Direct Dimethyl Carbonate Production from Carbon Dioxide and Methanol

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Abstract

The use of captured CO_2 as a raw material is a quite old concept that has however received more and more attention recently. Indeed, carbon capture units are increasingly being developed as well as new technologies for the storage, the utilisation and the transformation of this captured CO_2. This is driven by the increasing necessity to move towards more sustainable production processes and to mitigate greenhouse gases emissions.

The storage of CO_2 in earth's layers being a cost only technology, the alternative consisting in the production of novel chemical products or key substitutes to fossil-based chemicals seems attractive. In this perspective, two processes for dimethyl carbonate (DMC) production from captured CO_2 are discussed. The selected pathways both differ from usual dimethyl carbonate units in the selected raw materials and in the choice of energy used. Both processes rely on the direct synthesis of DMC from methanol and carbon dioxide. Each implies the utilisation of a dehydration agent to consume the water produced by the direct reaction and leading to a yield increase. Both alternatives are designed for an annual production of 20,000 tonnes of DMC and their respective mass and energy balances are simulated in Aspen Plus. Subsequently, a techno-economic analysis is performed to asses the viability of each process. From those analyses, it turns out that the direct synthesis of DMC using 2-cyanopyridine (2-CP) as dehydration agent leads to a revenue of 37 M€/year whereas the use of ethylene oxide (EO) as dehydration agent leads to 47 M€/year revenue. The difference comes from the ethylene glycol produced and sold. However, if the net present value (NPV) is regarded, the production of dimethyl carbonate using 2-cyanopyridine seems to be the most interesting production process.

In order to end up with a process as sustainable as possible, a sustainable way for methanol production is studied. This one implies the production of hydrogen from water electrolysis which is discussed as well. The results show that the electrolysis cell consumes around 40 kWh/kg of H_2 produced. This consumption is a hint showing the important energy requirements to produce methanol in a sustainable way. However, if renewable energy resources are considered, this process would be an attractive alternative compared to the classical methanol consumption in terms of CO_2 emissions. Nevertheless, the production cost of this methanol coming from renewable resources should not be neglected as it is shown that it is around 1,799 €/tonne while the actual purchase cost is 423 €/tonne. A whole energetic integration with the DMC production unit could be considered to optimise the overall energy consumption.

Introduction

This article is written in a context where climate change takes a preponderant place in most of scientific discussions. In recent years, the necessity to overcome climate issues by mitigating greenhouse gases emissions has become crucial for industries. Reducing those emissions can be made possible by using renewable energy resources, capturing carbon dioxide, finding applications and transformations for this captured CO_2, etc.

Each year, the European Committee for the Use of Computers in Chemical Engineering Education (EURECHA) initiates a 'Student Contest Problem' for which different groups of students throughout Europe are proposed to suggest solutions responding to a chemical engineering problem. This year, the proposed topic concerns CO_2 utilisation through the manufacture of a chemical product using captured CO_2 as raw material and renewable energy resources in France. This product must be a substitute to fossil-based chemicals and the process needs to demonstrate its contribution to different sustainable goals (*1*). This thematic appears to be increasingly important nowadays regarding the recent events caused by climate change. Those last years, the occurrence of fires, storms, drought, and other weather events has been increasing and historically calm regions have started to be the focus of attention due to these types of climate events. South of France, especially, knew historic fires last year but Siberia has also experienced a drought period leading to fires (*2*). Within this general context, captured CO_2 may have an interesting positive impact on global

warming. Even if it consists in a secondary measure in the fight against global warming, it may bring interesting perspectives for industries. The primary measures being to reduce and avoid fossil-based chemical products and greenhouse gases emissions.

In 2020, Covid crisis had an impact on CO_2 emissions (-6.4%) (*3*), but this was quickly mitigated by the significant recovery of all activities in the year 2021. It is required to think out of the box in order to increase the ability to move away from fossil fuels and create carbon-neutral processes and this article is a small step in this direction.

The article first presents an overview of dimethyl carbonate and the reasons testifying its production. Then, two main alternative processes are presented and then compared based on energy requirements and cost estimations. It is followed by a section concerning the production of methanol (MeOH) used in DMC production in a sustainable way. Eventually, perspectives for this project and answers to Eurecha assessments are presented.

1. Dimethyl carbonate as an interesting chemical product

Dimethyl carbonate (DMC) can be used for different purposes such as solvent, methylating agent, fuel additive but it also finds an application in polycarbonate production. The direct synthesis of DMC from CO_2 and methanol seems to be an interesting alternative compared to the utilisation of toxic phosgene what could lead to a sustainable production of polycarbonate as ultimate product (*4*). From a study published in 2020 (*5*), it can be seen that a high level conversion (85.2%) can be reached with a zirconium (IV) acetylacetonate ($Zr(acac)_4$) catalyst leading to a carboxymethylation with a selectivity up to 99%. The old way of producing polycarbonate (PC) from DMC was far less efficient (only few percents of conversion). It shows that DMC clearly appears as a high potential chemical, for its usual application but also in the field of polymer chemistry.

Furthermore, PC is a product that is used in many industrial sectors (medical, electronics, automotive, construction,...). Then, even if more than 315,000 tonnes of DMC per year is already known to be produced in the world (*6*), the amount of PC produced in Europe per year overcomes 1.5 million tonnes (*7*). It can be observed in Figure 1 that 11% of Europe PC consumption is attributed to France while it produces negligible amount of PC. There is thus a real need of polycarbonate production within its territory to reduce France's dependency on polycarbonate importations. This could be achieved by using the DMC produced by a sustainable way discussed in this article.

Sustainable way for dimethyl carbonate production Considering the current ecological and political situation (at least
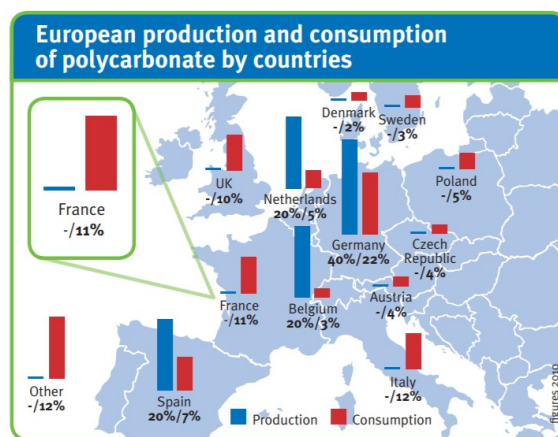

Figure 1. European production and consumption of polycarbonate by countries (*8*)

in France and Europe), it is nowadays more and more important to turn towards renewable energies and neutral carbon processes. The energy transition and the limitations of greenhouse gases emissions will constrain future industries to produce in a more environmentally friendly way. This inevitably also applies to DMC production. Looking for more sustainable processes has also an economic interest for industries as using captured CO_2 and renewable energies helps to obtain a negative carbon balance sheet preventing the payment of ecological taxes. However, it must be ensured that the project remains profitable, what is discussed in the following parts of the article.

DMC production goal Concerning the objectives of production, a good target for the production quantity seems to be of 20,000 tonnes of DMC per year. This value is chosen as it represents less than 10% of the worldwide DMC production and considering that this production could greatly contribute to polycarbonate manufacture. The goal here is not to overestimate the production but rather to provide a first capacity guess that can be further updated.

Source of CO_2 A first step to choose the source of CO_2 that is used in the process is to look for the price of CO_2 available in France. Based on a paper of Leeson et al. (*9*) in addition with EUETS website (*10*), a first correct price approach can be done. From this paper and website, it seems that hydrogen production industries enable to offer low cost CO_2, and that three of them (producing enough CO_2 for the processes studied in this article) exist in France. The first one is 'Air Liquide Hydrogene Port Jérome' that produces 200,000 tonnes of CO_2 per year. The second one is 'Air Liquide Hydrogene Lavera SMR' with a production of 180,000 tonnes of CO_2 per year and the third one is 'Alfi Belle-Étoile Hydrogene' with a production of 97,000 tonnes of CO_2 per year.

The more convenient site is identified regarding the space available near the CO_2 production industry, the accessibility

of the site (airport available, harbour, highway...) and the area in which the site is located (high population or industrial area). Based on this information, *'Alfi Belle-Étoile Hydrogene'* appears to be the best option because of its ideal position along the Rhônes, very close to railways and having a central position in the country allowing easier interactions with future customers. Moreover, there is already enough free space (+/- 130,000 m^2 as can be seen in Figure 2) around 2.5km to the north of the hydrogen plant.


Figure 2. Possible location of the future plant

It is estimated that around 55,000 m^2 are required based on the desired production quantity and by comparison with the needed space for the DMC production plant in *Shandong Shida Shenghua Chemical Co., Ltd.* (*11*) and the two methanol production plants from *Methanex* in Medicine Hat ((*12*)) and from *Oman methanol company* (*13*).

2. Processes pathways

The direct synthetis route of DMC is thermodynamically difficult due to the equilibrium limitation of the following reaction:

$$CO_2 + 2CH_3OH \rightleftharpoons (CH_3O)_2CO + H_2O$$
$$\Delta_r H^0 = -20.1 \text{ kJ/mol} \quad (1)$$
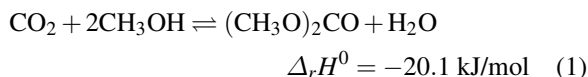
In order to increase the yield of methanol and carbon dioxide (CO$_2$) transformation into dimethyl carbonate, it is necessary to apply a fundamental principle to shift equilibrium towards the products. This principle does not play on the exothermicity of the reaction (enthalpy change of reaction = -20.1 kJ/mol (*14*)), but rather on the consumption of the by-product. Indeed, the idea is to consume water to shift the equilibrium to the right and to increase the production of DMC. In order to achieve this shifted equilibrium, two different processes are studied. The first one uses 2-cyanopyridine (2-CP) to consume water and to form 2-picolinamide (2-PA) which is recycled later in 2-cyanopyridine for having an interesting recycling loop, and the second one uses ethylene oxide (EO) that leads to the production of ethylene glycol (EG) which

can be sold on the market.

Those two processes are compared in order to select the more sustainable and profitable one. The comparison of both models is conducted with Aspen Plus V11.0. The amount of DMC produced is the same in both cases (20,000 tonnes/year) and the basis for the economical analysis of both processes comes from the method developed by Turton et al. (*15*).

3. Dimethyl carbonate synthesis with 2-cyanopyridine as dehydration agent

Concept In this section, the production of DMC from carbon dioxide and methanol assisted by 2-cyanopyridine as the dehydration agent is detailed and mainly based on an article published by Ohno et al. (2021) (*16*). A catalyst made up of CeO$_2$ is also used to overcome the thermodynamic limitation of the reaction (*16*, *17*).

The two reactions occurring in the process consist in the direct synthesis of DMC from CH$_3$OH and CO$_2$ and the hydration reaction of 2-cyanopyridine into 2-picolinamide:

$$CO_2 + 2CH_3OH \rightleftharpoons (CH_3O)_2CO + H_2O \quad (2)$$

$$C_6H_4N_2 + H_2O \rightleftharpoons C_6H_6N_2O \quad (3)$$
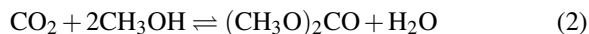
As mentioned before, both reactions are catalysed by cerium (IV) oxide (CeO$_2$). From different researches detailed by Ohno et al. (*16*), it is indicated that 2-cyanopyridine is found to be one of the most effective nitriles to be used as a dehydration agent to solve the encountered equilibrium limitation. Moreover, it is mentioned that reactive distillation is used in order to recover this 2-cyanopyridine from 2-picolinamide to avoid waste of dehydration agent. CeO$_2$-based catalyst is used for both reactions and allows to achieve 96% MeOH conversion into DMC by the efficient removal of water with 2-cyanopyridine (*16*, *18*).

Modelling and simulation Based on the process flow diagram (PFD) realised by Ohno et al. (*16*), a similar flowsheet is designed with Aspen Plus in order to produce 20,000 tonnes/year of DMC. The UNIQUAC model is used to describe the thermodynamics of the process and properties for 2-CP and 2-PA are estimated via Group Contribution Methods (GCMs) using Joback method (*19*). The components used in this process are methanol (MeOH), carbon dioxide (CO$_2$), 2-cyanopyridine (2-CP), 2-picolinamide (2-PA), water (H$_2$O) and dimethyl carbonate (DMC).

Concerning the two reactions catalysed by CeO$_2$ modelled in the process, the kinetics established by Honda et al. (*17*) are used. It should be mentioned that a third reaction is considered in the process which is the regeneration of 2-CP by
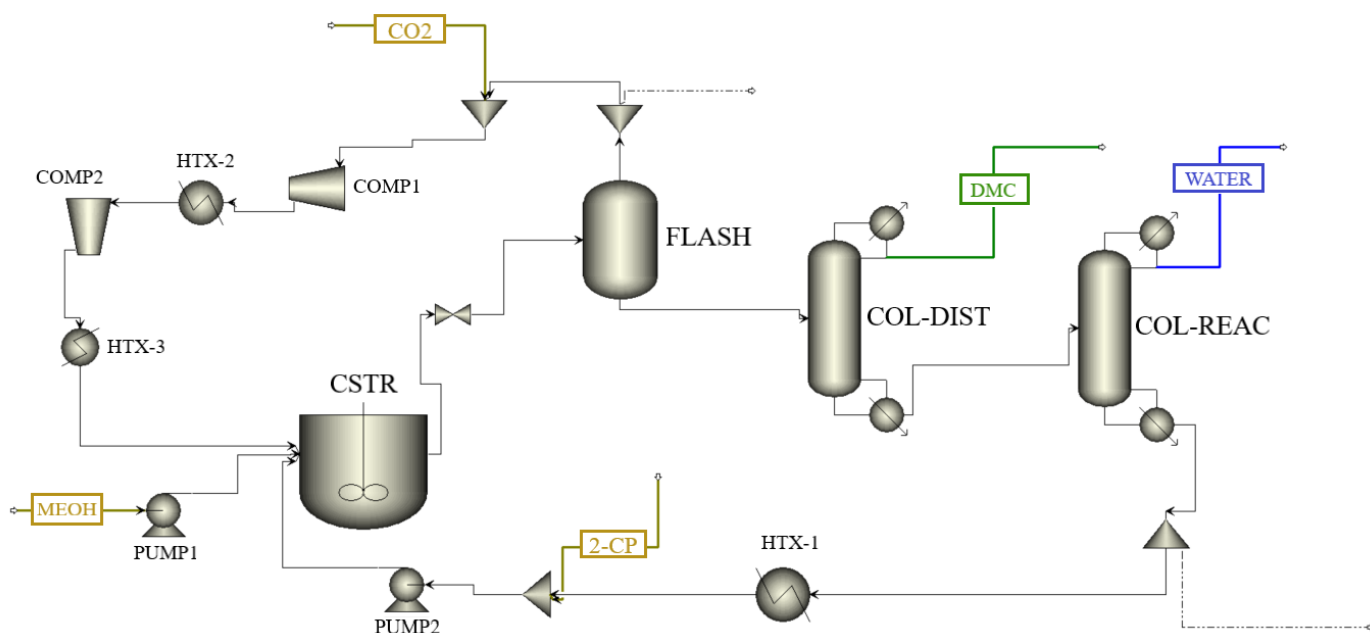
Figure 3. Process flow diagram for dimethyl carbonate synthesis using 2-CP as dehydration agent

dehydrating 2-PA in a reactive distillation column. This reverse reaction is considered at equilibrium (*16*).

The process flow diagram of the production of dimethyl carbonate using 2-CP as the dehydration agent is shown in Figure 3. To detail the process briefly, it consists in a continuous stirred-tank reactor (CSTR) where the two above-mentioned reactions occur. It is followed by a flash separation between unreacted CO_2 and other compounds. This stream of CO_2 is recycled, mixed with fresh CO_2 and sent back to the reactor. The other outlet stream of the flash tank (FLASH) containing the DMC is sent to a distillation column (COL-DIST) to separate DMC from 2-PA and other unreacted components. The last step is the regeneration of 2-CP by dehydrating 2-PA in the reactive distillation column (COL-REAC). The 2-CP is recycled and mixed with fresh 2-CP before sending it back to the reactor. A small fraction of 2-CP is not recycled and ends up at the top of the reactive distillation column within the wastewater stream.

The reactor operates as an isothermal CSTR at 120°C and 30 bar, and its residence time is set to 10 min (*20*). The flash separation is operated under adiabatic conditions at atmospheric pressure. Compared to the process of Ohno et al. (*16*), some adjustments on the column are made in order to achieve the purity (between 99.6 and 99.9 wt-%) and the quantity (20,000 tonnes/year) of DMC required. Indeed, the process shown in Figure 3 is designed for a production around 6 times higher than in the process of Ohno et al. (*16*).

Results In the simulated process, a production of 20,063 t/year of DMC is achieved with a mass-purity of 99.8 %. Only CO_2 is present as impurity into the product stream (less than

0.03 wt-%). The DMC yield based on MeOH feed is higher than 99.6 %. Even if the conversion in the reactor is high (99.96 %), a small amount of DMC (9.7 kg/h) is lost in the water stream at the top of the reactive distillation column. In this column, an almost complete regeneration of 2-CP from dehydration of 2-PA is achieved. This corresponds to a recycled flow of 2,879 kg/h of 2-CP leading to a fresh feed of 26.69 kg/h. Concerning the 2 main reagents, a fresh feed of MeOH containing 1,788 kg/h is required as well as a fresh feed of 1,232 kg/h of CO_2.

Looking at the first distillation column, 7 stages seem enough to separate effectively DMC from 2-PA due to their large difference in boiling point at atmospheric pressure (90°C and 263°C, respectively). A quick look at the temperature and concentration profiles leads to the same conclusion. Figures 4 and 5 show the temperature and composition profiles of the column. Only 2-PA and DMC are represented as they are the main compounds in the inlet stream of the column.
As can be seen in Figure 4, a high temperature is reached at the bottom of the column (stages 6-7) what already suggests that a high amount of heating energy is required.
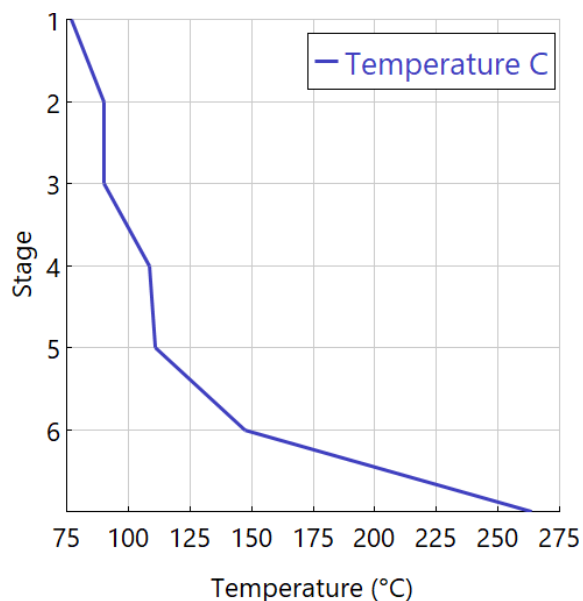
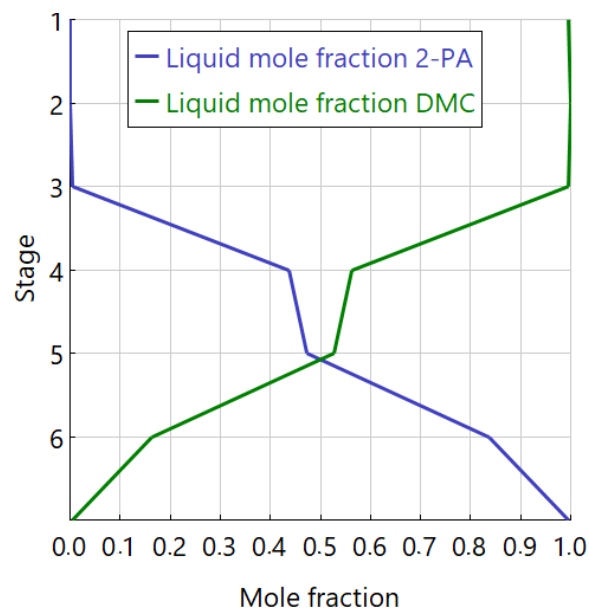**Figure 4.** Temperature profile in COL-DIST

Figure 5. Composition profile in COL-DIST

Based on Figure 5, the two top stages seem to be unnecessary. However, according to Ohno et al. (*16*), the two first stages should have a small variation of composition which is not really noticeable here. Then, the decision to keep 7 stages is made based on this information.

For the second column, the dehydration reaction of 2-PA into 2-CP occurs from stage 5 to stage 9 according to the model of Ohno et al. (*16*). This column counts 9 stages and internals are modelled as sieve trays. The two columns are modelled using the Radfrac package in Aspen Plus and the interactive

sizing mode is applied in order to have an order of magnitude for the size of the columns. The first one has a height of 3.75 m and a diameter of 0.61 m while the second one has a height of 4.25 m and a diameter of 1.22 m.

Compressors and pumps are used to achieve the optimal pressure of 30 bar (*17*). Heat exchangers modelled as coolers in the first place are included to increase the efficiency of compression and to avoid a too big increase in temperature. The energy consumption for each unit is shown in Tables 1 and 2. As can be seen, the reboilers and condensers of the two columns are the largest utility requirements. Of course, as the synthesis of DMC is an exothermic reaction, a huge amount of cooling energy is required in the CSTR in order to keep the temperature constant. The total electricity power requirement is about 205 kW.

Unit	Electricity demand (kW)
COMP1	120.91
COMP2	67.74
PUMP1	6.49
PUMP2	10.35
TOTAL	**205.48**

Table 1. Electricity requirements by unit for the process using 2-CP as the dehydration agent

Unit	Heating demand (kW)	Cooling demand (kW)
HTX-1		173.67
HTX-2		31.35
HTX-3		156.05
COL-DIST	711.37	355.49
COL-REAC	1,611.55	1,091.32
CSTR		842.06
TOTAL	**2,322.92**	**2,649.94**

Table 2. Heating and cooling energy requirements by unit for the process using 2-CP as the dehydration agent

For the column condenser, cooling water is used due to its higher overall heat transfer coefficient compared to air. The temperature of condensation in the two columns (respectively 77 °C and 99.5 °C) enables to use water at ambient temperature. For the heating demand, high-pressure steam at 284 °C (40 bar) can be used in order to reach the 263 °C and 232 °C required respectively in the reboilers of the distillation column and of the reactive distillation column.

Heat integration To avoid unnecessary energy consumption, a heat-exchanging analysis can be made in order to observe a possible heat-exchanger network. In this work, only a quick calculation of potential energy savings using a Grand Com-

posite Curve (GCC) is made. A ΔT_{min} of 10 °C is considered for the heat consumption analysis.
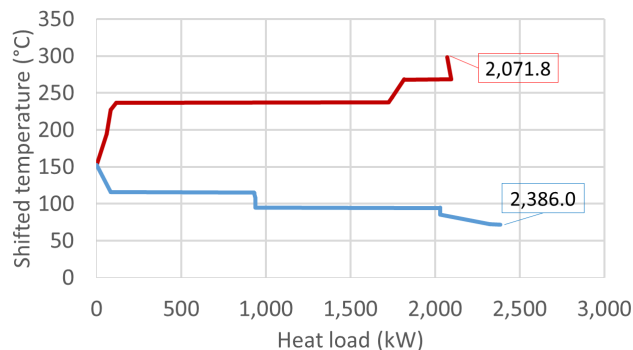

Figure 6. Grand composite curve for the process using 2-CP as a dehydration agent

In Figure 6, the GCC is represented showing the heating and cooling utilities required. This leads to 2,071.8 kW of heating utilities and 2,386.0 kW of cooling utilities. If these values are compared with the values found in Table 2, it corresponds to potential energy savings of around 10% which is non-negligible.

4. Dimethyl carbonate synthesis with ethylene oxide as dehydration agent

Concept In the alternative presented in the following, DMC is still produced through its direct synthesis in which methanol reacts with carbon dioxide (see Equation 1). As already explained in the previous section, the reaction is not spontaneous and limited to an equilibrium. It is required to use a dehydrating agent to withdraw water from the system, thus shifting the equilibrium of the reaction. This alternative uses ethylene oxide as a dehydrating agent to take advantage of its reactivity towards water to form ethylene glycol:

$$(CH_2CH_2)O + H_2O \longrightarrow HO-CH_2CH_2-OH \quad (4)$$

This alternative seems to be interesting given the fact that this reaction is very well known as around 60% of ethylene oxide production is transformed into ethylene glycol (21), however it is only viable if the product formed can be sold. Indeed, regarding the high cost of ethylene oxide as a raw material (22), this process cannot be economically viable if ethylene glycol is not recovered to be sold.

The simulation of this process is mainly based on a recent paper published by Wu and Chien (2020) (23). They propose in their article different alternatives to produce DMC through the direct synthesis and come to the conclusion that the most effective configuration from an economical point of view is the one represented in Figure 7. This configuration is an example of process intensification because the dehydration reaction

(Equation 4) takes place in a distillation column which is in turn called a reactive distillation column (RDC). The different reagents are fed to this column from which methanol and carbon dioxide exit in the gaseous phase to be sent to a side reactor in which the DMC synthesis takes place. The exit of this reactor is sent back to the reactive distillation column where the water formed in the reactor reacts with ethylene oxide to form ethylene glycol. This later exits the RDC in the liquid phase along with the produced DMC to be further separated in a distillation column.

Some differences can be noticed between the process flow diagram presented in Figure 7 and the one from the original paper (23). In this work, the compression and heating or cooling of the reagents entering the RDC is considered while it is not the case in the reference article. Another difference is the presence of a heater just after the reactor. As it is explained in the following section, the modelling of the reactor by Wu and Chien (23) presents some uncertainties regarding the results they obtained. Consequently some modifications are done for this part of the process and discussed in the following.

Simulation and modelling As the scope of this report is not focused on a detailed modelling of the process, only the key points are presented as well as the main differences brought compared to Wu and Chien's work (23). In this regard, the two reactions taking place within this process are first discussed. DMC production, described by Equation 2, takes place in an isothermal continuous stirred-tank reactor (CSTR). This reaction occurs in the gas phase and is assumed to reach chemical equilibrium. Wu and Chien (23) regressed the reaction equilibrium model from experimental data (24) and derived an equation describing the temperature dependence of the equilibrium constant. However, as it is shown by Redeker et al. (25), the equation derived by Wu and Chien (23) presents some points of uncertainty. It comprises the fact that the data used to fit model parameters are taken at 12 bar while the reactor is modelled at 15 bar and that the reported model parameters do not fit the experimental data. Redeker et al. (25) hence derived a new equation:

$$\ln (K_{eq}) = 223 - \frac{40,700}{T} - 0.32T, \quad \text{where } T \text{ is in K} \quad (5)$$

that seems to better fit the experimental points and that is consequently used in this work.

The second reaction i.e. the dehydration reaction (Equation 4) takes place in the reactive distillation column, more precisely in the liquid phase on each tray of this column. This reaction is described with the following kinetics model:

$$r \, (\text{mol.s}^{-1}.\text{cm}^{-3}) = 3.15 \times 10^9 \exp\left(\frac{-9,547}{T}\right) x_{EO} x_{H_2O} \quad (6)$$

where x_{EO} and x_{H_2O} are the molar fractions of ethylene oxide and water, respectively. Looking at the high value of the
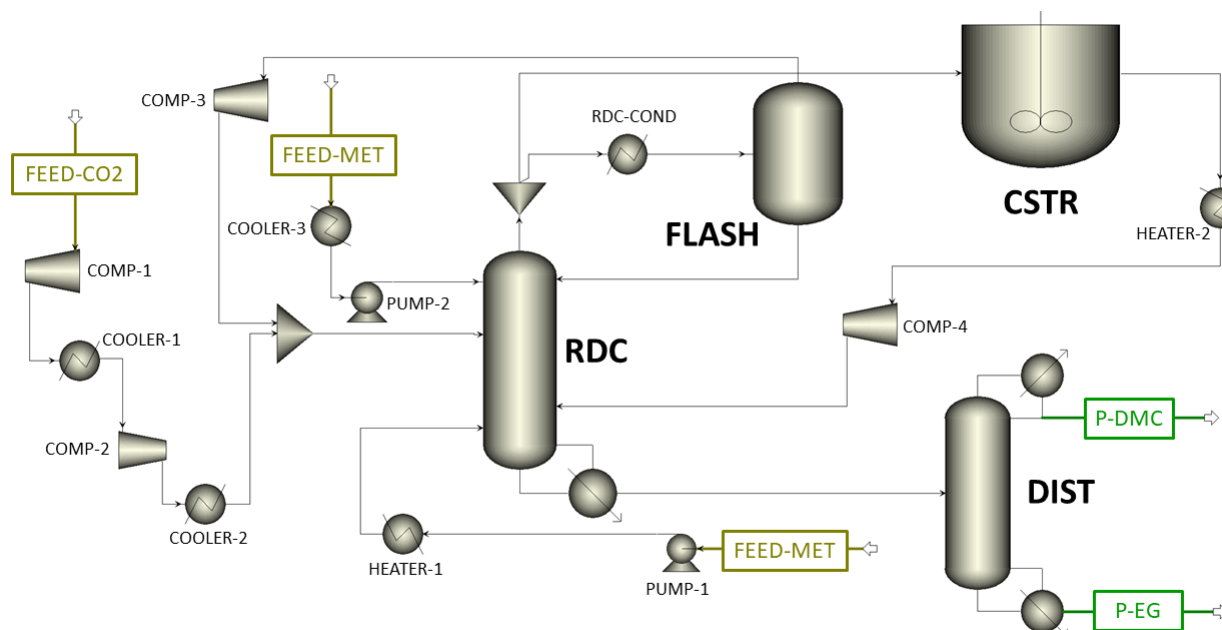
Figure 7. Process flow diagram for dimethyl carbonate synthesis using ethylene oxide as dehydration agent

pre-exponential factor, it seems that this reaction has pretty fast kinetics justifying the utilisation of ethylene oxide as a dehydration agent. The activation energy also influences the kinetics, however the value is not so high in this case (around 79 kJ/mol) suggesting that the kinetics should be fast (*26*). The value of the activation energy is calculated by multiplying the factor 9,547 in the equation above by the ideal gas constant, R, equal to 8.314 J/(mol*K).

As already said, this work considers the compression and the heating or cooling to the adequate temperature of the reagents. The fresh CO_2 is assumed to come from a post-combustion capture unit where it is available at 40°C and 2.5 bar (*27*, *28*). In order to reach the entrance conditions (32.85°C, 15 bar), it is chosen to compress the gas stream with two compressors with inter-stage cooling in order to not overcome a pressure ratio of 4 (*29*). This compression line is designed by minimising the cost of utilities used in the two compressors and in the two coolers. The objective function to minimise is thus:

$$C_{comp} = C_{elec} \cdot W_{comp} + C_{cooling} \cdot Q_{coolers} \qquad (7)$$

where C_{comp} is the total cost of the utilities used in the compression line, C_{elec} is the electricity cost, W_{comp} is the energy required by both compressors, $C_{cooling}$ the cost of cooling water and $Q_{coolers}$ the cooling duty required by both coolers. The variables of this optimisation are the pressure ratio of each compressor and the exit temperature of the cooler set between the two compressors. It is assumed that the coolers are cooled down by cooling water entering at 30°C and leaving at 40°C.

The results of this optimisation lead to impose a pressure ratio of 2.44 for the first compressor, 2.49 for the second one and an intermediate cooling temperature of 35°C which is the lower bound of the variation domain of this variable. It is quite logical as the compression work decreases with the temperature, and that compression work is much more costly than cooling. The cost of utilities can be found in the section discussing the cost estimation of this process (see Section 5).

Methanol and ethylene oxide being liquid at the desired conditions, their pressure is raised using a pump. For the modelling, it is assumed that the methanol is obtained from the process described in Section 6, justifying the utilisation of a cooler as it leaves the process at 64.2°C and atmospheric pressure. In order to avoid this cooling step before the entrance in the column, it would be interesting to study the impact of using methanol at 64.2°C in that column. Concerning the ethylene oxide it is assumed that it is obtained at 20°C and 2 bar because it is generally stored under pressure to have it in liquid phase in which it is free of explosion hazard (*30*).

Another point of discussion concerns the reactor. Wu and Chien (*23*) mention in their work that the reactor is an isothermal CSTR operating at 109°C and 15 bar and having a cooling duty of 0.91 MW. They also mention that the reactor outlet sent back to the column has a temperature of 141°C after the compressor. This temperature is a first questioning point because it would mean that the stream leaving the reactor, which is thus at the same temperature as the reactor i.e. 109°C, is

heated up to 141°C just by going through the compressor. This could be possible as the compression increases the temperature of the stream, however the simulation shows that this temperature cannot be reached within this compression step. Indeed, an increase in temperature of around 32°C should be achieved for a pressure increase of around 0.2 bar. The simulation shows that this compression step only slightly increases the temperature (less than 1°C for an isentropic efficiency of around 72%). Moreover, in case there is no heater after the reactor, the stream leaving the reactor would contain a too big liquid fraction (around 56 mol-%) that would be detrimental for the compressor. Another questioning point is the heat duty of the reactor calculated by Wu and Chien (*23*). When simulating the reactor at an operating temperature of 114°C and entering temperature of 140°C , the heat duty calculated is -10.7 MW. The difference between this value and 0.91 MW cannot be explained only by the difference in the amount of DMC produced (around 15 ktonnes/year against 20 ktonnes/year in this work). It is supposed that Wu and Chien (*23*) combined the duty of their reactor with the duty of a heater not represented in their flowsheet. If this assumption is correct, it means that this heater raises the temperature of the reactor outlet before it enters the compressor to evaporate the liquid fraction of the stream. The positive heat duty of this heater would counterbalance the negative heat duty of the reactor leading to the value announced by Wu and Chien (*23*). These assumptions are the reasons why the reactor is followed by a heater in the process presented in this work. It should be mentioned that raising the temperature of a stream before it enters a compressor does not appear as an optimal design option, however it avoids the presence of liquid in the compressor. Given the relatively slight pressure increase in the studied compressor, it would be of interest to study the impact of removing this later.

Results As stated above, the objective of this process is to produce 20,000 tonnes/year of DMC. To reach this production objective, stoechiometric amounts of reagents are introduced in the process: the methanol makeup is twice as large as the carbon dioxide makeup while the ethylene oxide one is equal to this later. It is assumed that the reagents are obtained 100% pure but the investigation of the impact of impurities on the design of the process could be interesting as a next step to improve this modelling. It can already be mentioned that the presence of impurities in the reagent makeups would require the inclusion of a purge stream to prevent an accumulation of these impurities. This process requires 1,221 kg/h of CO_2, 1,778 kg/h of methanol and 1,222 kg/h of ethylene oxide to produce 2,507 kg/h of DMC and 1,716 kg/h of ethylene glycol. The DMC produced has a mass purity of 99.7% what falls in the purity ranges observed on the market (*31*). The mass purity of the produced ethylene glycol is 99.99%.

The energy requirements of this process can be found in Tables 3 and 4 in which the electricity demand and heating and cooling requirements are separated. It can be seen in Table 4

that the heating and cooling demand of this process is much bigger than for the process using 2-CP. This difference is questionable as both processes use the same technology (direct synthesis with dehydration agent) to produce the same amount of DMC. It is interesting to observe that the main contribution to these heating and cooling requirements comes from the reactor section i.e. from the reactor itself and the heater following it. The uncertainties on this section of the process are mentioned in the previous section. In this later, it is assumed that Wu and Chien (*23*) combined the cooling demand of the reactor with the heating demand of the heater as a single cooling demand. If this was done as well in this case, then the total values given in Table 4 would become 1,999.3 kW for the heating demand and 2,777.8 kW for the cooling demand. It turns out that these values are quite close from the one observed for the 2-CP process in Table 2. However, for the cost estimation described below and for the remaining of this article, the values presented in Table 4 are used because there is no evident reactor-heater configuration that would allow to combine the heating and cooling duty of both blocks as a single cooling requirement. Given these uncertainties on the reactor section modelling, the results presented should be taken with care.

Unit	Electricity demand (kW)
COMP-1	27.3
COMP-2	27.6
COMP-3	1.9
COMP-4	45.5
PUMP-1	1.7
PUMP-2	3.1
TOTAL	**107.1**

Table 3. Electricity requirements by unit for the process using EO as the dehydration agent

Unit	Heating demand (kW)	Cooling demand (kW)
RDC	1,859.4	938.2
DIST	117.8	361.2
CSTR	0	11,089.2
HEATER-1	22.1	0
HEATER-2	9,692.8	0
COOLER-1	0	28.8
COOLER-2	0	28.2
COOLER-3	0	25.0
TOTAL	**11,692.1**	**12,470.6**

Table 4. Heating and cooling energy requirements by unit for the process using EO as the dehydration agent

Heat integration In order to seek the minimal energy consumption of this process in terms of heating and cooling requirements, a pinch analysis can be performed as it is done for

the 2-CP process with the same ΔT_{min} (10°C). The grand composite curve is shown in Figure 8 to find the pinch temperature of the process, separating the area where heating is required from the one where cooling is required. It must be mentioned that this analysis is performed only to estimate the potential of the process in terms of energy savings. The analysis is not taken as far as the total modelling of an heat-exchanger network being the reason why the process is modelled with heaters and coolers and not with heat exchangers.
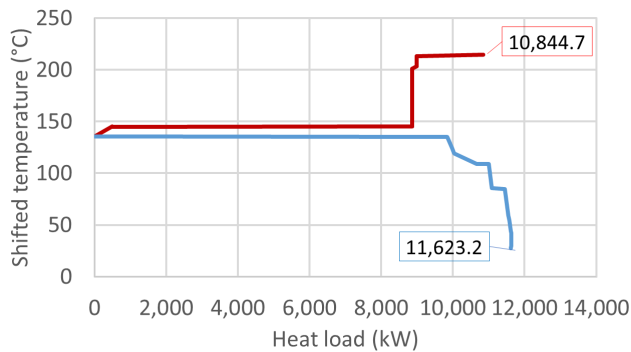
Figure 8. Grand composite curve for the process using EO as a dehydration agent

The results of this pinch analysis show that the minimum heating utilities required by the process are 10,844.7 kW corresponding to an energy saving of 7.2% with respect to the value in Table 4. Concerning the cooling utilities, the potential energy saving is 6.8% as the minimum cooling requirement is 11,623.2 kW.

5. Cost estimation

As explained in the beginning of this article, the aim is to identify a sustainable process reusing CO_2. In order to do it, both alternative processes require to be compared based on their energy consumption (as described in previous sections) as well as on their cost requirements. An initial cost estimation is thus performed for both processes. The same methodology and the same assumptions are used to estimate the cost of these processes. The applied methodology is the one described by Turton et al. (15) in which the estimation is made up of a capital expenditures (CAPEX) and operating expenditures (OPEX) calculation followed by a cash flow analysis.

The different correlations proposed by Turton et al. (15) to calculate the CAPEX of each piece of equipment have been derived in 2001. In order to take the inflation into account, the calculated costs must be updated with an index called CEPCI which is calculated for each year. In August 2021 the CEPCI value was 735.2 (32) which is used in this work. Concerning the OPEX estimation and cash flow analysis, some assumptions are used including an annual cost of 35,876 €/year for a machine operator (33), a tax rate of 26.5% (34), a depreciation of equipment following the MACRS method over 6 years as described by Turton et al. (15). The project life is assumed to be 12 years including two years for the start-up of the project and then 10 years of operation according to what is proposed by Turton et al. (15). The plant lifetime may be longer than 10 years but the point here is to compare the profitability of both alternative processes what can already be done for a duration of 10 years as it is shown in the following. The price of the different chemicals used in the process are summarised in Table 5 in which the minimum and maximum values can be found. For the following estimations, the mean value is calculated and used. For the methanol and ethylene oxide, only one value has been found in the literature explaining why there is only one value for these chemicals. The cost of the land necessary for the process (as discussed in Section 1) can finally be found in this table as well. This cost is given without VAT which is equal to 5.8% (35) and which is used in the calculations.

Chemical	Minimum price (€/kg)	Maximum price (€/kg)
DMC	0.84	2.39
EG	0.61	0.86
CO_2	0.013	0.067
2-CP	2.65	4.059
KOH	0.86	1.67
H_2O	0.12	0.36
MeOH	0.423	0.423
EO	1.594	1.594
Surface (m^2)	Minimum price (€)	Maximum price (€)
1	9	11
55,000	495,000	605,000

Table 5. Price of the different chemicals found in the described processes (22, 36, 37) and land price excluding VAT (38)

Concerning the heating and cooling utilities used in the process, the data used come from Turton et al. (15). It is chosen to use cooling water for cooling utilities as in both alternative processes, the temperature never reaches values that are low enough to require the utilisation of refrigerated water. Cooling water is available at 30°C and is assumed to observe a temperature variation of 10°C within each exchanger where it is used. Concerning heating utilities, low pressure steam available at 160°C (3.5-4.5 bar), medium pressure steam at 184°C (15-17 bar) and intermediate pressure steam at 254°C (28.5 - 29.5 bar) are used. An exception is made for both reboilers of the 2-CP process in which a temperature greater than 254°C is required. In that case, high pressure steam at 284°C is used (250-300°C at 40-43.2 bar) but its cost is supposed to be equal to the intermediate pressure steam cost by lack of data. An alternative to this high pressure steam at high temperature could be to use heating oil instead for the two reboilers of the

2-CP process. The cost of each utility can be found in Table 6.

Type of utility	Cost (€/GJ)
Cooling water	0.337
Low pressure steam	4.04
Medium pressure steam	4.25
Intermediate pressure steam	5.04

Table 6. Cost of utilities (Turton et al. (*15*))

The last assumptions regarding this cost estimation concerns the way the different equipment are sized to estimate their CAPEX. In the following section, it can be seen that the CAPEX of each class of units is given in terms of their respective C_{BM}. This corresponds to the bare module cost, updated for 2021 with the CEPCI, of a piece of equipment that includes the estimation of the CAPEX and the material and pressure factors. These factors enable to correct the cost estimation depending on the selected material and the operating pressure of each block. As no specifications are required for the different raw materials and products passing through the different pipes and blocks, carbon steel is considered for each piece of equipment.

To estimate the CAPEX of a heat exchanger, its surface area is required. As already mentioned, all exchangers are modelled as heaters, thus it is not possible to obtain this surface area from the Aspen Plus simulation. The surface areas are estimated with the following equation:

$$Q = U \cdot A \cdot \Delta T_{lm} \tag{8}$$

where Q is the heat duty of the heat exchanger expressed in kW, U the heat transfer coefficient in kW/(m^2*K) which are estimated for each exchanger based on heuristic rules and ΔT_{lm} the logarithmic mean temperature difference in K. In order to estimate the CAPEX of a reactor and a flash vessel, their respective volume must be known. To estimate these volumes, a retention time of 10 min is assumed for a liquid phase and 1 min for a gas phase. Based on these assumptions and the flow rate leaving the reactor or the flash tank, it is possible to estimate their volume. This volume is then doubled in the case of a flash tank to ensure sufficient space for the gas to leave. The estimation cost of distillation columns is also based on their volume that is determined by using their respective diameter and height resulting from the Aspen Plus simulation and approximating them as cylinders. Regarding compressors and pumps, their shaft power is the only parameter necessary to calculate their respective CAPEX.

DMC via 2-CP as dehydration agent A cost estimation of the plant is made following the different assumptions described in the beginning of this section. The C_{BM} of the different units involved in the process is shown in Table 7.

Units	C_{BM} (€)
Compressors	372,421
Pumps	63,778
Heat exchangers	892,043
Reactor	235,208
Flash vessel	27,737
Column vessel	110,891
TOTAL	**1,702,081**

Table 7. C_{BM} of different units required in the process

Concerning the OPEX estimation, it leads to a total cost of manufacturing without depreciation of 11.1 M€/year. Moreover, revenue is calculated based on a selling price of DMC of 1,842 €/tonne and leads to 36.95 M€/year. Based on those calculated values a cumulative cash flow diagram is illustrated in Figure 9. As a first approximation, it is considered that the plant is bought at the beginning of the project (end of year 0) and that the building of the plant takes 1 year.
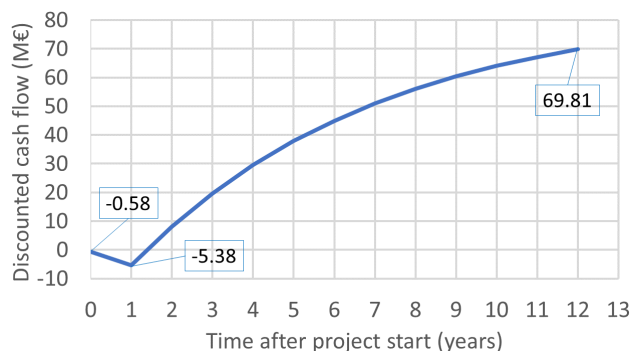

Figure 9. Cumulative cash flow diagram of dimethyl carbonate process using 2-CP as the dehydration agent

As can be seen in Figure 9, the first expense, equal to 580,000€, corresponds to the land purchase. The discounted cash flow after 12 years has a positive value of 69.81 M€. In order to investigate how it evolves with the selling price of DMC, a sensitivity analysis is conducted. From Table 5, different selling prices of DMC between the minimum and maximum value are considered. Figure 10 shows how the discounted cash flow evolves if the selling price of DMC varies between 0.84€/kg and 2.38€/kg.

From Figure 10, it can be seen that even if the price of DMC is the lowest, the discounted cash flow after 12 years is sill positive and reaches 11.81 M€. On the other side, with high selling price of DMC, this discounted cash flow reaches 102 M€ after 12 years.

Similar analyses can be made to understand how the cost of 2-CP impacts the discounted cash flow diagram and influences the minimum price for selling DMC to have a zero cumulative cash flow after 12 years. However, it has small
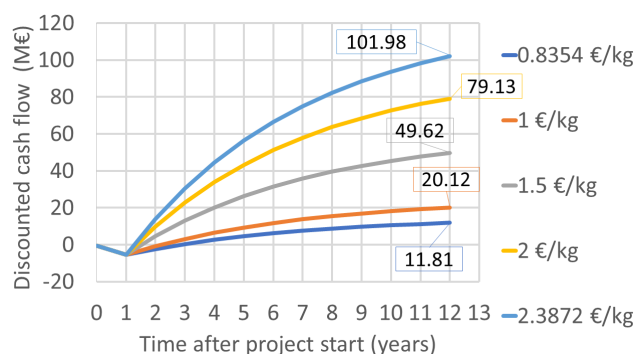
Figure 10. Evolution of cash flow diagram depending on the selling price of DMC

impact both on the cash flow diagram and minimum price of DMC. Indeed, if the price of 2-CP is 0.5 €/kg, the minimum selling price of DMC reaches 0.59 €/kg, while if the price of 2-CP reaches 5 €/kg, the minimum selling price of DMC only increases to 0.66 €/kg.

The main costly raw material is MeOH which costs approximately 6 M€/year. Then, its price variation has supposedly a bigger impact than 2-CP. As can be seen in Figure 11, the minimum selling price of DMC leading to a zero cumulative cash flow after 12 years evolves quite a bit. Indeed, between a methanol price of 300 €/tonne and 600 €/tonne, the minimum selling price of DMC increases by 55%. Figure 12 illustrates the variation of methanol price over the 3 last years and gives credit to the choice of prices used in Figure 11.
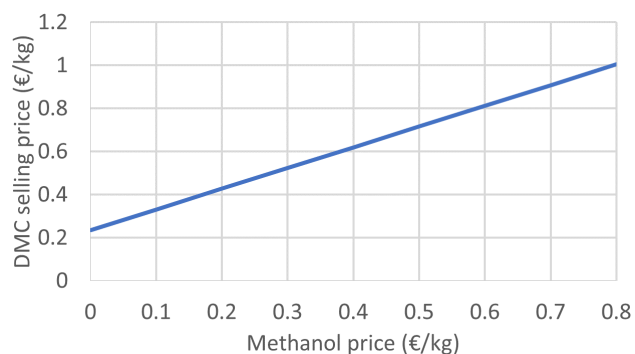
Figure 11. Break-even curve considering methanol price

From Figures 11 and 12, one realises that producing methanol internally may avoid being too dependent on market prices and thus be less vulnerable to market variations. Moreover, a sustainable production of methanol could also decrease the environmental impact of DMC production as well as its contribution to global warming. This part on sustainable methanol production is discussed in Section 6.

DMC via ethylene oxide as dehydration agent The cost estimation for this process is also made following the different
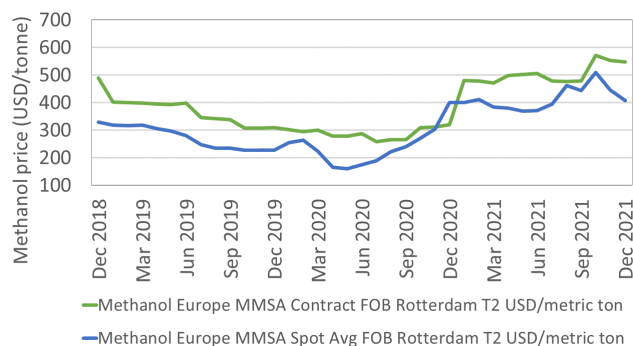
Figure 12. Methanol price evolution (*39*)

assumptions described in the beginning of the present section. The C_{BM} of the different units involved in the process is shown in Table 8.

Units	C_{BM} (€)
Compressors	244,715
Pumps	39,829
Heat exchangers	1,305,455
Reactor	548,937
Flash vessel	28,643
Column vessels	756,045
TOTAL	**2,923,624**

Table 8. C_{BM} of the different units required in the process

Concerning the OPEX estimation, it leads to a total cost of manufacturing without depreciation of 31.43 M€/year. The revenue is calculated based on a selling price of DMC of 1,842 €/tonne and a selling price of EG of 732.3 €/tonne, leading to a value of 47 M€/year. Based on those calculated values the corresponding cumulative cash flow diagram is illustrated in Figure 13. It is also considered that the plant is bought at the beginning of the project (end of year 0) and that the building of the plant takes 1 year.
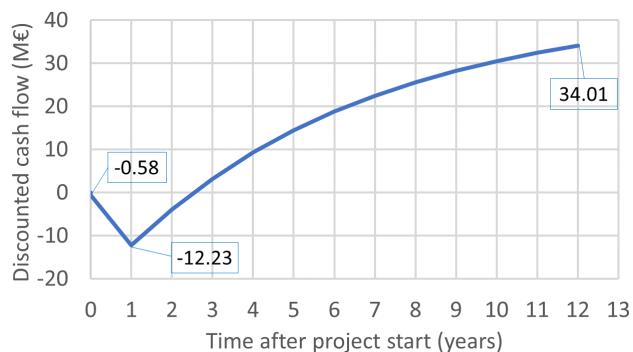
Figure 13. Cumulative cash flow diagram of dimethyl carbonate process using EO as the dehydration agent

The main cost with respect to raw materials concerns ethylene oxide which costs approximately 15.6 M€/year. Then, it can be supposed that its price variation could have a major impact on the profitability of the process. This can be observed by calculating the DMC selling price leading to a zero cumulative cash flow after 12 years as a function of ethylene oxide price i.e. by constructing the break-even curve of the process. It can be seen in Figure 14 that the minimum selling price of DMC observes a quite large variation. Indeed, between a price for ethylene oxide of 1000 €/tonne and 2000 €/tonne, the minimum selling price of DMC increases by 76.9%.
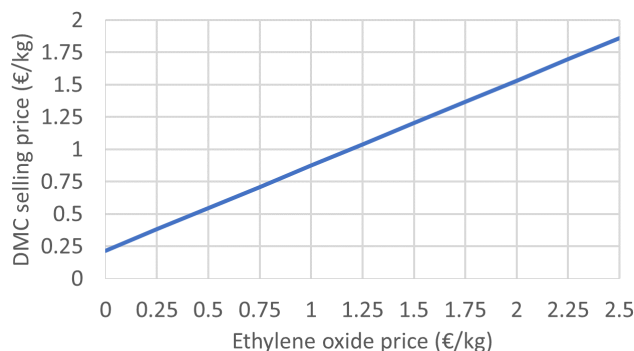

Figure 14. Break-even curve considering ethylene oxide price

Economical comparison of the 2 processes As can be seen through this section, direct synthesis process using 2-CP as dehydration agent seems to lead to higher benefit due to lower capital expenditure and operational expenditure. Moreover, the selling price of DMC is less impacted by the dehydration agent. Even if the direct synthesis process using ethylene oxide contributes to produce ethylene glycol, the return on investment could not counterbalance the higher expenditure as comparison to 2-CP process while the dehydration agent is recycled as long as possible with a minimum of fresh-feed. The CAPEX estimated for the ethylene oxide process is around 40% greater than the one observed for the 2-CP process. This can be explained by the fact that the EO process is operated at an average pressure of 15 bar while the 2-CP process is roughly operated at atmospheric pressure (excluding the reactor which is operated at 30 bar). This difference has first an impact on the number of compressors that must be used and also on the pressure factors that increase the CAPEX for the equipment operated at high pressure. Moreover, the 2-CP process is mainly operated in the liquid phase meaning that to reach the 30 bar required in the reactor, a pump can be used. After a first techno-economic analysis, the 2-CP process seems to be the most interesting option. However, it must be remembered that some uncertainties are raised in previous sections concerning the modelling of the EO process. Those uncertainties may affect this cost estimation especially the OPEX part due to the unknowns in term of cooling and heating utilities requirements.
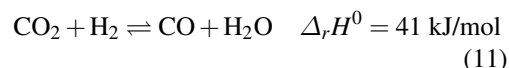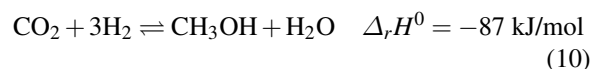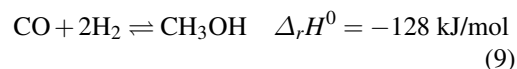
6. Methanol synthesis in a sustainable way

Concept Worlwide methanol is mainly synthesised from natural gas (around 52%), coal (around 35% and mainly in China) and coke oven gas. The first step of methanol synthesis is the formation of syngas from the catalytic reforming of natural gas or the gasification of coal. The synthesis gas obtained from catalytic reforming arrives at a temperature of around 830°C, under a pressure of around 18 bar and with the following composition in volume: H_2 (72%), CO (13%), CO_2 (8%), impurities (water, methane) (*40*). It is then cooled to around 250°C and compressed to a pressure between 50 and 100 bar for the methanol synthesis reaction in an adiabatic fixed bed reactor with $Cu/ZnO/Al_2O_3$ catalyst (*41*).

The main disadvantage of this kind of process is the raw materials (natural gas and coal) which are fossil resources. They are therefore limited in time and do not represent a sustainable source of energy. Another more sustainable way of producing methanol is to use carbon dioxide that comes from the flue gas stream of an industry or carbon dioxide that is present in the air that reacts with hydrogen to produce methanol. There are two issues with these methods: first, they require carbon dioxide capture to produce a concentrated CO_2 gaseous stream and then, they require a sustainable production source of hydrogen and those are two expensive processes.

In order to produce DMC using raw materials which are not coming from fossil resources, the idea is to model a process that can produce methanol without using fossil resources. This is why the two main reagents are carbon dioxide, from a carbon capture unit, and hydrogen produced from water electrolysis. In this section, an Aspen Plus simulation of methanol synthesis is considered including water electrolysis with an alkaline cell to produce hydrogen.

Reactions There are three chemical reactions that occur in the reactor, two exothermic reactions that produce methanol by hydrogenation of CO_2 and CO and the reverse water-gas shift (RWGS) reaction:

$$CO + 2H_2 \rightleftharpoons CH_3OH \quad \Delta_r H^0 = -128 \text{ kJ/mol} \tag{9}$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \quad \Delta_r H^0 = -87 \text{ kJ/mol} \tag{10}$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad \Delta_r H^0 = 41 \text{ kJ/mol} \tag{11}$$

The overall methanol yield is up to 80% when the stream leaving the reactor is recycled (*42*). The $Cu/ZnO/Al_2O_3$ catalyst has been studied and approved for its use for the production of methanol from CO_2 (*43*). It has a porosity of 0.4, a density of 1775 kg_{cat}/m^3 and a particle diameter of 5.5 mm (*41*). This catalyst allows to avoid the methanation reaction which is a competitive reaction for the CO_2 hydrogenation reactions.
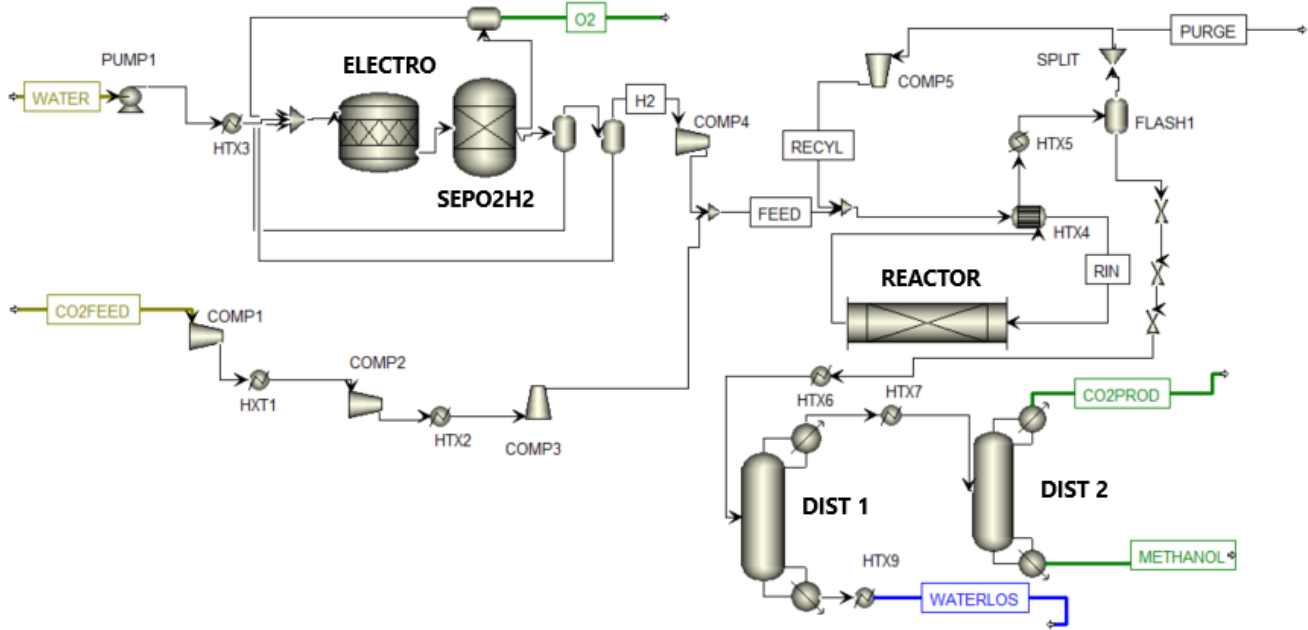
Figure 15. Process flow diagram of the methanol synthesis

However, copper-based catalysts have poor activity for CO_2 hydrogenation at low temperature (T < 500 K) which leads to a low conversion per pass. An increase in temperature facilitates CO_2 activation, but undesirable CO and H_2O are formed through the RWGS reaction which leads to an increase in H_2 consumption per tonne of methanol produced (*44*). New type of catalysts that are active at lower temperature are investigated to overcome the low conversion per pass of CO_2 to methanol but are not used massively in industries yet (*45*).

The kinetic model for methanol synthesis and the reverse water-gas shift reaction on a commercial $Cu/ZnO/Al_2O_3$ catalyst has been studied and validated on a bench scale setup, operating between 180 and 280°C and at pressure up to 100 bar (*46*). The reactor used is an adiabatic fixed bed working at a temperature of 210°C and a pressure of 78 bar. The reactions are highly exothermic which means that the reactor temperature should be low to increase the conversion but not too low so that the catalyst remains active.

Modelling and simulation Based on the process flow diagram designed by Van-Dal and Bouallou (*41*), an equivalent process flow diagram (see Figure 15) is implemented in Aspen Plus in order to produce the quantity of methanol that is necessary to produce 20,000 tonnes of DMC per year. To achieve this annual DMC production, it is required to produce around 14,400 tonnes of methanol per year. The property method based on the Redlich–Kwong–Soave equation of state with modified Huron–Vidal mixing rules is used for the high pressure streams of the reactor cycle streams. A mix property method (liquid phase with NRTL model (activity coefficient model) and gas phases following Redlich-Kwong equation

of state) is used for low pressure streams (less than 10 bar) what concerns the streams of the water electrolysis and the distillation columns. In order to produce the right amount of methanol, the quantity of CO_2 and H_2 must be varied such that the stoichiometric ratio of 3 moles of H_2 for 1 mole of CO_2 is respected.

First of all, the hydrogen coming from the alkaline electrolyzer is compressed to 78 bar to reach the pressure of the reactor. The stream CO_2FEED is coming from a CO_2 capture process at a pressure of 2.5 bar and its molar fraction is supposed to be 1 as the impurities are not considered in this work, as mentioned above. It passes through three compressors with inter-cooling stages to reduce the total energy required to pressurise it to 78 bar. Hydrogen and carbon dioxide are mixed with the recycling stream which is composed of 80 mol-% of H_2, 15 mol-% of CO_2 and 5 mol-% of CO.

This mixed stream COLD is at a temperature of 82°C and is heated up to 210°C by the outlet of the reactor. The conversion per pass of methanol in the reactor is 4.6% considering the kinetics described by Van-Dal and Bouallou (*41*). The reactor has a volume of 2.4 m^3 with a bed voidage of 0.5. The outlet stream of the reactor is cooled to 15°C to enter the flash tank that separates hydrogen from the stream to be recycled as it is a really expensive reactant. The recycled stream is partially purged and the purge stream is burned to produce steam. The stream leaving the flash tank at the bottom contains CO_2, methanol and water. This stream passes through valves to be depressurised to atmospheric pressure. Water is separated in the first column which has been calculated to be

about 20 m tall, 1.14 m in diameter with an HETP of 0.6 m and to be a sieve tray column with a tray efficiency of 0.7. CO_2 is separated in the second column which is calculated to be 12 m tall, 0.28 m in diameter with an HETP of 0.6 m and to be a sieve tray column with a tray efficiency of 0.7. This second column is used to get pure methanol which cannot be obtained with a flash tank separation. To produce 1,800 kg/h of methanol with a purity of 99.8 mol-%, the amount of CO_2 required is 3,250 kg/h and the amount of hydrogen is 441 kg/h.

Knowing the flow rate of hydrogen needed, the modelling of an alkaline cell that produces 441 kg/h of hydrogen is performed in Aspen Plus. The alkaline cell is supposed to lead to a fractional conversion of water of 60% and to work at 73°C and 7 bar (*47*). Using the process model, it is calculated that a 17.5 MW electrolysis cell is necessary to produce 441 kg/h of H_2.

Cost Analysis The cost analysis is done following the bare module estimation method described by Turton et al. (*15*). The CAPEX is calculated for all the different units of the Aspen Plus model. The values to be known are the area for the exchangers, the power for the compressors, the volume for the columns, the reactor and the flash tanks. For the electrolyzer it is assumed that the price for a water alkaline electrolyzer is around 750 €/kW (*48*).

The CAPEX analysis gives a total cost of 14.2 M€. The cost of the electrolyzer is equivalent to 93% of the total CAPEX. The cost for renewable energy is fixed to be equal to 166 €/MWh (taking into account the cost of electricity and the necessity to buy green certificates to ensure consumption of electricity from renewable resources (*49*)) which leads to an overall OPEX of 25.2 M€/year with 93% of the OPEX being the cost of electricity for the electrolyzer. To have an idea about the profitability of this methanol model it is assumed that the lifetime of the equipment is 20 years. Knowing that the amount of methanol produced is 14,400 t/year, the production value over 20 years can be known and the methanol price to reach profitability can then be calculated. This price is 1,799 €/tonne while the current purchase cost of methanol is 423 €/tonne (see Table 5). A process with such a great loss of money does not require an accurate cost evaluation and this simplified cost analysis is sufficient to understand that with a price of electricity as high as 166 €/MWh, this process is unfeasible. The graph illustrated in Figure 16 shows for which price of electricity it would be interesting to look furthermore into detailed cost calculation. It would occur when the cost to produce methanol is equal to the cost to buy methanol which happens for an electricity price equals to 32.6 €/MWh what can be seen in Figure 16.

In the article from Pérez-Fortes et al. that has been published in 2015 (*50*), it is stated that the cost of producing methanol from CO_2 is 2.5 times higher than with the conventional process leading to a break-even point for methanol
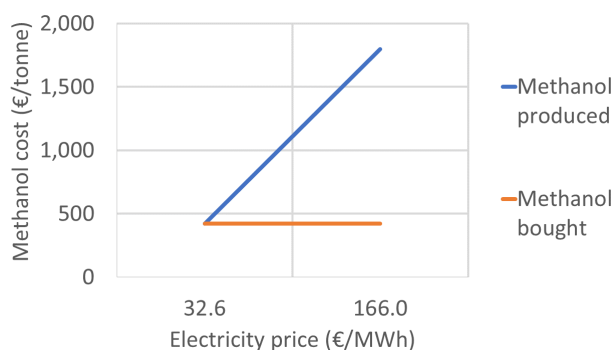

Figure 16. Influence of electricity price on methanol cost

value of 1057.5 €/tonne. Here the methanol price for the break-even point has been calculated to be 1,775 €/tonne which is the consequence in the increase of electricity price that increases the cost of H_2. The cost of H_2 in the mentioned article is 3,090 €/tonne while in this study it is calculated to be 6,800 €/tonne which roughly means that the price of electricity is more than two times higher in this case.

7. Conclusion & Perspectives

Different points can be discussed to conclude this article. It was shown that a sustainable production of dimethyl carbonate using non-fossil-based chemical compounds and renewable energy resources seems to be possible. A first fundamental work was done here with the economical and feasibility study of DMC production process even if a global techo-economic analysis for the whole process combining methanol production and dimethyl carbonate production needs to be done.

Heat-integration of the combined methanol and dimethyl carbonate process could be investigated in order to have a better view of the overall cost but also of the overall energy requirements. In other words, a deeper analysis of the process as a whole should be conducted before giving a real conclusion concerning the viability of this process.

A complete Life Cycle Assessment (LCA) is also something that could be done in order to look at the global warming potential of each process. Indeed, this would maybe lead to other conclusions concerning the sustainability of each process and thus to the choice of the best alternative. A proper LCA could therefore be an additional decision parameter in the choice of the best alternative process.

Even if the direct synthesis of dimethyl carbonate using 2-cyanopyridine as dehydration agent seems to be more interesting than the other process using ethylene oxide, some key points like the reactor section for the process using EO need to be further explored.

As a conclusion, this entire work can serve as a basis for

further research into the reuse of CO_2 as raw material but also for building an integrating process combining different production processes.

8. Acknowledgment

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