 tons of formic acid per year.

This would not be a problem in CO<sub>2</sub> input terms, because even if there were not enough carbon capture facilities at the moment, since we are accounting for the carbon capture, if

the whole process is profitable then building a carbon capture facility to supply CO<sub>2</sub> to our process would be profitable.

But, regarding formic acid production, 36500 tons per year is a world consumption magnitude, which means that equilibrium would be altered and probably it would become necessary to look for other uses for formic acid. Nevertheless this is not an economic study; one of those should be done in order to address these circumstances.

## 7 Conclusion

This analysis showed that electricity is the main contributor to the impacts, so using a clean energy source will result in an overall environmental friendly process. Compared to the main route for producing formic acid, the methyl formate one, a fairly big decrease in impacts can be obtained.

There have been some uncertainties in the study that have led to the use of approximations, mainly in the energy and infrastructure part, but still the results obtained are not expected to be far from reality.

Economic viability remains unknown, and the bigger energy consumption of the process compared to the methyl formate one can be a challenge.

In order to make a full comparison between this process and the methyl formate one, more detailed data on this process will be needed, especially regarding costs. Also, a full detailed study must be done on the methyl formate process to be able to compare both correctly.

Finally, this analysis indicates that the electrochemical reduction of CO<sub>2</sub> to produce formic acid is an interesting process from the environmental point of view, but it is not clear that this makes up for the higher energy consumption. More analysis should be carried out in the economical part in order to reach a final conclusion.



## Sources

Agency, U. E. (17 de October de 2010). *Defining Life Cycle Assessment (LCA)*. Obtained from <http://www.gdrc.org/uem/lca/lca-define.html>

Chemical, H. (s.f.). *Chemical Economics Handbook - Formic Acid*. Obtained from <http://www.ihs.com/products/chemical/planning/ceh/formic-acid.aspx?pu=1&rd=chemihs>

*Ecoinvent*. (s.f.). Obtenido de Swiss Centre for life Cycle inventories: [www.ecoinvent.ch](http://www.ecoinvent.ch)

J. Beck, R. J. (Spring 2010). *Electrochemical conversion of carbon dioxide to hydrocarbon fuels*.

*PubChem 284*. (s.f.). Obtained from <http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?cid=284>

Singh, B. (2011). *Environmental evaluation of carbon capture and storage technology and large scale deployment scenarios*.

*Ullmann's encyclopedia of industrial chemistry - Formic Acid*. (s.f.). Obtained from [http://onlinelibrary.wiley.com/doi/10.1002/14356007.a12\\_013.pub2/full](http://onlinelibrary.wiley.com/doi/10.1002/14356007.a12_013.pub2/full)

## Appendix and Formulas

### Mass & Molar flows

Attending to the properties of the process addressed by DNV, the following mass and molar flows have been obtained for a functional unit output of 100tons 85wt% formic acid. The numbers of the flows are referred to this diagram:

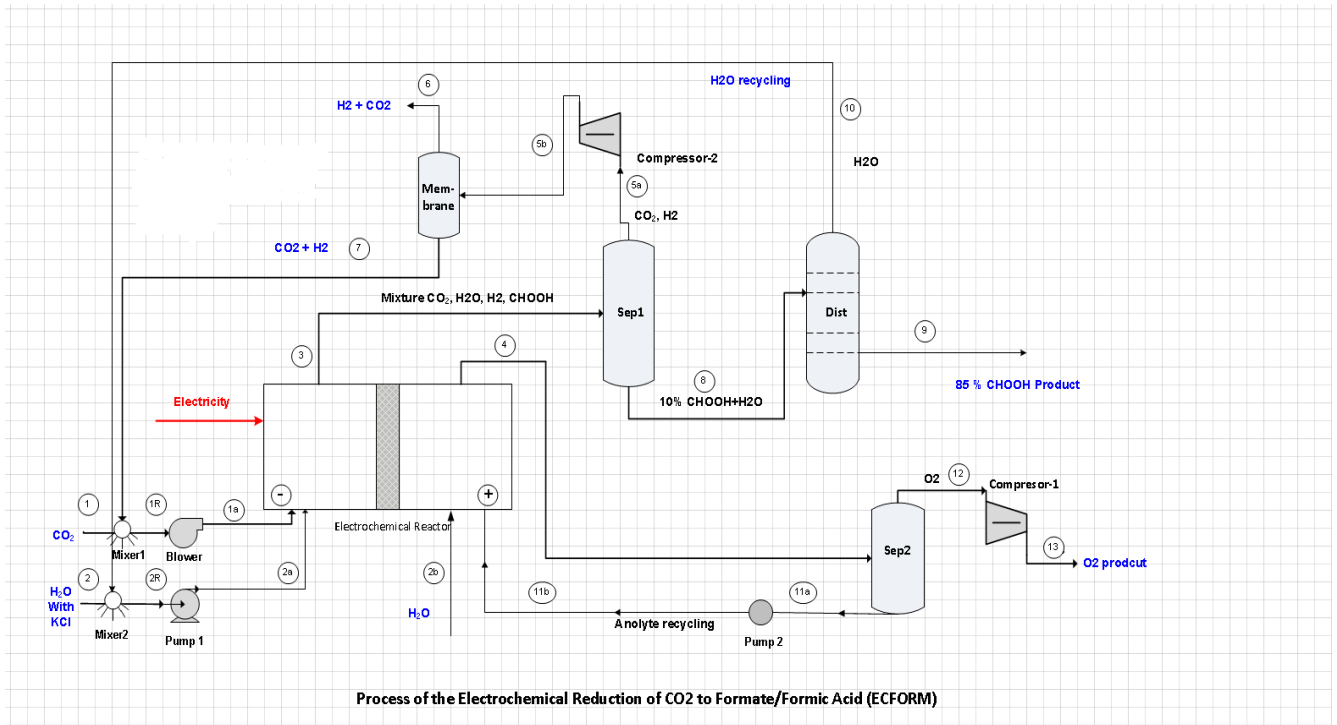


Table A1. Mass flows for the production of 100 ton HCOOH 85 wt% /day

Mass flows (ton/day)	1	2	3	4	5	6	7	8	9	10
CO <sub>2</sub>	81.3		460.7		460.7	0.01	460.7			
H <sub>2</sub> O		48.3	765.0					765.0	15	750
HCOOH			85.0					85.0	85.0	
H <sub>2</sub>			0.55		0.55	0.47	0.08			
O <sub>2</sub>				34.0						

Table A2. Molar flows for the production of 100 ton HCOOH 85 wt% /day

Molar flows (Mmol/day)	1	2	3	4	5	6	7	8	9	10
CO <sub>2</sub>	1.84		10.47		10.47	0.0002	10.47			
H <sub>2</sub> O		2.68	42.5					42.5	0.83	41.7
HCOOH			1.84					1.85	1.85	
H <sub>2</sub>			0.28		0.28	0.235	0.04			
O <sub>2</sub>				1.06						

Flow line 11 only contains anolyte, and since we are neglecting it for the environmental study it is not shown in the table. The other flows that are not shown in the tables can be easily derived from the figure.

The formic acid that appears in the tables is formic acid 100% pure; this is the reason why there is only 85 tons of formic acid output (flow 9). If you mix those 85 tons with 15 tons of water you get 100tons of formic acid 85wt%, which is our functional unit.

### Calculations used for electricity in carbon capture and CO<sub>2</sub> supply

As mentioned before, we are considering the process “capturing CO<sub>2</sub> and supplying it to the electrochemical reactor” as part of our system. This way, we get an electricity consumption for capturing the CO<sub>2</sub>.

For logical reasons, we assume that the electricity used for capturing the CO<sub>2</sub> comes from the same power plant that emits this CO<sub>2</sub>. This way, the electricity used for capturing the CO<sub>2</sub> also emits CO<sub>2</sub> that can be captured using the same process. This creates a cycle that will be solved using a couple of equations and the data provided in Bhwana Singh’s thesis [6].

The data can be simplified to the following:

- 1KWh of electricity produced by a power plant with CC captures 901g of CO<sub>2</sub>.
- To capture 1 kg of CO<sub>2</sub> 0.343 KWh of electricity is required.

So, the point here is that we will need less electricity than what we could expect in the beginning because from the electricity we use we already get some CO<sub>2</sub>.

If we say X = CO<sub>2</sub> captured in a “direct” way and Y= CO<sub>2</sub> captured as a byproduct of electricity production:

If we sum both we will have the total CO<sub>2</sub> needed to run the process (81.3 ton).

- $X + Y = 81.3$

And the electricity consumption must be the same at both sides of the equation:

- $X * 0.343 = Y / 0.901$

From solving the system we get the results: X = 60.83 ton; Y = 19.17 ton

So the electricity we really need for capturing the CO<sub>2</sub> is:

$$60.83 * 0.343 = 20.86 \text{ MWh/100ton HCOOH 85wt}$$

For the base case of our process, where we use all the electricity from a coal power plant with CC, the way of getting the real electricity consumptions is the same as in here.

There will be much more CO<sub>2</sub> produced as an electricity byproduct than what is needed for our electrochemical reactor, so we will take the CO<sub>2</sub> we need and the rest will be considered to be stored (CCS). All the data for these processes can be obtained from Bhwana Singh's PhD. (Singh, 2011)