

# Ethanol Production by catalytic hydration of ethylene

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## Abstract

This paper discusses all the aspects of the process of ethylene hydration to produce ethanol. A short summary gives all the information known and found about the studied process. Afterwards, the necessary cost to implement this process is presented and analyzed. A literature review shows a glimpse of the other kinds of processes used in the industry to produce ethanol, detailing the catalysts used as well as the different raw materials. An overview of the ethanol properties is also displayed in this paper. Finally, the Life Cycle Analysis (LCA) gives the environmental aspect of the ethylene hydration process, underlying sections of the process to improve such as the heat integration.

## Keywords

Ethanol - Process - Ethylene - Hydration - LCA - Market - Feedstock

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## 1. Introduction

This project was devoted to the study of ethanol production by catalytic hydration of ethylene. A process for the ethanol synthesis has been developed and the operating conditions optimized in order to reduce production costs. Before the extended literature review, a summary of the work done will be presented.

The purpose of this extended literature review is to compare our process with those found in the literature. Firstly, the cost of our process will be analyzed. Secondly, our process is compared to similar production processes of synthetic ethanol using oil-based products as raw materials.

Afterwards, different ways of producing ethanol will be discussed and compared to our process. To end this literature review, a broader society overview including market, toxicity,... will be made.

Lastly, the LCA of the process will be discussed to acknowledge the impacts of the considered process.

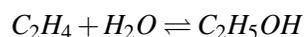
## 2. Summary of our process : catalytic hydration of ethylene

This process is mainly used to produce ethanol as a solvent. Considering the entire ethanol production, this type of process represents only 7% of the production (Roozbehani, Mirdrikvand, Moqadam, & Roshan, 2013; Mohsenzadeh, Zamani, & Taherzadeh, 2017).

Indeed, producing ethanol via this process is more expensive than using techniques such as fermentation. This is due to the price of ethylene, which fluctuates enormously according to the geographical area. Three large companies produce synthetic ethanol: Sasol in South Africa, SADAF in Saudi Arabia and Equistar in the USA. (Roozbehani et al., 2013).

### 2.1 Our process

The process displayed in the FIGURE 8 was the subject of an in-depth study this year. The following equilibrium describes the main reaction:



Because of the equilibrium, the operating conditions play an important role in conversion. Part of the work done this year was useful to determine the optimal conditions for a maximized conversion, taking into account

the imposed constraints. However, ones must be careful about the fact that other components are present in the process due to impurities in the ethylene feed.

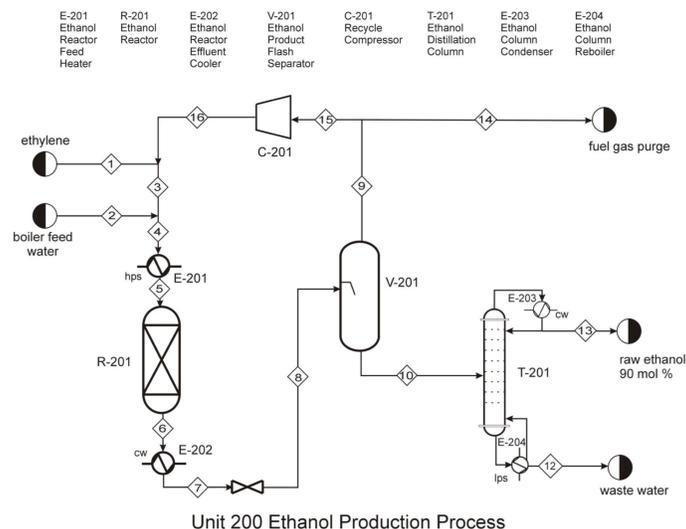


Figure 1 – Our process flowsheet

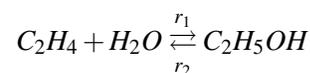
### 2.1.1 Thermodynamics

The thermodynamics part was devoted to determine the properties of all the components of our process. To reach this goal, the properties for the pure components at different temperatures and pressures have to be determined. Then, the properties of ideal and real mixtures can be found. The real mixture properties will depend on the choice of the thermodynamic model. These data will be used in the other sections for the design of all unit operations. In this way, concerning the pure components, the Peng-Robinson model was chosen to describe them. For the mixtures, the model that fits the better the experimental data of binary mixtures was chosen. For this case, the NRTL-RK is the most accurate model.

### 2.1.2 Kinetics and catalysts

Three main reactions are occurring within the studied process:

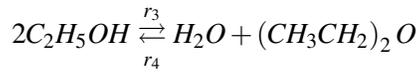
- Ethylene hydration:



with

$$r = r_1 - r_2 = \frac{k_1 \cdot p_E \cdot p_W - k_2 \cdot K_A \cdot p_A}{\{1 + K_E \cdot p_E + K_W \cdot p_W + K_A \cdot p_A + K_{DEE} \cdot p_{DEE}\}^2}$$

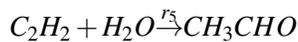
- Ethanol dehydration:



with

$$r = r_3 - r_4 = \frac{k_3 \cdot p_A^2 - k_4 \cdot p_W \cdot p_{DEE}}{\{1 + K_W \cdot p_W + K_A \cdot p_A + K_E \cdot p_E + K_{DEE} \cdot p_{DEE}\}^2}$$

- Acetylene conversion into acetaldehyde:



with

$$r = r_5 = k_5 \cdot p_{Acetylene}$$

In the kinetics and catalyst part, it was first shown that with Langmuir Hinshelwood reaction mechanisms, it was possible to find back the reaction rates of gas-phase hydration of ethylene, ethanol dehydration and acetylene conversion into acetaldehyde. Then, it has been demonstrated, for the chosen operating conditions, that the limiting step of ethylene hydration was the chemical reaction and not the diffusion mechanisms. It has therefore been shown that the catalyst operates in chemical regime. It also has been proven that the catalyst could be considered as isothermal. Based on this, the design of the process' reactor as isothermal and the use of chemical rates were appropriate.

### 2.1.3 Reactor

In the reactor part, the main reaction that occurs is the one that leads to the production of ethanol as mentioned previously:



In order to design the reactor correctly, the reactor had to be numerically modeled in the software Aspen so that the influence of the parameters such as the pressure, the temperature and the steam to ethylene ratio can be studied.

The goal is to maximize the conversion of the main

ethylene reaction by determining the optimal conditions. The other two undesired reactions leading to the formation of the diethylether and acetaldehyde do not have a significant conversion variation when the parameters of the reactor are varied. Thanks to the optimizing tool of Aspen, the parameters converged to the optimal parameters and it had to be verified that the results make sense by performing many sensitivity analysis. The final reactor parameters obtained are the following:

Parameter	Unit	Value
Pressure	atm/bar	60.2/61.7
Temperature	°C	246.5
Steam/ethylene at the input	-	2.4

Table 1 – Operating conditions of the reactor

The operating conditions shown in the Table 1 were fixed such that there is only a vapor phase in the reactor. If the temperature decreases or if the steam-to-ethylene ratio is higher than 2.6, the liquid phase will start forming. Increasing the pressure above 60.2 atm will not lead to a significant and interesting increase in the conversion. Additionally to that, it would increase significantly the cost of the compressor.

The type of reactor considered is an isothermal plug flow reactor. Because knowing that the reaction is exothermic, if an adiabatic reactor was chosen, this will lead to an increase of temperature in the reactor, leading to a decrease of conversion due to the kinetics. Also the total volume of the reactor considered is about  $620m^3$  with a bed void fraction of 0.383. The maximum ethylene conversion obtained is about  $\pm 10\%$ . In order to respect the design of a typical tubular reactor, the length over diameter ratio should be at least equal to 5. Additionally to that, the pressure drop has a negligible influence on the conversion. Which means the length of the reactor doesn't matter as long as the total final chosen volume is respected.

### 2.1.4 Separation process

The separation process is composed of a flash unit as well as a distillation column. The purpose of the flash unit is to separate ethanol as well as water from the other undesired components like ethane, methane,...

Concerning the other unit, the distillation column aimed to obtain the ethanol at the desired purity i.e. 82 molar% and therefore, its main goal was to eliminate most of the water.

The flash was designed in order to get a liquid outlet big enough to meet our quantity specifications. Indeed, 30 000 tonnes of ethanol at 82 molar% purity were required per year. The varied parameter was the temperature inside the flash as it determines the ratio between vapour and liquid outlets. The optimal working temperature is 85 °C.

The distillation column was designed in multiple steps, as this unit is much more complex than the latter unit. At first, short-cut methods were used to get an order of magnitude of the column parameters, i.e. the number of stages, the feed stage position, the reflux ratio, the reboiler heat duty and the tray spacing.

The McCabe-Thiele method was then used to refine our results.

Finally, the last step consisted in implementing the distillation column on Aspen as well as the flash unit. This final step was useful to know the true composition at the inlet of both units allowing even more precise results.

For each of the steps mentioned, the optimal column was chosen to minimise the costs related to that separation unit. The costs comprise the equipment cost and the utility cost. By analysing the influence of the column parameters, it has been understood that the two main parameters influencing the most the costs are the reflux ratio and the reboiler duty. Decreasing these parameters led to a decrease of the utility cost, which is the main fraction of the total cost.

However, one has to be careful that this decrease of the reflux ratio and the reboiler duty has a limit as it may induce a possible dry up within the column.

For the combination minimising the reflux ratio and reboiler duty values, the number of theoretical stages has been set in order to meet the desired specifications in quantity as well as in purity.

### 2.1.5 Heat integration

The aim of the heat integration is to minimise the energy consumption of the process. Once the different parts of the process have been optimised, the streams and the units that need to be heated or cooled are identified and coupled in heat exchangers.

The pinch analysis allows to determine the hot and cold utilities that are still needed: 13612.4kW for the hot utility and 18529.3kW for the cold one. Indeed, a huge amount of heat is required at the start of the process to vaporise the water under such pressure, and a great deal of cooling water is used to cool the stream exiting the reactor. Once the heat exchangers network has been included, the final flowsheet presented on FIGURE 2 is obtained.

### 2.1.6 Costs

The costs of the process have finally been calculated. The annual capital cost (CAPEX) and the annual operating cost (OPEX) have been taken into account. Costs linked to the infrastructures (grassroots plant costs) and costs linked to the personal have been evaluated more precisely to obtain the overall annual cost.

Costs of the raw materials were determined using the market price some months before the Covid-19 crisis. Unfortunately, as the overall annual cost is larger than the income of the process and the building of a new plant, this process for ethanol production is not profitable. The cost analysis will be presented in the section 3 in more details.

Reflux ratio	Reboiler duty	Number of stages
2.93	6075 kW	31

Table 2 – Optimal parameters of the distillation column

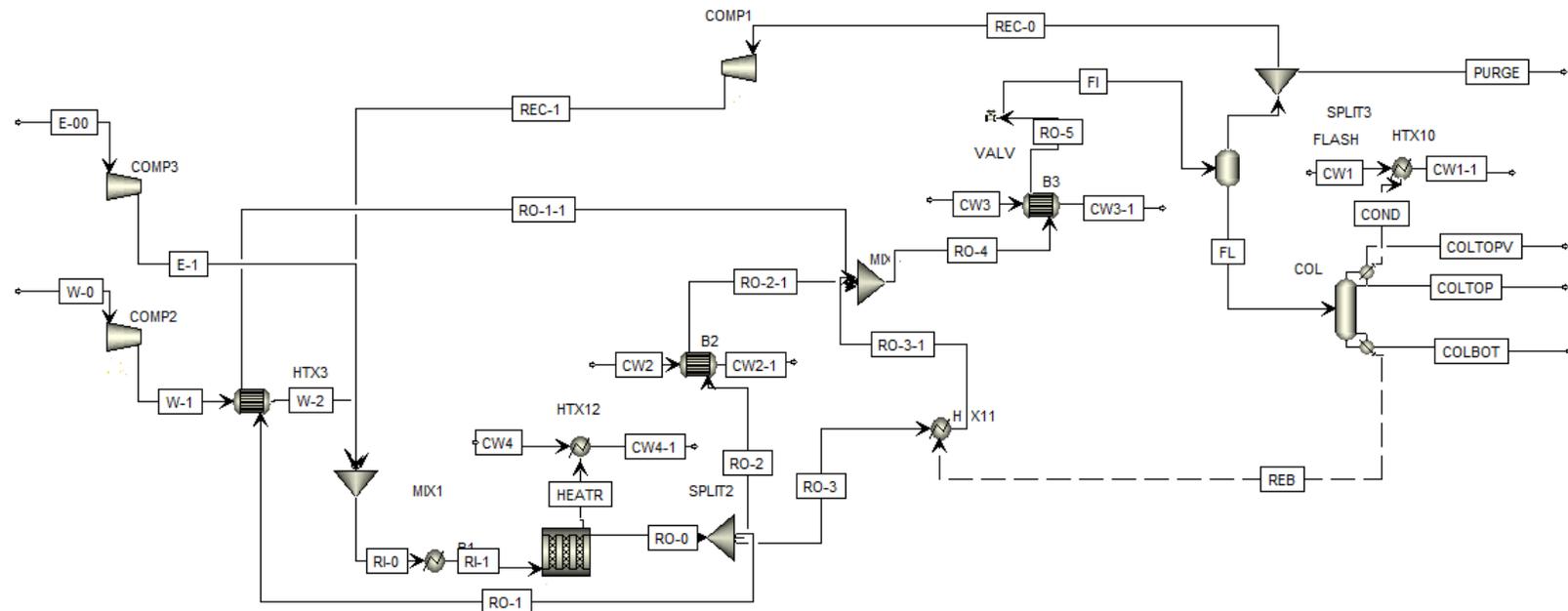


Figure 2 – Final flowsheet

### 3. Cost analysis

#### 3.1 CAPEX

The CAPEX is the cost for all the fixed structures such as buildings, laboratories, process units or lands.

To calculate the CAPEX, the bare module cost is firstly calculated. This is the raw cost of each specific unit of each specific unit, where the installation Then, the total module cost is calculated. It corresponds to the cost and transport are taken into account. There is no corrosive compounds in the process, so the plant can be built in carbon steel.

The detail of the bare module cost and the total module cost of each unit is present in the APPENDIX 7.1.

Finally, the grassroots plant cost is computed. This cost takes into account, in addition of the total module cost, others costs like auxiliary facilities (administration buildings, cafeteria and more), land or unexpected costs and fees. Its formula is present in the APPENDIX 7.1.

For this process the total grassroots plant cost is about **12 781 k\$**.

#### 3.2 OPEX

The OPEX is a day-to-day cost that depends on the needs of the process such as electricity, water treatment, raw materials, maintenance and cost of workers.

The OPEX (operation expenditure) part consists in calculating the annual total manufacturing costs (COM) which are based on: the direct manufacturing costs, the fixed manufacturing costs and the general expenses. The direct manufacturing costs (DMC) takes into account costs such as raw materials, waste water treatment, utilities (electricity, cooling and heating water), operating labour and other direct costs.

The fixed manufacturing costs (FMC) are the costs that cover the depreciation cost, the local taxes and insurance and the plant overhead costs.

The general manufacturing costs (GE) take into account the administration costs, the distribution and selling costs and the research and development costs.

The different costs are calculated by following the formulas explained in the referenced book (Whiting, Shaeiwitz, Bhattacharyya, Turton, & Bailie, 2013). A summary of the OPEX result costs is displayed in the following TABLE 3. The operating labor cost was calculated depending on the number of units operating in the process. The number of operators required per shift ( $N_{WP}$ ) is 3. Which leads to a total number of operators required

( $N_{OL}$ ) about 14.

Different costs	Cost (k\$/yr)
Operating labor	817
Raw materials	11660
Water treatment	13
Utilities	9309
Fixed capital investment	12780
Depreciation	1278
Cost of manufacturing <i>COM</i>	<b>31617</b>

Table 3 – OPEX costs

### 3.3 Cash flows

In order to analyse the profitability of the project involving both capital expenditures and yearly operating costs, cash flow diagram has to be drawn by using the discounted and the non-discounted approach.

As reminder, the discounted approach takes into account the time value of money by including the inflation rate into the calculations.

One of the hypothesis that were made is that the working capital was assumed to be 0 as a first approximation. Usually the typical values of the working capital ranges between 15% and 20 % of the fixed capital investment. But even without these additional expenses, it can be seen in the FIGURE 3 that this project is far from being profitable because all the other expenses cannot be covered over time. This is because the annual net benefit is negative (-8 M\$). For an usual profitable business, the slope of the cash flow is positive when the plant is ready to operate i.e. after its construction.

However, in our case, it can be observed that after the first year, the cash flow (discounted and non-discounted one) continues to decrease instead of increasing.

According to this reference (*New capacities, weaker downstream markets to weigh on ethylene in 2020*, n.d.), the price of ethylene bought is around 0.35 \$/kg. And knowing that with the actual price of ethanol 0.72\$/kg (according to (*Ethanol T2 FOB Rotterdam Including Duty Swap Platts Future*, n.d.)), a negative benefit is obtained, if we wanted to balance our costs with our profits, it would be necessary to raise the price of ethanol to 0.98\$/kg. But this solution cannot be achieved in reality.

An alternative solution is to do a scale-up which means increasing the size of the company, leading to an increase in the production size. Therefore, the cost of

production per unit product will decrease. It might be interesting to study the economical effect if the plant would produce more than 30 000 tonnes of ethanol per year.

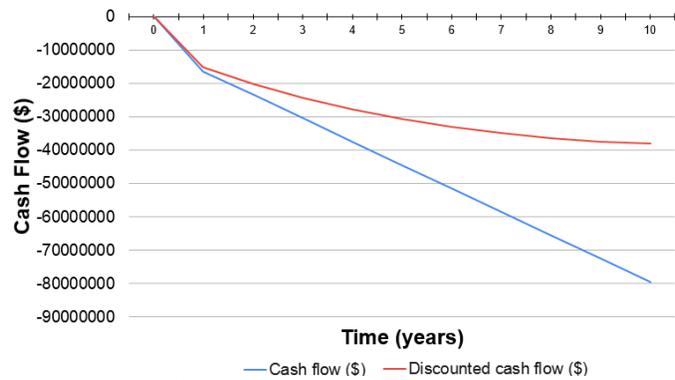


Figure 3 – Cash flow diagram

## 4. Literature Review

### 4.1 Catalytic Hydration of Ethylene: Other Processes

In order to determine whether the results obtained make sense or not, a comparison between the latter and the results found in the literature will be made. Different catalysts will be mentioned and compared with the one chosen for this project, i.e. zirconium tungstate.

#### 4.1.1 Catalysts

##### Phosphoric Acid

Phosphoric acid supported by inert materials<sup>1</sup> has been used as catalyst in the hydration of ethylene for years and is still the most widely used catalyst in the industry thanks to its high selectivity (98.5%) The phosphorus content of the latter catalyst is between 50 and 80 % in weight of the total mass of the catalyst. The reaction is an electrophilic addition reaction where a  $\pi$  bond is broken, involving the formation of two covalent bonds. The reaction mechanisms involved in this catalytic reaction are the following.

- Transfer of a proton from phosphoric acid to ethylene and formation of a  $CH_3CH_2^+$  carbocation

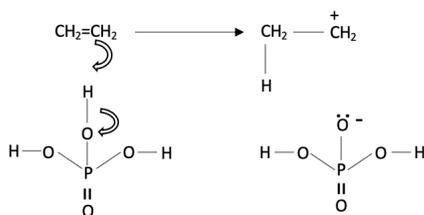


Figure 4

- Reaction of the latter  $CH_3CH_2^+$  carbocation with a water molecule



Figure 5

- Catalyst regeneration

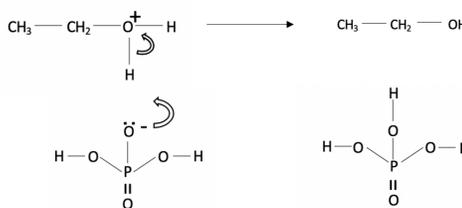


Figure 6

As described by (Hidzir, Som, & Abdullah, 2014) and (Matar & Hatch, 2001), the hydration of ethylene is done in a fixed bed reactor with phosphoric (V) acid coated onto a solid silicon dioxide as a catalyst. The following operating conditions were described:

P (atm)	T (°C)	Steam to ethylene ratio (S/E)
70 - 80	250 - 300	0.6

Table 4 – Operating conditions

These operating conditions lead to a conversion of 4% to 5% of the ethylene into ethanol. Therefore, the remaining ethylene is recycled into the process. Nevertheless, the high concentration of phosphoric acid has consequence such as corrosion of the reactor (Isobe, Yabuuchi, Iwasa, & Takezawa, 2000). For this reason, Isobe et al. (Isobe et al., 2000) have studied the influence of phosphoric impregnated metal phosphate on the conversion of ethylene to ethanol. The reaction takes place in a pack bed reactor at a temperature of 473K and at a pressure of 1 atm. The following results have been obtained:

Catalysts	Rate of EtOH formation ( $\mu\text{mol}/\text{min}/\text{g} \cdot \text{cat}$ )
Ge	0.47
Zr	0.064
Ti	0.26
Sn	0.94
H3PO4/SiO2	0.13

It can be seen that the Sn-based catalyst is the most efficient compared to the classical  $H_3PO_4/SiO_2$  catalyst. However, and this is one of the reasons why another catalyst was chosen in our process (Zirconium Tungstate), phosphorous compounds are responsible for environmental pollution (Katada et al., 2008).

<sup>1</sup>Materials such as porous silica or alumina-silica.

### Zirconium tungstate

In the article proposed by (Momose, Kusumoto, Izumi, & Mizutani, 1982), the zirconium tungstate is used as a catalyst for the reaction and the following results were found (see TABLE 5).

P (atm)	T (°C)	S/E	Selecivity EtOH
68	280	2.1	94 - 99%

Table 5 – Results found in the literature

The above tables show the consistency of our results. Indeed, in our case, an ethylene conversion of 9% is reached with a temperature of 246.5°C and a pressure of 60.2atm, which is quite good compared to the literature. The advantages of using such a catalyst are :

- For a given pressure, the ethanol yield increases with the temperature.
- With an optimal water/ethylene ratio, the ethanol yield is even bigger.

The disadvantage is:

- Regarding the acetaldehyde, the catalyst is subject to a reduction reaction when ethanol is present so that acetaldehyde is produced.
- For a given pressure, the quantity of acetaldehyde increases significantly above the temperature for which the ethanol yield is obtained.

The selectivity is around 94-99 mol% if the water/ethylene ratio is well chosen.

### Corrole – based catalysts

The use of metal-based catalyst in acidic medium for ethanol production has been widespread for a long time. Nevertheless, this type of catalyst has the great defect of conducting secondary reactions leading to undesired products such as diethylether, acetaldehyde, etc... To solve this type of problem, corrole-based catalysts are studied (see Figure 7). In the article proposed by (Hassani, 2020), three types of corrole M (M=B, Al and Ga) were studied by the density functional theory, which is a quantum chemistry theory. The hydration of

ethylene on corrole Ga shows the best results with an energy barrier of 0.93eV. This study shows that these catalysts could be used in ethanol production.

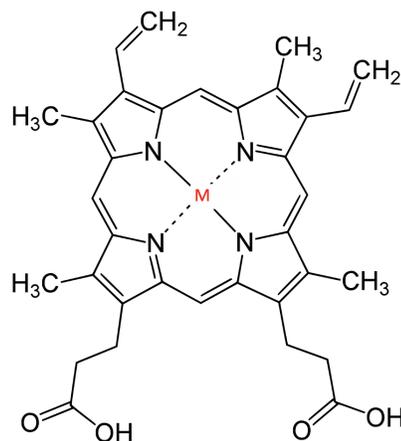


Figure 7 – Corrole molecule

### 4.2 Comparison with previously obtained results

Along time, the calculations became more and more precise. Therefore, it is a good idea to make a comparison with the previously obtained results to understand the evolution of the values obtained.

The comparison will be conducted on results obtained before (part 1 of the project) and after receiving the definitive statement of the project (for part 2 and part 4 of the project). The idea is to compare the results obtained when different assumptions are used and when new pieces of data are taken into account (such as the catalyst between part 2 and part 4). The TABLE 6 gives that comparison over different parameters of the system such as the ethylene conversion (EC), feed flowrate (FF), pressure (P), steam to ethylene ratio (S/E), temperature (T) and reactor volume (RV).

Param.	Part1	Part2	Part4	literature
EC (%)	90	16.3	10	7-8
FF (kmol/h)	135.622	1870.1	1822	/
P (atm)	10	40	60.2	68
S/E	1	2	2.4	2.1
T (°C)	227	227	246.5	280
RV (m <sup>3</sup> )	unspecified	294.5	620	/

Table 6 – Comparison of some parameters of the system before, after receiving the definitive statement and scientific literature

By looking at TABLE 6, the evolution of the parameters is really noticeable for all of them. New assumptions were added at each stage (e.g. : kinetics, catalyst,...). It led to changes in the values of those parameters to validate the assumptions of the system. Those new assumptions forced the system to become closer and closer to the real one.

#### 4.3 Other process: Fermentation

Alcoholic fermentation is a process transforming sugars into ethanol in an anaerobic environment by using yeasts. The following equation describes the phenomenon:



Generally, this type of process is used for the production of bio ethanol and alcoholic beverages.

In the context of bio-fuel production, three types of generation can be distinguished according to the raw material used for the fermentation (Balat, Balat, & Öz, 2008):

- First generation: feedstocks are agricultural biomass.
- Second generation: feedstocks are lignocellulosic biomass.
- Third generation: feedstocks are algae biomass.

At the end of 2013, the european parlement capped the first generation of bioethanol to 6% of the total consumed energy in the transportation sector. The second and third generations peaked at 2.5% (et environnement par sia partners, 2015).

#### 4.3.1 First generation: Corn ethanol industry

Agricultural biomass has been used for a long time; ethanol is produced from corn. Large groups such as ADM or POET still use this method of producing ethanol today (Gray, Zhao, & Emptage, 2018). Two methods can be used to produced ethanol from corn (Caballero, Trugo, & Finglas, 2003):

- Dry milling
- Wet milling

The difference between the two processes is the pre-treatment of corn (Caballero et al., 2003). As regards wet milling, in order to prevent bacterial growth and facilitate the separation of the various components of the grain, corn kernels are soaked in sulfur dioxide solution during 30 hours. In dry milling, the grains are crushed directly after being washed in a 15% moisture environment. ADM and POET use both wet and dry milling to produce respectively 6.66 billion L/year and 6.05 billion L/year (Chan & Reiner, 2018). The FIGURE8 shows how ethanol is produced by dry or wet milling.

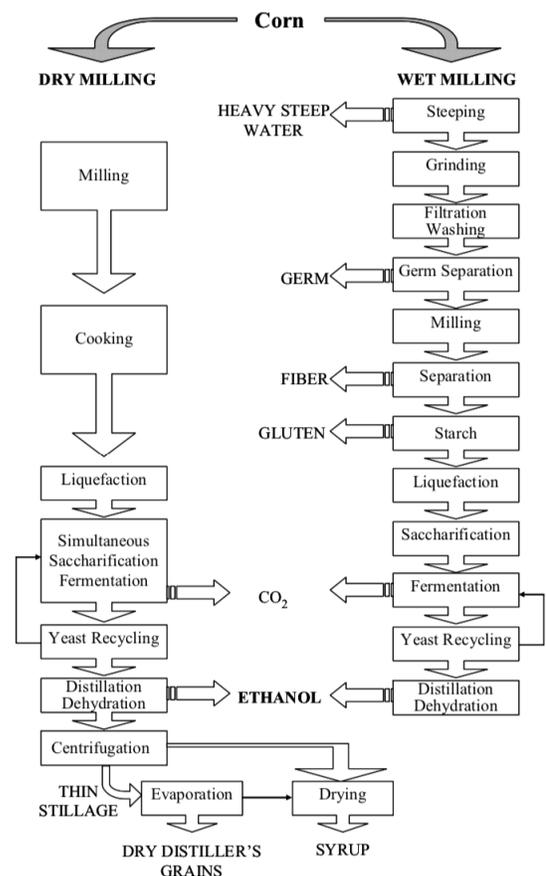


Figure 8 – Diagram of ethanol production from wet or dry milling

### 4.3.2 Second generation : Lignocellulosic ethanol industry

This type of fermentation uses lignocellulose as a raw material. It is hydrolysed in order to release the sugars necessary for fermentation and therefore, for the production of ethanol. The advent of this type of raw material is mainly due to two factors.

First, corn ethanol production is limited to 56,78 billion L/year, this limit ensures that sufficient corn starch remains for human and animal consumption (of Energy, 2019). Second, using cellulose as a feedstock would reduce greenhouse gas emissions by more than 85% compared to reformulated gasoline due to the energy balance (Wang et al., 2011). Since 2014, POET has launched a lignocellulosic ethanol production line. FIGURE 9 shows how ethanol is produced from lignocellulosic feedstock:

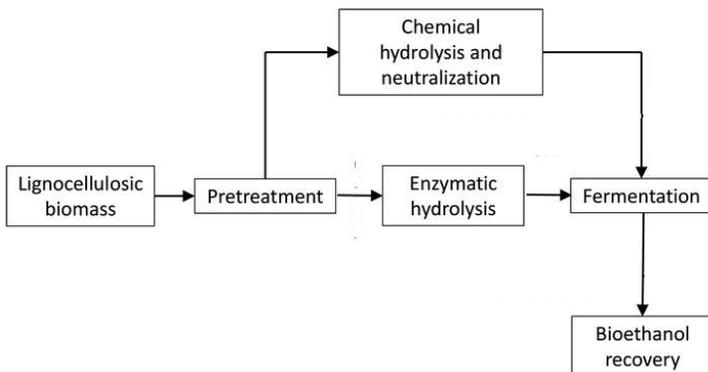


Figure 9 – Diagram of ethanol production from lignocellulosic feedstock

Nevertheless, cellulosic fermentation has disadvantages :

1. Cellulose reduces the effective yield of the biomass.
2. Lignocellulosic fermentation has a higher cost because a pretreatment is needed to extract the holocellulose<sup>2</sup> from the lignin(Martel, 2011).
3. Obtaining glucose from biomass is followed by energy<sup>3</sup> losses from (Frenzel, Hillerbrand, & Pfennig, 2014):

- (a) The general agricultural process that includes crops cultivation and transport as well as the production of fertilizers;

<sup>2</sup>Cellulose and hemicellulose combined.

<sup>3</sup>Value allowing to measure the quality of an energy.

- (b) The methods, from the literature, used to isolate the carbohydrates.

### 4.3.3 Third generation: Algae, Bacteria

The fermentation is done from algae, bacteria. This type of fuel is still being developed. It would further reduce greenhouse gas emissions because a part of the  $CO_2$  is recycled to feed the algae via photosynthesis. On the other hand, cultivating these algae is highly energy consuming and is thus expensive (et environnement par sia partners, 2015).

### 4.3.4 Feedstock origin

On a global scale, in 2014, the majority of biofuel was made from corn ethanol (41%), 19% of the biofuel was made with sugarcane ethanol, 18% of the biofuel produced was biodiesel made from vegetable oils, 15% of the global biofuel production came from unspecified feedstock (ethylene,...), and finally, 2% of the biofuel produced was made from wastes. FIGURE 10 shows these data in a more graphical way (Richter, 2018).

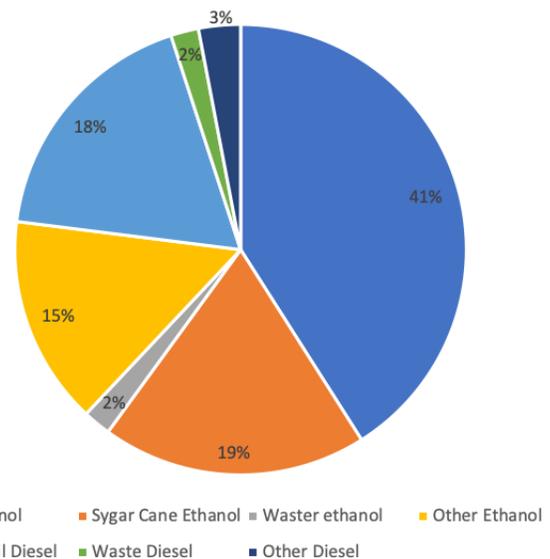


Figure 10 – Shares of bioethanol and biodiesel types from different feedstock in global biofuel production in 2014

## 4.4 Comparison of all processes

From a cost perspective, corn ethanol is the cheapest with a production cost of \$0.15/L (Koehler & Wilson, 2019) (Olsson, 2007). The two milling ways have a different cost distribution: for wet-milling, 39% of the cost price is feedstock and 61% production costs. On

the other hand, the costs distribution for dry-milling is 50/50. Second-generation fuels are more expensive with a production cost of \$0.5/L (Mark, Detre, Darby, & Salassi, 2014). Pre-processing accounts for 30-40% of the cost, which is why the costs are higher.

The price of raw materials has an impact on the production costs. Indeed, the price of corn or cotton does not vary in the same way as the ethylene price, which is linked to the oil court and therefore varies more strongly. Moreover, the geographical location impacts a lot the ethylene price as can be seen in TABLE 7 below (Lewandowski, 2019):

	USA	Europe
Ethylene Price per ton (\$)	350	1000

Table 7 – Ethylene price

In addition, access to raw materials such as corn, cotton, wood is easier than for ethylene, produced either from oil or from shale gas. It should be noted that some reaction by-products can be valued. Indeed, concerning the corn fermentation, in addition to ethanol production, oil can be recovered and used as food. The ethanol production by direct catalytic hydration of ethylene allows the production of diethylether (DEE) in small quantities but still valuable.

The above mentioned processes also have different yields. Concerning the first generation fuel, from 2.28kg of corn 1L of ethanol is obtained. For second generation fuels, the yield depends on the type of hydrolysis. For instance, if hydrolysis is made by a diluted acid, 1L of ethanol is obtained per 5.29kg of raw material, which is quite big compared to the first generation fuel. (Hoover & Abraham, 2009) TABLE 8 summarizes the various points discussed above.

#### 4.5 Ethanol overview

##### 4.5.1 Market

The ethanol market is broken down as follows (Source: Mordor Intelligence) :

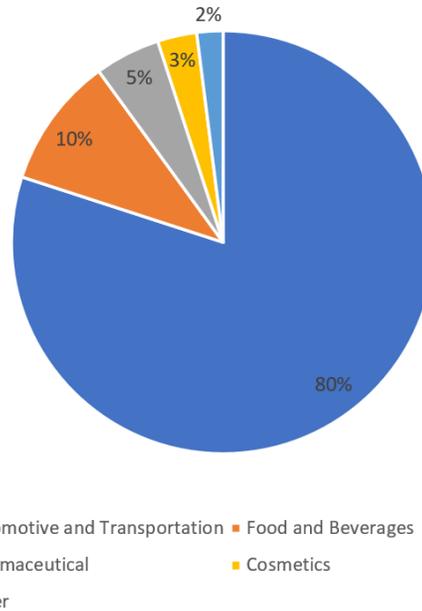


Figure 11 – Distribution of ethanol market

The biofuels market is the largest, followed by the beverages, chemical, pharmaceutical and cosmetics markets. The two largest producers of bioethanol are the USA and Brazil with, respectively, 60.780 and 29.980 billion litres produced in 2018. ADM and POET are two major bioethanol manufacturing companies in the USA. In Brazil, the Cosan company dominates the bioethanol market (FIGURE 12). Concerning synthetic ethanol, there are companies such as Sasol in South Africa or SADAF in Saudi Arabia.

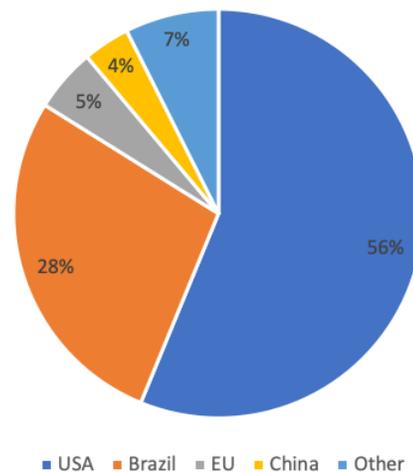


Figure 12 – Distribution of ethanol production. Source: Statista

The biofuel market is buoyant. Indeed, it is part of an ecological reasoning, allowing to reduce greenhouse

	Production Costs	Yield	Access to raw material	By-products
Corn Fermentation	\$0.15/L	2.28kg → 1L	Easy	Valuable
Cellulosic Fermentation	\$0.5/L	5.29kg → 1L	Easy	No
Catalytic Hydration of Ethylene	\$0.86/L	6.44L H <sub>2</sub> O, 570L C <sub>2</sub> H <sub>4</sub> :1L EtOH	More difficult	Less valuable

Table 8 – Comparison of all processes

gas emissions. This market development is supported by the following FIGURE 13, which shows the evolution of this market.

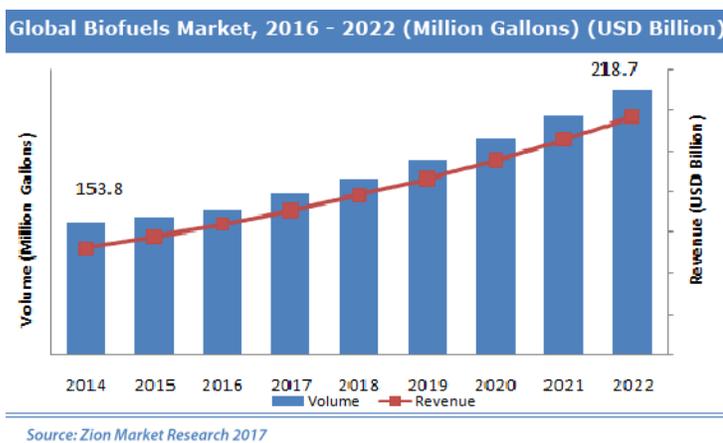


Figure 13 – Biofuel market

#### 4.5.2 Raw materials uses

Ethanol can be used as a reagent in various reactions.

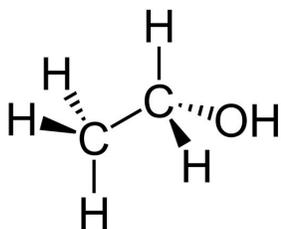


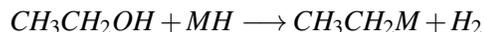
Figure 14 – Ethanol molecule

Indeed, it is a weak acid with a pKa of 16. In addition, the oxygen of the hydroxyl group gives it a nucleophilic character which involves it in several reactions (Wymann, 1990), for example:

- Dehydration reaction with alkene formation, which corresponds to the reverse of the studied reaction

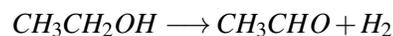


- Acid base reactions:

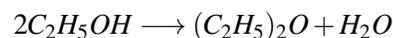


More specifically and concerning our project, ethanol may be involved in reactions leading to the formation of undesired products such as:

- Acetaldehyde



- Diethyl ether (DEE): This is a 2nd order nucleophilic substitution (S<sub>N</sub>2).



Other uses of the ethanol as a final product can be : alcohol drinks, fuels such as bioethanol, solvent and medicinal use.

#### 4.5.3 Toxicity and Environment

##### Toxicity

Ethanol can be absorbed by the body via inhalation of the gases or absorption of the liquid. Regardless of whether it is gaseous or liquid, the toxicity of ethanol is related to its concentration.

When absorbed, at low blood concentration (0.2 to 0.5 g/L) symptoms such as decreased reflex and attention are observed. At medium concentration (0.5 to 1g/L), nausea, vomiting, impaired motor functions and slowing of cognition may appear. At high concentration (1 to 3 g/L), there are risks of loss of consciousness and coma and, finally, beyond 3 g/L, there are risks of death.

The possible symptoms of ethanol inhalation can be (for Biotechnology Information, n.d.) : cough, headaches, drowsiness, nasal irritation and narcosis.

According to the HSDB<sup>4</sup>, ethanol has carcinogen<sup>5</sup> properties (for Biotechnology Information, n.d.).

<sup>4</sup>A toxicology database whose information are assessed by a scientific review panel.

<sup>5</sup>It can cause cancer.

## Environment

Concerning the environmental impact of ethanol production from corn fermentation, there are several points which are needed to talk about (rethink ethanol, n.d.) :

- Even though the carbon emissions are reduced, more volatile organic compounds are emitted. Thus, more tropospheric ozone is created from biofuels than regular fuels.
- Due to the increase of need, more and more nitrate and phosphore, coming mainly from fertilizers, is thrown away into the rivers,... it increases the growth of algae and thus decreases the quantity of oxygen inside water. Therefore, it increases the eutrophication phenomenon.
- Safety hazards can occur during ethanol transportation by train or truck. If an ethanol fire happens, it is not possible to put it out with water only.

When ethanol is produced by the ethylene hydration, the energy consumption is 62 megajoules per kilogram of produced ethanol. On the other hand, ethanol production from natural raw materials, despite its disadvantages, needs only 19 megajoules per kilogram of produced ethanol. If, for a certain reason, the produced ethanol is unsaleable, the need to recycle the ethanol becomes necessary (OCDE, 2000).

### 4.5.4 Recycling

There are two different ways to recycle this solvent:

1. Custom regeneration<sup>6</sup>
2. Solvent elimination

The main advantages of custom regeneration are (Tradebe, n.d.-a):

- An effective reduction of ethanol wastes. Thus, the environment impact and additional costs are reduced.
- A reduced need to buy pure solvent<sup>7</sup>. Therefore, production costs are reduced.

<sup>6</sup> *Regénération à façon* in french

<sup>7</sup> Ethanol is also used as a solvent.

- It offers a better protection against price fluctuations.

Concerning the solvent elimination, the transportation of the ethanol can be done via a tanker or a hybrid vehicle (Tradebe, n.d.-b).

The solvent elimination process is made of the following steps (Tradebe, n.d.-b) :

1. An evaluation of possible treatment itineraries and advantages for a specific trash flux is made.
2. For complex mixes and to confirm studies on paper, a sample is taken on the production site by a highly qualified representative.
3. As soon as the samples are received, analyzes are made by the highly qualified technical staff. A commercial report is then sent.
4. The results of that report will be commented for the client. The client will also be informed about the best methods of thrash manipulation. Other alternatives are also presented to the client.
5. A commercial offer detailing the particular demands and specifications is given. Knowing that recycling offers more advantages than eliminating, the company offers a wide choice of options that are the most appropriate.

### 4.5.5 Ethanol alternatives

If there are problems with ethanol such as shortage , finding alternatives to ethanol can be a good thing.

### 4.5.6 In the case of Bioethanol

Using butanol (e. ramey, n.d.) can be an alternative for biofuels. Using ethanol in fuels to make E85 will damage the car engines if those aren't adapted to the bioethanol (rethink ethanol, n.d.).

Some of the advantages by switching from ethanol to butanol can be (e. ramey, n.d.) :

- No modifications of the engine are necessary to run the vehicle with butanol.
- In the case of bioethanol, there is still a certain amount of fossil fuel in the mix. In the case of butanol, a fuel made of 100% of butanol can be used.

## 5. Life-cycle assessment (LCA)

A life-cycle assessment, or LCA, is a methodology for assessing environmental impacts associated with all the stages of a product's life from cradle to grave. For instance, in the case of a manufactured product, it covers a range of activities from the extraction of raw materials (cradle), through the production and distribution of energy, manufacture and use of the product, to the recycling or final disposal of materials composing it (grave).

LCA study involves a thorough inventory of the energy and materials required across a process and assesses the corresponding emissions to the environment. Therefore, the goal of this tool is to improve the overall environmental profile of a product by helping decision makers to compare the impacts when choosing between different options. Moreover, it helps to support policy and to optimise a process.

In this project, we decided to focus the LCA analysis on three main parts of the cycle of ethanol production from ethylene hydration :

- Raw materials supply
- Transport
- Energy used in the process

Nowadays, the United States is the major producer of ethanol in the world with more or less 55% of the total production (Demmon, 2019). Therefore, the production unit is chosen as being located in the USA. Moreover, the analysis is performed based on the annual production designed to produce 30 000 tons of ethanol. The results obtained for the environmental impacts associated with all the stages of ethanol production are evaluated thanks to a simulation software called SIMAPRO and will be expressed for the production of 1kg of ethanol. The databases are Ecoinvent and the impact assessment method is CML-IA baseline V3.05.

Different hypotheses will be put throughout the development of this life-cycle assessment. So, it has to be taken as a tool intended to get an order of magnitude of the environmental impacts and not a precise evaluation.

### 5.1 Raw material supply

In this part, the impacts of the procurement of raw materials are studied. The process considered is ethanol

production via direct hydration of ethylene. Water and ethylene are the two main reactants used in this process. Therefore, environmental impacts for ethylene and water production are evaluated.

#### 5.1.1 Ethylene

In order to evaluate the environmental impact of ethylene production, it is important to study the way ethylene is produced and the raw materials used in this process.

First, it is assumed that ethylene production comes from steam cracking. This method consists of heating the naphtha fraction of oil, in the presence of water vapor (around 30 to 100 % by weight) to obtain compounds such as ethylene, propylene, etc which are precious for the chemical industry. In this case, only ethylene is valuable. To get an idea, at the output of the unit, with a charge of naphtha, one has a yield of about 25 % to 30 % of ethylene.

Concerning the steam cracking, oil, steam and the energy needed are all taken into account for the LCA analysis.

In the ethanol production unit, **25 870 tons** of ethylene with a purity of 86% are needed each year. All calculations corresponding to the production of it will be made with respect to this value.

#### 5.1.2 Water

The ethanol production unit is a big consumer of water. Indeed, a huge amount of water is used as a raw material. As said previously, this plant is based on ethanol production via direct hydration of ethylene and has a ratio 1:15 between the molar fluxes of ethylene and water at the entrance of the process. Each year, **246 000 tons** of pure water are needed as reactant in the process.

Most of the time, water used for industrial activities is taken from groundwater, rivers or lakes, often by the industrial operator himself. Let's say that in our case, the ethanol production unit is right next to one of these water sources. Once withdrawn, the water is said to be "raw". It is sometimes used as such but is generally subjected to a treatment (disinfection, clarification, ...) before use and especially when it is used as a raw material in the process.

Finally, before industrial wastewater can be discharged into the environment, it must be subjected to purifica-

tion in order to comply with the standards.

All of these steps will have an environmental impact and can be estimated with the simulation software.

## 5.2 Transport

First, an important hypothesis that has been made is to assume that the ethanol production unit is right next to the ethylene production unit. More and more plants which are related try to set up this system in order to reduce the cost and the environmental impacts related to transportation. Moreover, as said previously, the ethanol production unit is near a water source so there is no need for water transport either.

A second assumption was to locate the production plant in the USA precisely in Texas. Indeed, firstly, the US are the biggest consumers of ethanol in the world. Then, according to the TABLE 9, Texas is the biggest oil producing state in the United States. That implies a lower environmental impact to transport the oil from the source to the refinery.

Ranking	Oil production [million of barrels]
Texas	1850.1
North Dakota	512.3
New Mexico	339.8
Oklahoma	211.8

Table 9 – Crude oil production in the United States in 2019, by state, REFERENCE (Statista, 2020)

Concerning the way to transport the oil, it is presumed that this raw material is transferred by pipeline. Indeed, according to the REFERENCE (Conca, 2018), pipelines requiring significantly less energy, is cheaper to operate than trucks or rail (about 5\$/barrel versus 10\$ to 15\$/barrel) and have a lower carbon footprint. An approximate distance for oil transportation by pipeline in the state of Texas is assumed to be 500 km. This oil will be transported in liquid phase by pipeline. And, in order to improve the fluidity of crude oil before it enters into the device, the crude oil is always heated to a certain temperature (a little higher than the ambient).

## 5.3 Energy used in the process

Every process needs energy to function in order to power the equipment. In the ethanol production unit, the main sources of energy are electricity, vapour and

cooling water. In the following, the way these energies are produced will be described.

The electricity used in this process is produced by on-shore wind turbines with a power installed above 3 MW. To get an idea, a wind turbine of 2 MW generates annually 4500 MWh. Surprisingly wind energy in the United States is growing. In 2018, the United States ranked 2<sup>nd</sup> in the world for wind power production with more than 20% of the world total. Moreover, Texas is by far the largest producer of wind energy in the country with a quarter of the installed wind power of the country (Wikipedia, 2020). Therefore, producing electricity with wind turbines is a good assumption as the ethanol production unit is located in Texas. The electricity consumption in this process is at high voltage and allows to power the three compressors and represents an overall power of 5155 kW. This large value is due to the fact that the compressor (COMP1) requires a huge net work because it compresses the recycle stream, which has a big volume, from 5 to 61,68 bar. Note that this recycle stream is in vapor phase. Therefore, the ethanol production unit has a high consumption of electricity with an annual consumption of 41,2 GWh.

Moreover, a large amount of heat is required in order to warm up the fluxes at the desired temperatures. Thanks to the heat integration, it was found that an annual heat duty of 116 GWh is required for the overall process. This heat will be provided by vapour produced with a boiler. The boiler burns oil as fuel and the heat given off will transform water into steam. This vapour is then routed to the different heaters of the unit production.

Concerning the cooling system of the process, water taken from a river or a lake is considered as cooling fluid. A volume of 1050 m<sup>3</sup> of water per year is used to cool flows and the equipment. Cooling helps manage and maintain the temperature of the production process and components. Furthermore, prevention of overheating of the equipment helps increase the productivity and reduces maintenance cost of the machine.

A last source of energy that can be considered in the process is the purge recovery. Indeed, the purge is used as fuel gas and its combustion allows to recover thermal energy. Burning the purge allows to spare a lot of energy in this process because the purge is a very important flux and represents an energy economy of 108 GWh per year, which is not negligible.

## 5.4 Environmental impacts

The environmental impacts associated with all the stages of the ethanol production are evaluated thanks to the simulation software SIMAPRO and will be expressed for the production of 1kg of ethanol. Nowadays, the world is in an energy transition phase towards renewable energies. Therefore, it can be interesting to compare the environmental impacts of two different factories, one producing electricity with fossil fuels and another with wind turbines. It was decided to focus this analyse on five impact categories :

1. **Abiotic depletion (fossil fuels)** refers to the depletion of nonliving resources and more particularly fossil fuels. It is expressed in terms of *MJ* which is related to the equivalent energy extracted.
2. **Global warming (GWP100a)** results of greenhouse gases concentration in the atmosphere such as carbon monoxide, methane, nitrogen oxide which let in sunlight but capture reflected heat by earth. Each greenhouse gas has a different warming effect that can be calculated on the basis of a reference value : the warming potential of  $CO_2$  and is expressed in terms of the equivalent amount of carbon dioxide ( $kg\ CO_2\ eq$ ).
3. **Human toxicity** reflects the potential harm of chemicals released into the human environment and covers a number of different effects such as irritation effects, carcinogenic effects,... Health risks of exposure in the working environment are not included. It is expressed in terms of equivalent amount of dichlorobenzene ( $kg\ 1,4\text{-DB}\ eq$ ).
4. **Fresh water aquatic ecotoxicity** refers to the impact on fresh water ecosystems, as a result of emissions of toxic substances to air, water and soil. It is expressed in terms of equivalent amount of dichlorobenzene ( $kg\ 1,4\text{-DB}\ eq$ ).
5. **Acidification** refers to emission which increases acidity of water and soils and has a wide range of impacts ecosystems and materials (buildings). It is expressed in terms of equivalent amount of sulfur dioxide ( $kg\ SO_2\ eq$ ).

The impact of the process on the main pollution factors is shown in the TABLE 10. This makes the comparison between the use of wind turbines or fossil fuels to produce electricity. All data have been calculated for the equivalent of 1 *kg* of ethanol produced.

Label	Unit	Wind turbines	Fossil fuel
Abiotic depletion (fossil fuels)	MJ	56.58	68.29
Global warming (GWP100a)	kg $CO_2$ eq	1.45	2.54
Human toxicity	kg 1,4-DB eq	0.056	0.55
Fresh water aquatic ecotoxicity	kg 1,4-DB eq	0.032	0.67
Acidification	kg $SO_2$ eq	0.004	0.0071

Table 10 – Comparison of the environmental impacts between two same process using wind turbine or fossil fuel to produce electricity.

A first observation is that producing electricity by wind turbines has a much less impact on the environment. Furthermore, regarding the FIGURES 15 and 16, the relative % of energy recovered from the waste stream of the process (purge) is much more important when wind turbines are used as the environmental impacts decrease. It should be noted that the environmental impacts linked to the construction of the wind turbines are not taken into account for the life cycle analysis of the process.

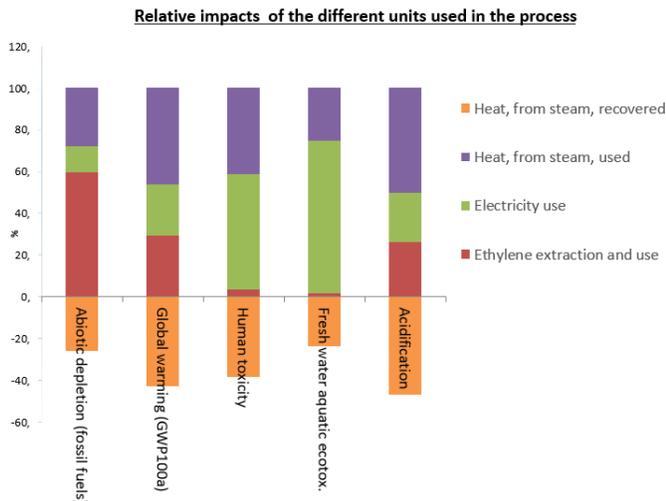


Figure 15 – Electricity produced from fossil fuels

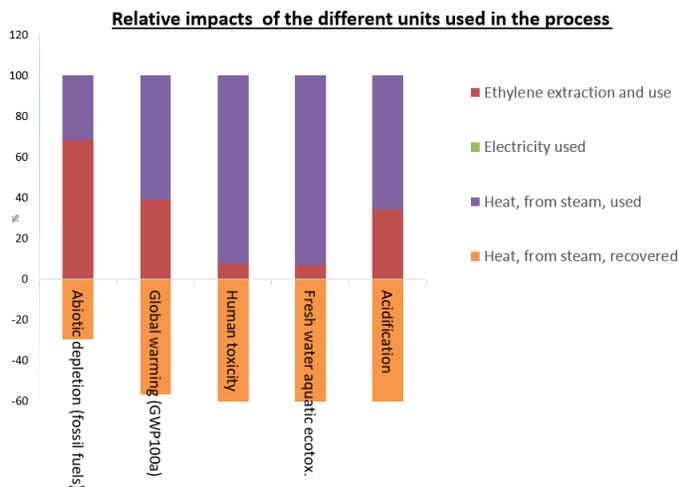


Figure 16 – Electricity produced from wind turbines

Now, regarding the environment, it makes more sense to work by producing electricity from wind turbines. This model is thus chosen for the process.

Then, to get an idea of the real impact of the process on the environment, a comparison between our process and a typical one of ethanol production from the software SIMAPRO has been done in the TABLE 11. The data of the table have all been computed for a production of 1 kg ethanol with a purity equal to 82% .

Label	Unit	Process with Wind turbines	Typical process from SIMAPRO
Abiotic depletion (fossil fuels)	MJ	56.58	32.9
Global warming (GWP100a)	kg $CO_2$ eq	1.45	0.96
Human toxicity	kg 1,4-DB eq	0.056	0.08
Fresh water aquatic ecotoxicity	kg 1,4-DB eq	0.032	0.053
Acidification	kg $SO_2$ eq	0.004	0.003

Table 11 – Comparison of the environmental between the process and a typical one from the software SIMAPRO.

From the TABLE 11, one notices several relevant information about our process :

- The "abiotic depletion" and "global warming" parameters are 1.5 times higher than the average for our process. That means that it is more energy consuming than a typical process. It is explained by the fact that the recycling stream in our process is big and undergoes several increases/decreases of its temperature.
- In terms of toxicity, the process is within the standards. One notices that the value of the "fresh water aquatic ecotoxicity" of our process is smaller than the one from the software. It means that the waste water is discharged in the sea and is correctly cleaned.
- Concerning the acidification, the process is a little higher than the standards.

#### 5.4.1 Conclusion

To conclude this LCA, based on the comparison between the environmental impacts between our process and a typical one from the software SIMAPRO, it can be considered that the ethanol unit production developed in this

project can be validated. Indeed, the results obtained for the different impact categories are of the same order of magnitude.

Therefore, it can be seen that a life cycle assignment is an important study for the development of a new production unit because it allows to validate or not the feasibility and the viability of the project. By carrying out this study, it can be seen that the way electricity is produced has an important influence on the environmental impacts. Indeed, producing electricity with wind turbines allows to have a lower environmental footprint. However, it should not be overlooked that wind turbines can cause other disturbances such as noise, landscape degradation,... Moreover, this type of renewable energy is said to be intermittent so it can be critical for a production unit if ever the supply of electricity is not sufficient.

Furthermore, this analysis can be used to help decision makers to optimise the process. Indeed, it was noticed that the heat used in the process represents an important part of the overall environmental impacts. Therefore, it can be interesting to optimise the heat integration. Then, it can also help to support policy in order to comply with the standards.

## 6. Conclusion

In this report, a summary of the work done since the beginning of the year has been presented. Moreover, a deeper analysis of the costs of the studied process was made. It has been shown that with our current knowledge of the process, it turns out to be non-profitable. This is however a crude analysis, which appears to be inaccurate, as this process is implemented in the industry. A more complex and deeper analysis should therefore be made to highlight the inaccuracies in our cost analysis.

Furthermore, the literature review highlighted the fact that ethanol production is done in several different ways, the most valuable today being corn fermentation. It also highlighted the growing place of ethanol in the biofuel industry.

Finally, a life cycle assessment of our process was realised. It allowed to validate our process as results of the same order of magnitude as with the simulation software were found.

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## 7. Appendix

### 7.1 CAPEX costs

#### Bare and total module cost

Specificity of each unit in order to calculate the bare and total module cost is presented in the TABLE 12.

Unity	Working pressure (atm)	Heat surface exchange ( $m^2$ )
HTX1	61	123
HTX2	61	74.6
HTX3	61	20*

Unity	Working pressure (atm)	Net work required (kW)
COMP1	/	5118
COMP2	/	450*
COMP3	/	450*

Unity	Working pressure (atm)	Volume ( $m^3$ )
REACTEUR	61	619
FLASH	5	4.75

Table 12 – Specificity required for the cost of each unity

The values with \* means that the value in the flowsheet is under the minimal value required to the construction of the unity. So the minimal value for the construction was taken in our calculation and is present in the TABLE 12.

The working pressure of compressors was not searched because there is no need to know it in order to calculate their total module costs. The bare module costs of the compressors takes already the pressure into account. Details about column cost was made by the separation group in the previous reports.

The bare module and total module cost of each unit are presented in the TABLE 13.

Unity	Bare module cost (k\$)	Total module cost (k\$)
HTX1	3.8	53
HTX2	4.2	59
HTX3	6.5	91
COMP1	1309	5237
COMP2	204	818
COMP3	204	818
REACTEUR	183	2562
FLASH	6.3	25.1
COL	80	320
<b>TOTAL</b>	<b>2002</b>	<b>9983</b>

Table 13 – Bare and total module costs of each unit

Formulas used to calculate the bare module cost and the total module cost come from the general assignment.

#### Grassroots plant cost

The grassroots plant  $C_{GR}$  is expressed with the following formula (Whiting et al., 2013):

$$C_{GR} = 1.18C_{TM} + 0.5C_{BM} \quad (1)$$

where  $C_{TM}$  is the total module cost and  $C_{BM}$  is the bare module cost.