

# Dimethyl ether, A review of production processes and a modeling of the indirect route

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## Abstract

Dimethyl ether (DME) can be considered as a potential substitute to traditional fuels and, thus, receives a great industrial interest. This paper exposes the two main DME production processes: the direct route, where DME is directly produced from syngas and the indirect route which involves the upstream methanol production. This paper also presents a modeled DME production plant (through indirect route) of a capacity of 116 kton/yr. This simulation was performed in Aspen Plus software using the UNIQUAC thermodynamic model. DME is produced through the dehydration of methanol under  $\gamma\text{-Al}_2\text{O}_3$  catalyst in a adiabatic fixed-bed reactor. The proposed model allows to reach a DME yield and purity of respectively 93.1 % and 99.6 mol %. A cost analysis was performed. OPEX and CAPEX are evaluated to 66,987 k\$/yr and 3,780 k\$. The economical balance shows that benefices of the production plant widely depend on the price of the methanol feed stream. A life cycle analysis of the process shows a good agreement between the modeled process and Ecoinvent data base.

A literature review was also performed to investigate other ways to produce DME. Improvements can be achieved within the indirect route. The literature review shows that using silica embedded  $\gamma\text{-Al}_2\text{O}_3$  or zeolite catalyst can enhance the DME conversion up to 86% and 94% respectively. The process integration of the indirect DME production was also considered and more particularly the use of a reactive dividing-wall column. Direct DME production from syngas is also presented as well as a European associated project (FLEDGED) which targets to produce DME fuel from biomass.

## Keywords

DME — Dimethylether — Methanol Dehydratation — Aspen Modeling — Process Intensification — FLEDGED

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## Introduction

Dimethyl ether, also called metoxymethane, is an organic gas in standard condition that can be obtained through several synthesis pathways. Dimethyl ether, usually abbreviated to "DME", has several applications but has attracted industry attention in recent years as a potential substitute for conventional fuels.

In this context, it is interesting to study synthesis processes that could be competitive on the DME market. Therefore, a DME production process using a modified indirect synthesis pathway has been investigated. This is a process whose raw material would be a mixture of 88 mol-% methanol, 11 mol-% ethanol and 1 mol-% water, in order to have a less expensive feedstock. This mixture must therefore be separated before entering the reaction zone. However, a complete methanol/ethanol separation is not possible. Therefore, reactions due to ethanol and its by-products have to be taken into account. In this paper, the process study will not consider this first separation, including for cost calculations and life cycle analysis. It will be assumed that the required methanol purity can be achieved through a distillation step.

Before presenting the modelling steps of this new process, a presentation of the DME market, its main applications, a small point on toxicity as well as a presentation of the two main synthesis routes are carried out.

Afterwards, the design results of the new process studied will be compared with those that can be found in the literature. In addition, alternatives to further improve the process will be explored.

Finally, the second synthesis path and a special case of this type of synthesis will be discussed.

## 1. Dimethylether

### 1.1 Market

#### 1.1.1 Producing and consuming countries

DME market is divided into five key regions: Asia, Europe, America, Latin America (LATAM) and Middle East and Africa (MEA) as seen in FIGURE 1.

Asia dominates the market in particularly thanks to China which is the main producer and consumer in the world with more than 85% of the shares. This is mainly due to the use as domestic fuel and the constantly growing automobile industry [2] in this region. Moreover, others countries such as Japan, India and South Korea are expected to be the fastest growing countries. This growth is due to regulatory conditions in these countries which promote the use of DME.

Europe has a significant smaller part in the market where the key contributors are Germany, U.K. and Italy, with a major utilization in the automobile industry [3]. It is followed by America where the market is hold by U.S. Finally, Latin America and MEA are expected to grow with the utilization as transportation fuel.

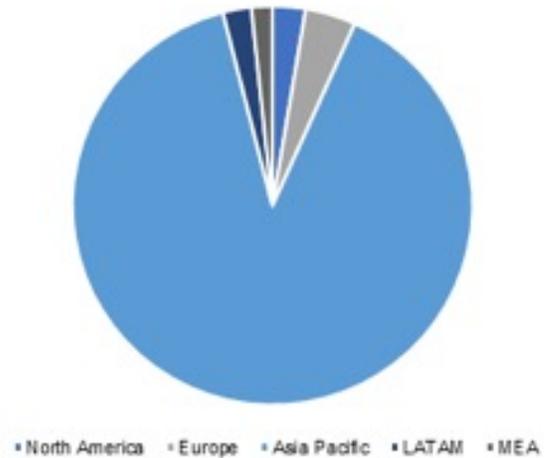


Figure 1. Distribution of the market of DME in the world [1]

#### 1.1.2 Producing companies

The major producing companies in the world for the DME market are listed below (among others) [3]:

- Azko Nobel N.V (Netherlands)
- China Energy Limited (China)
- The Chemours Company (U.S.)
- Mitsubishi Corporation (Japan)
- Royal Dutch Shell plc (Netherlands)
- Ferrostaal GmbH (Germany)
- Grillo Werke AG (Germany)
- Jiutai Energy Group (China)
- Oberon Fuels (U.S.)
- Zagros Petrochemical Company (Iran)

#### 1.1.3 Price

In March 2020, the price in China for DME (99% or above) was approximately 2,790.000 RMB/ton which corresponds to 356.07 €/ton [4].

### 1.2 Main Uses

There is a few number of applications for DME such as aerosol, propellant, chemical feedstock, transportation fuel or refrigerant.

In the last few years, Liquefied Petroleum Gas (LPG) blending emerges as the major application [2]. Indeed, scarcity of LPG poses a threat. Moreover, its low toxicity, high cetane number and good flammable properties make DME a good substitute to LPG. Also, DME can be produced from different raw materials such as methanol, biomass and syngas which support an increase of the production and the market. In China, LPG is mixed with DME and is used for cooking or other applications in household and industry [5].

Dimethyl ether can also be used as green refrigerant. Indeed, its global warming potential is much lower than those of chlorofluorocarbons and it has zero ozone depletion potential [6, 7].

Moreover, another major application of DME is its use as feedstock for the synthesis of other products (e.g.: dimethyl sulfate, methyl acetate, light olefins) [6]. DME can also be converted into acetic acid through carbonylation thanks to Monsanto process.

### 1.3 Toxicity

The utilization of DME is environment-friendly since its combustion is greener compared to traditional fuels (less NO<sub>x</sub>, CO and HC emissions) [6] and its global warming potentials are low compared to chlorofluorocarbons which are traditionally coolants (now forbidden) [8]. DME is known to be a stable chemical compound, relatively non-toxic and easily stored. However, high exposition can lead to headaches, dizziness, lightheadedness, and even loss of consciousness [9]. Also, it is highly flammable and can cause fires.

## 2. Synthesis methods

There are two main ways to produce DME: the first, which is the historical one, is the indirect route where DME is obtained by the dehydration of methanol and the second, which is more efficient, is the direct route where DME is produced directly from syngas in a single stage thanks to bi-functional catalysts [6]. For both routes, the feedstock can be coal, natural gas, oil or biomass. Indirect and direct processes are schematized in FIGURE 2.

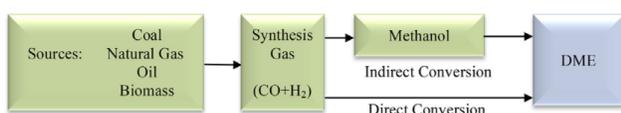
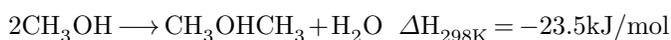


Figure 2. Dimethyl ether production diagram[6]

These two conventional DME production processes will be briefly presented in the following sections.

### 2.1 Indirect synthesis method

Historically, DME has been produced from syngas in a two-step process: methanol is first produced and purified and then converted to DME in a second reactor. The conversion of methanol to DME occurs through a dehydration as seen in the following equation.



Theoretically, as the dehydration of methanol to DME is an exothermic reaction, the DME production is favored at low temperature. The catalysts used to conduct this reaction are of solid-acid type.

### 2.2 Direct synthesis method

More recently, a direct synthesis method has been developed. This route allows the synthesis of DME directly from syngas: the methanol production and dehydration occurs in a single reactor and using bi-functional catalysts. The reactions involved in this process as well as the flowsheet of the DME production plant will be presented in the section “Direct synthesis method”.

Compared to the indirect route, the direct method leads to much lower DME production costs [6].

## 3. Modeling the indirect production process

### 3.1 Goal of the integrated project

In this section, the production of DME through a slightly modified indirect process is modeled. The flowsheet of the basic indirect process is shown in FIGURE 3. The idea in this work is to feed the process with a methanol/ethanol mixture instead of pure methanol. Indeed, this reduces the cost of the feedstock. The process input stream must therefore undergo a first distillation to separate methanol and ethanol. The ethanol is then stored for later use to produce diethyl ether. It should be noted however that the following study is limited to the DME production process after the separation of methanol and ethanol.

The different phases of this process design as well as the results obtained are presented in this section of the article.

### 3.2 Thermodynamic

A key part of the modeling of a chemical process is the estimation of the thermodynamic properties. The selection of the thermodynamic model used is critical; if chosen badly, it will eventually lead to huge mistakes and dramatic consequences.

Six different properties were studied: the density  $\rho$ , the heat capacity  $C_p$ , the entropy  $S$ , the enthalpy  $H$ , Gibbs energy  $G$  and the vapor pressure  $P^v$ . They were studied with the conditions of three key locations: the feed, the inlet of the reactor and the outlet of the reactor.

The properties were first studied for pure components, then for ideal mixtures and finally for real mixtures using several thermodynamic models such as SRK, PSRK, PR, VTPR, ideal, NRTL and UNIQUAC.

The results obtained with those models were compared to experimental data available in NIST and Dechema, but due to their lack of data for the desired set of conditions, the results were compared to that of CoolProp which is a software using the best-fitting thermodynamic model with regards to the components and the conditions.

VTPR turned out to be the best model for pure components properties calculation and UNIQUAC the most suitable one for the calculation of real mixtures properties: UNIQUAC has therefore been used all along the project to evaluate thermodynamic properties. Figure 4 is a recall showing that UNIQUAC model values are the closest one to CoolProp values, justifying its choice.

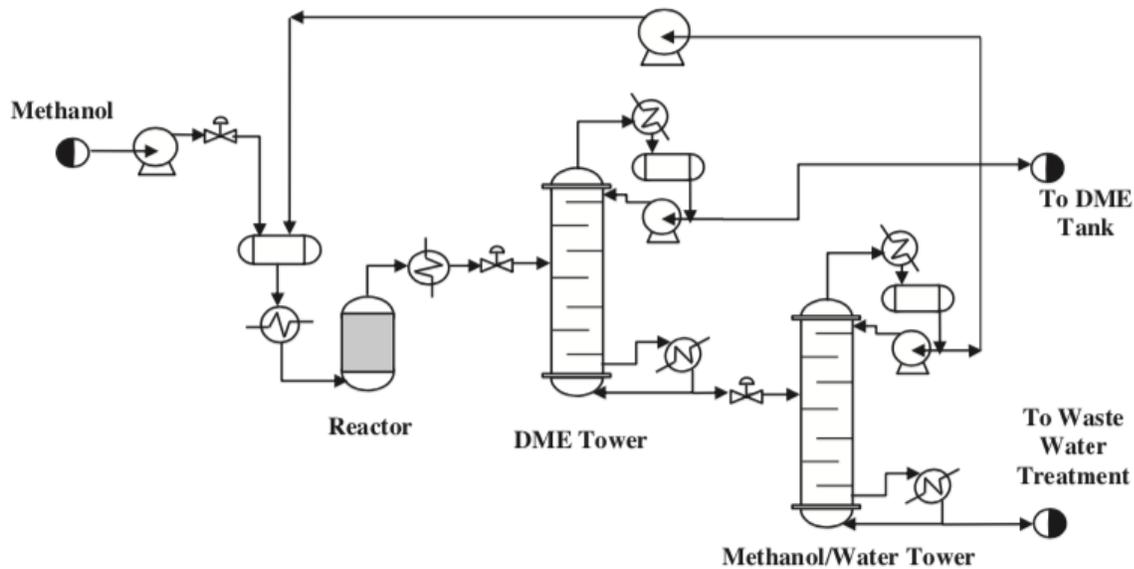


Figure 3. Flowsheet of the indirect process [6]

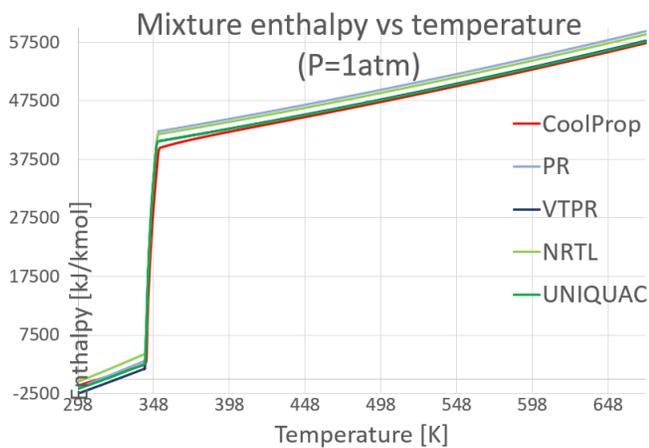


Figure 4

### 3.3 Reactor

The reactor is the main part of the process and had to be designed properly. First, the behavior of the reactor has been modeled in Matlab. Two models have been implemented. One for an isothermal reactor and another one for an adiabatic reactor. The modeling has been made thanks to the CRE algorithm which describes the mass balance equations for all reactants and products as a function of reactor volume. For the adiabatic reactor it describes the heat balance too. This algorithm contains also the kinetic laws of the reaction taking place in the reactor.

These models give the conversion as a function of the reactor volume as main result. It allows to size approximately the reactor before the implementation in Aspen. As previously said, Matlab is used here to perform a first study of the reactors and to become familiar with its behavior. Because of that, to begin this first study, some parameters such as inlet temperature and inlet composition are fixed. For the isother-

mal reactor, the inlet temperature is equal to 350°C. For the adiabatic one, the inlet temperature is 250°C. By looking at catalyst properties and behavior, these temperatures are not the most interesting to obtain a volume as small as possible for a given production. A sensibility analysis is then performed to determine the most interesting temperature. This sensibility, as well as sensibility analysis which study pressure and composition, is detailed in the following paragraph. However, for this part of the project, pressure is fixed at 15 bar and inlet flux is composed of 98% of methanol, 1% of ethanol and 1% of water. For the isothermal reactor as for the adiabatic reactor a conversion of 0.7 has been fixed and it leads to a reactors volume of 65.02 m<sup>3</sup> and 101.4 m<sup>3</sup> respectively as it can be seen in FIGURE 5.

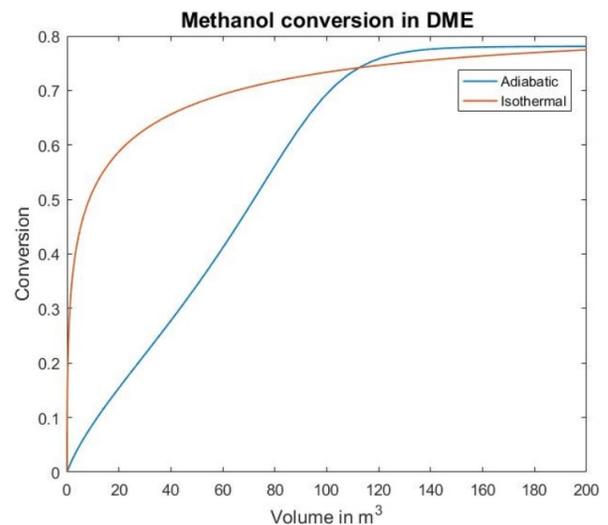


Figure 5. Conversion as a function of the volume for both reactor in Matlab

The next step is the modelling of both reactors in Aspen. After entering kinetic laws, sensitivity analyses are conducted in Aspen and Matlab to find the optimal operating conditions. The pressure, the temperature and the composition are the key parameters studied. The effect of the variation of these parameters on the reactor is studied through the methanol conversion and the corresponding reactor volume.

The first analysis determined that the optimum pressure is 15 bar for both reactors. Regarding the impact of the other parameters varied, a compromise had to be made between having a better conversion and having a smaller reactor volume. For the isothermal reactor it was finally chosen to have an inlet temperature of 395°C, a methanol:ethanol ratio of 95.72:0.59 (in mole percentage) and a conversion of 66.39%. Those values led to a reactor volume of 4.82 m<sup>3</sup>. For the adiabatic reactor, the inlet temperature is 296.85°C, a MeOH:EOH ratio of 96.86:0.49 and 66.39% conversion were found. The volume is then 14.58 m<sup>3</sup>.

### 3.4 Separation

In order to achieve the required purity of DME, the separation units have to be designed properly. As can be seen on the flowsheet in FIGURE 3, two separation columns are needed. In both columns, multi-component mixtures have to be distilled. The assumption of binary mixture has been made in order to be able to design the units; therefore, two components were separated in each column thanks to the difference between their boiling points.

The first column D-201 was used to obtain DME with a purity of 99.5% from the binary mixture DME-methanol and the second one to recycle much methanol as possible from the binary mixture methanol-water.

After that, a first approximation of the number of theoretical stages was obtained thanks to the short-cut method. This gives an idea of the height of the columns. However, this method is based on several assumptions that are not always verified. A McCabe Thiele diagram was therefore drawn for each column to obtain more precise values for the number of theoretical stages. Note that this number is always given as a function of the reflux ratio. The height and area have been calculated in Excel and Matlab. Afterwards, the internals ensuring an effective mass transfer between the liquid and gas phases flowing in counter-current in the column have been studied. Based on the total costs (investment and operating costs), the optimal reflux ratio and the type of internals were chosen. It was found for both columns that a packing of ceramic rings is the most interesting choice.

The results obtained via Excel and Matlab have been validated in Aspen. To improve the process, some sensitivity analysis were performed, namely the variation of the reflux ratio, reboiler and condenser duties with the number of theoretical stages *N* using the DSTWU model. Those analyses lead to *N*=12 and *N*=20 for D-201 and D-202 respectively. The reboiler duties were respectively 2593 kW for D-201 and 6136 kW for D-202. For the simulation of the entire process,

the Radfrac model has been used since it offers more options and its characteristics are closest to that of real columns.

### 3.5 Catalysis

When designing a reactor, a major step is the choice of the catalyst. For this process, Al<sub>2</sub>O<sub>3</sub> has been used. The kinetics used made the assumption of a chemical regime inside the catalyst pellet. In order to validate this assumption, the catalyst has been studied. First, since the reactor is not isothermal, it was necessary to check that the pellet could be considered as isothermal. Then external and internal diffusion limitations have been studied.

To validate the isothermal assumption, we calculated the ratio between two adimensional numbers (the thermal and mass transfer Biot number) at the inlet and at the outlet of the reactor. Because this ratio is sufficiently high, the temperature of the pellet surface is considered as the same as the film one. Afterwards the temperature profile inside the pellet was studied. Weisz modulus has been used to determine the maximum temperature at the center of the pellet. This temperature was not so far from the surface temperature and thus the catalyst pellet can be considered as isothermal.

Then, external diffusion limitations were studied. In order to determine if external diffusion issues exist, the mass transport resistance fraction has been calculated at the outlet and at the inlet of the reactor. The conclusion is that there are no external diffusion issue because the value of the mass transport resistance fraction is sufficiently low. Thus, the concentration profile in the film can be considered constant.

Finally, the internal diffusion has been studied. Weisz modulus has been calculated at the inlet and at the outlet of the reactor and because its value is  $\ll 1$  the pellet can be considered to be in chemical regime. The maximum diameter of the pellet which allows to stay in chemical regime is 3.34 cm.

As a conclusion, the assumption used by the kinetics of the reactor has been validated. We were also able to derive the design of the pellet that will be used: sphere of 3 cm diameter.

### 3.6 Integration

Once all the process sub-units have been separately and correctly modeled and optimized in Aspen, the next step is the integration of the whole process. This was achieved by connecting those units together; the goal being the obtaining of a process where the entire block works and gives consistent results.

Some design specifications were implemented in order to fix three parameters: a conversion in the reactor of 66.39% (this value corresponds to 80% of the equilibrium conversion at 395 °C), a DME production flowrate of 312 kmol/hr (this leads to an annual production of 100,000 tons) and a DME purity of 99.5%. Those parameters being fixed, the amount of process's feed as well as the distillate vapor fraction that leaves the top of D-201 were varied simultaneously in order to reach the production requirements. Finally, the flowsheet of the whole process can be seen in FIGURE 6.

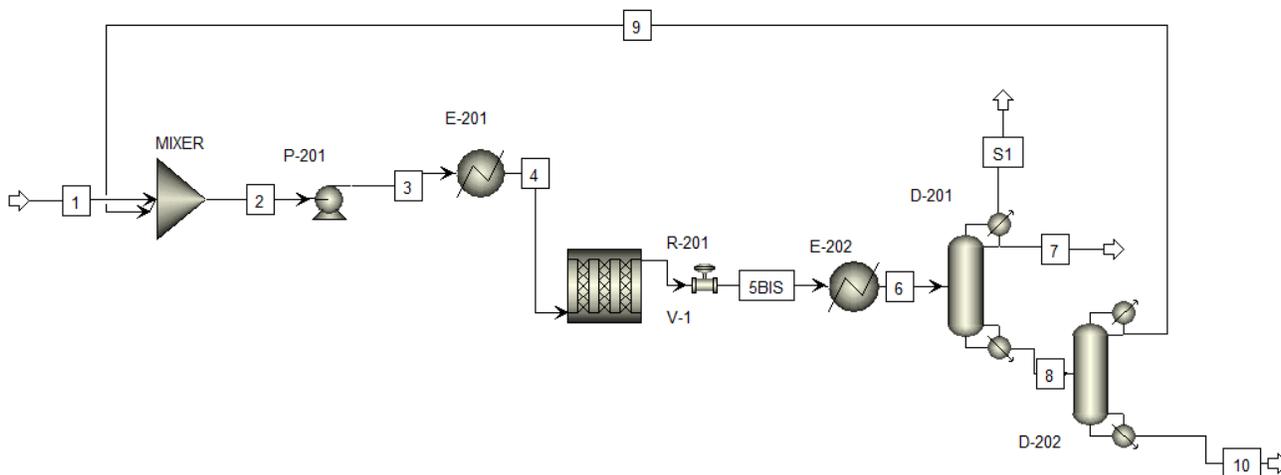


Figure 6. Flowsheet of the integrated process

### 3.7 Optimization

After ensuring that the process is working properly, the next step is its optimization. After noticing non-negligible losses of DME in stream S1 (ethylene removal stream above D-201) and methanol in stream 10 (water removal stream below D-202), the main goal of this optimization part was to minimize them.

To reduce DME losses, ethylene was firstly defined as an Henry's compound and secondly the impact of D-201 reboiler duty on the amount of DME lost was studied as shown in FIGURE 7. Working with a reboiler duty of 2408 kW for the adiabatic reactor and defining ethylene as an Henry's compound reduces DME flowrate in stream S1 from 25.53 kmol/hr to 9.29 kmol/hr.

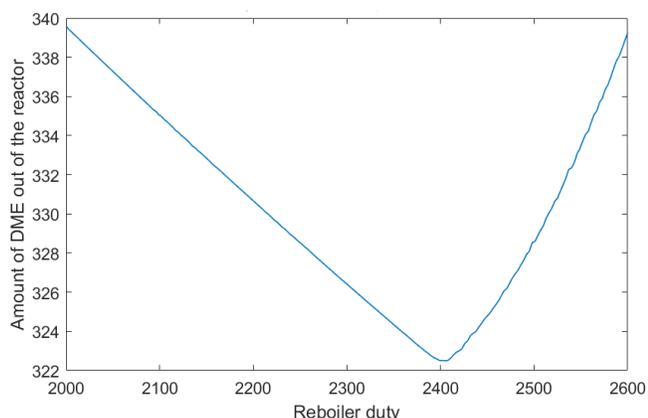


Figure 7. Amount of DME to produce in R-201 to reach the desired production and purity

To reduce methanol losses, the influence of D-202 reboiler duty on methanol flowrate has been studied as shown in FIGURE 8. It follows that at 6136 kW, the methanol loss is 86.76 kmol/hr compared to 7.28 kmol/hr at 8100 kW.

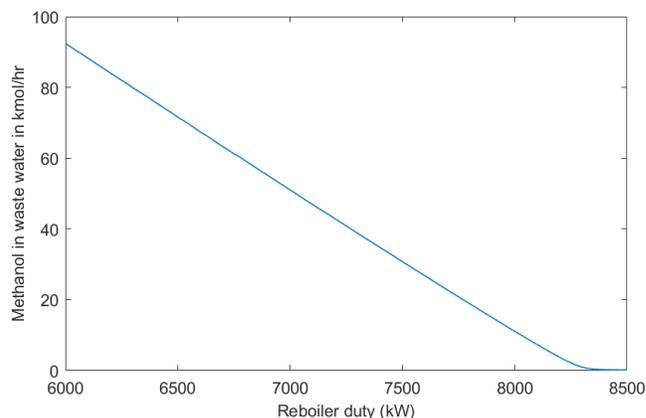


Figure 8. Amount of Methanol lost in the waste water stream

### 3.8 Choice of the reactor

Since the beginning of this article, computations and studies have been done for the two reactors considered. After the integration, results obtained are very close in both cases from a mass balance point of view. However, as detailed in the "Reactor" section, the inlet temperature of both reactors is not the same. The difference leads to a difference of energy needed to warm the reactor's inlet flux. To choose the reactor that will be used, a small cost analysis of reactors has been done. The construction costs of both reactors are computed with the *Turton* method [10]. The electricity price is the average electricity price in the US: 0.1319 \$/kWh, the steam price given in the *Turton* is 0.063 \$/kWh. Prices computation can be seen in TABLE 1. By using electricity as well as steam, the number of hours needed to compensate the construction cost difference is very small. Knowing that the plant should operate about 8,000 hours each years, even if 90% of the energy needed to warm the inlet flow is found in the process during the heat integration, the adiabatic reactor will become more interesting after a little bit more than one year. For a plant that should operate for at least 10 years, the adiabatic

R-201	Construction price (\$)	Electricity price (\$/hr)	Steam price (\$/hr)
Isothermal	73 242	2092.46	1010.85
Adiabatic	211 778	1804.12	871.56
Time needed to compensate construction cost difference		480 hours	995 hours

**Table 1.** Cost analysis for both reactors with electricity and steam as energy source

reactor seems to be the best choice.

Moreover, the conclusion is confirmed by looking at some similar plants in literature that, for the majority of them, also use an adiabatic reactor.

### 3.9 Heat integration

In order to optimize the energy efficiency of the process, a heat integration is performed. It allows to design the heat exchanges between the process streams as well as the utilities needed to run the process. Initially the hot and cold streams of the process are identified. By definition a cold stream is a flux that needs to be heated up and a hot stream is a flux that needs to be cooled. Based on the stream data, the Pinch Analysis method can be carried out. This method provides the load of the hot utilities, called the minimum energy requirement, as well as the load of the cold utilities required for the process. Another important value obtained with the Pinch Analysis method is the pinch point temperature. The pinch point is a separation between the heat source where no heating is required and the heat sink where no cooling is required. In other words, it is a separation between two thermodynamically different regions. Therefore, in order to achieve the minimum energy required with the heat exchanger network, heat must not be transferred through the pinch. Then, the results of the Pinch Analysis method can be used to build the heat exchangers network. It indicates the position of the heat exchangers as well as the different utilities used. In this case, steam is chosen as hot utility because it is more economical than electricity. Process water is used as cold utility since it has several advantages. Indeed, it is conceivable to resell it once heated to use it in the heating of buildings for instance. Furthermore, its price is quite low. The heat exchanger network is modeled in *Aspen*. As a result, the final flowsheet of the process is represented in FIGURE 9. The stream tables and a major equipment summary of this final process are given in APPENDIX 1 and 2, respectively.

### 3.10 Costs

Once the integration and heat integration have been done, the costs of the process can be computed. The computation of costs is divided in two sections: CAPEX which are the construction costs and OPEX which are operating costs.

#### 3.10.1 CAPEX

The computation of CAPEX is done thanks to the *Turton* method [10]. The method is composed of three steps. The

first one is the computation of the costs of the unit without taking pressure and material into account. This step is only based on type and size of the unit.

The second step includes the effect of pressure and material in the cost computation. In this case, all products that are in our process have an excellent or at least a good reaction with carbon steel [11]. This material will be chosen because of its low price.

The last step is the increase of the price of the unit in agreement with the increase of chemical engineering plant cost index (CEPCI). This index can correct the prices computed thanks to the *Turton* method. It adapts them to the actual situation.

Bloc	CAPEX from <i>Turton</i> (\$)	CAPEX from assignment (\$)
Pump1	20 461	10 000
Pump2	27 427	10 000
U1	198 166	343 994
U2	92 499	58 631
U3	236 378	382 284
U4	130 625	423 113
U5	152 985	161 015
HX1	15 683	50 000
HX2	16 713	50 000
HX3	17 790	50 000
R-201	226 814	1 000 000
D-201	149 190	500 000
D-201 COND	198 087	Ungiven
D-201 REB	320 900	160 455
D-202	132 553	500 000
D-202 REB	928 187	423 447

**Table 2.** Results of the CAPEX computation with *Turton* method and assignment method

TABLE 2 contains all the CAPEX costs for each unit computed with *Turton* method and with the method given in the assignment. It can be seen that the price of the reactor is a little bit higher than the price computed in TABLE 1. This is due to the fact that the flowsheet has been modified during heat integration. This modification leads to small modifications in flux of the process. These modifications lead to a small increase of reactor length to keep the desired conversion. This small increase is responsible for the cost increasing.

Main differences between the two costs evaluated are the reactor and columns costs. Indeed, prices computed for these units with the *Turton* seem very low. However, the *Turton's* prices will be used for the rest of this analysis. One should note that a verification of these prices with another computation could help to obtain a more accurate value of these prices.

These prices are those for each unit separately, to obtain the overall price with installation prices and unexpected costs,

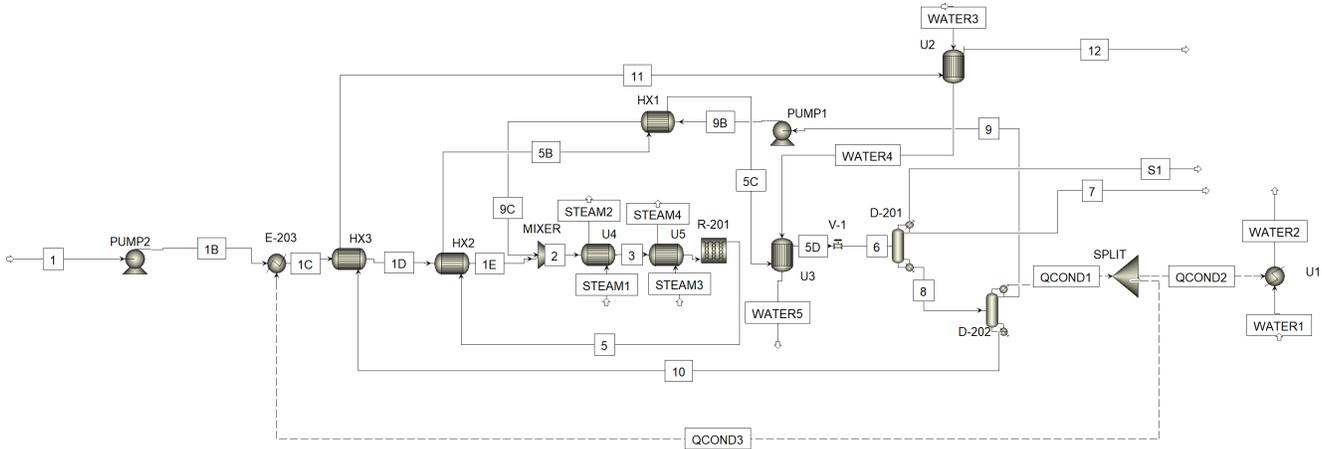


Figure 9. Final flowsheet of the process

the following equation can be used:

$$FCI = 1.18 * \sum C_{Unit} + 0.5 * \sum C_{0Unit} \quad (1)$$

where FCI are the CAPEX of the plant,  $C_{Unit}$  the prices of each unit in TABLE 2 and  $C_{0Unit}$  the prices of each unit after the first step of the *Turton* method.

Finally, the value obtained is:

$$FCI = 3,780,334 \$ \quad (2)$$

### 3.10.2 OPEX

The OPEX is composed of different types of costs. In this case, the main costs are the cost of utilities and raw materials. Utility costs are composed of steam and water that are used in heat exchangers, electricity that provides energy to pumps and catalyst that is used in the reactor.

As it can be seen in FIGURE 9, steam is needed in U4, U5 and in the reboilers of the columns, refrigerated water is needed for the condenser of column D-201. Finally, process water is used in U1, U2 and U3. This water is heated and can be used to provide heat in a building next to the plant for instance.

Prices of water and steam used are in the *Turton* [10]. The electricity price is 0.1319 \$/kWh. Finally, the catalyst price is approximated at 3\$/kg thanks to [12] and [13]. This price should be refined, but it can be seen in TABLES 3 and 4 that the price of the catalyst is negligible compared to raw materials price. It will then not influence as much the conclusions of this cost study, even with a higher catalyst price. Another parameter to take into account is the number of times the catalyst has to be replaced each year. This value is found thanks to the following formula:

$$\ln \frac{f_m}{1-f_m} = -\frac{4840}{T} - (3 * 10^{-5}) * (T - 520) * t + 8.9370 \quad (3)$$

where  $T$  is the temperature in Kelvin,  $f_m$  the fractional conversion and  $t$  the time in days. Once again, this formula is an approximation and the result should be refined. The formula

leads to a replacement of the catalyst twice a year. Knowing that, the total amount of catalysts needed each year is 11.55 tons. The results for utilities are in TABLE 3.

Bloc	Annual cost (\$/yr)
Steam	9 251 706
Cooling water	1 765 782
Process water	77 249
Electricity	29 082
Catalyst	34 632

Table 3. Cost of utilities

All these costs are utility costs of the process.

On the other hand, other costs such as waste water treatment, buying of raw materials and cost associated with employee salaries have to be taken into account.

Wastewater treatment cost is 56\$ for 1000 tons [10]. Actual price of methanol in the US is 313\$/ton [14]. Lastly, employees cost is computed thanks to the following formula:

$$N_{OL} = 4.5 * (6.29 + 31.7 * (P)^2 + 0.23N_{NP})^{0.5} \quad (4)$$

where  $P$  and  $N_{NP}$  are respectively the number of particular and non particular processing steps.

The number of employees needed can be computed. In this case, 14 people are needed. Knowing that the average annual payment for a chemical employee is 61 570 \$/year, cost of workers can be computed. All these costs are in TABLE 4.

OPEX	Annual cost (\$/yr)
Utilities	11 158 451
Wastewater treatment	4 225
Raw material	54 962 800
Employee's cost	861 980

Table 4. Results of OPEX costs

Thanks to this value and to the following formula [15],

the total manufacturing cost can be computed.

$$COM = \frac{C_{RM} + C_{WT} + C_{UT} + D}{0.810} + \frac{C_{OL}}{0.366} + \frac{FCI}{5.548} \quad (5)$$

The last missing value is the Depreciation. This value can be computed following this formula:

$$D = \frac{FCI * (1 - (1 - 0.2)^N)}{N} \quad (6)$$

where  $N$  is the operating time of the plant in years. With  $N = 10$ ,  $D = 337,442$  \$/year. With this value, the value of the total manufacturing cost can be computed.

$$COM = 85,089,338 \text{ $/yr} \quad (7)$$

### 3.10.3 Economical balance and Cash flow

Now that the costs are known, the economical balance can be realized. The price of the raw materials and the final product need to be known.

Two cases have been explored: buying methanol on the American market, or producing from natural gas. In both cases, the plant lays in the USA, in the state of New York or the state of Georgia and near of a river to have access to water (for the thermal circuit).

In the case of buying methanol. The price of the methanol depends on the price of the oil and follows it trends. It went down until 2017, then rose but the recent worldwide events decreased the price down to USD 313/MT [14]. As the price of the methanol is changing the price of the DME should be adapted depending on the price of the raw material.

In the case of producing the methanol from oil, considering a plant working with the *Hinol* process, the cost of the methanol is USD 247/MT [16]. This price considers the capital cost which is USD 792 MM for plant with a capacity of 1085 MM Gal/yr. In this case, the price of methanol would depend on the price of natural gas which is not fixed leading to adaptation of the selling price of the DME.

A cash flow is realized to see the evolution of the economics of the company. The profit is:

$$N_p = (R - COM) \times (1 - t) + Depreciation \quad (8)$$

The cash flow (CF) is then the flow of money of the company and now consider the FCI. As explained in the previous report, the discounted cash flow (DCF), based on the cash flow, is considered to take into account the effective discount rate ( $i_{eff}$ ) itself considering the inflation ( $f$ ) to adapt the discount rate ( $i$ ).

$$DCF = \frac{CF}{(1 + i_{eff})^k} \quad \text{with} \quad i_{eff} = \frac{1 + i}{1 - f} - 1 \quad (9)$$

The goal of a company is to propose a good product meeting standards set by the buyer but also to make benefits to attract

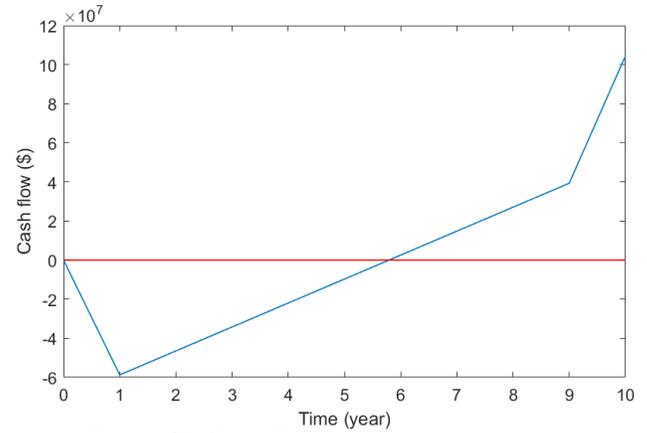


Figure 10. Cash Flow of the company

new investors and invest in research. In this idea, a profit margin has been chosen. The full refund of the investment should be achieved after around ten years. All these concepts in mind allow us to determine the minimal selling price of DME. FIGURE 11 shows the selling price of DME depending on the cost of methanol. Above the red line, the profit is above 10%. Under the red line, the profit is under 10%.

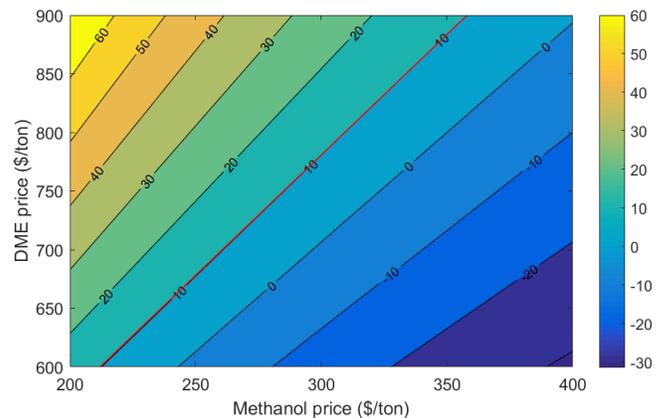


Figure 11. Percentage of benefits obtained each year as a function of methanol and DME prices

The *Turton* gives a price for DME of USD 841/MT [10]. FIGURE 11 shows that the price is beneficial for the two prices of methanol. Then, to avoid a massive additional investment and the build of whole additional plant, the decision to buy methanol is made. Considering these values, 14.4% of profit margin rate (equals USD 12.258 MM per year) is made. This profit margin can be used to pay dividends to the investors, invest in other plants or invest in R&D or quality control.

Afterwards, a proper DCF can be realized. The DCF presented in FIGURE 12 shows that during the first year the plants does not produce yet but is built and the first raw materials for one year are bought. After six years, the company is in positive. From that point, the company is making money and the economical balance is positive. Then each year the

company earns more and more money. The last year, no raw materials are necessary because they have bought the previous year leading to a pic of profit.

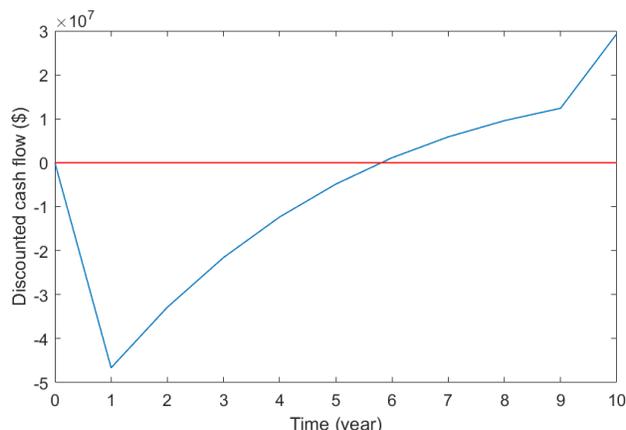


Figure 12. Discounted Cash Flow of the company

### 3.10.4 Discussion

The study of costs and the economical side of the plant shows that many things need to be considered. The market of chemicals based on petroleum product depends on the price of the oil/gas. For now, May 2020, the price of the methanol is very low due to the actual crisis and its impact on price of the oil. In this report the difference between a plant viable or not is quite thin. To have a plant viable in the long term, price of the DME should be adapted regularly.

## 3.11 LCA

The goal of this study is to perform a life cycle analysis of DME produced in USA in order to identify its potential environmental impacts from extraction to final disposal. Since no information was given about the packaging/distribution step, only the raw materials extraction, DME production and manufacturing have been taken into account.

### 3.11.1 Presentation of the situation

Before analyzing the results, a brief presentation of the system is made. The process is located in USA, therefore all the values are calculated based on the fact that the raw materials extraction and the DME production are carried out there. The raw material of the process is methanol produced from natural gas and transported by pipelines. As presented in the “Costs” section, methanol is produced on the production site of DME. All process inputs are resumed in TABLE 5.

The energy implemented to the system has two origins: electricity and water steam. The steam is produced by heating water with a reboiler and the electricity has a tension of 400V. TABLE 6 gives the total input of electricity, heat water and cooling water needed for the process.

Outputs are resumed by flow 7 (water) and 12 (DME) as can be seen in FIGURE 9. TABLE 7 shows the values of the process outputs.

Input	Value
Methanol[t/year]	172800.94
Cold water [kmol/h]	4800
Vapor [kmol/h]	1165.68
Pump(P-201) [kWh]	67088
Pump(P-202) [kWh]	153408
Condenser of D-201 [kWh]	-62693520
Reboiler of D-201 [kWh]	18960000
Reboiler of D202 [kWh]	64800000
U1 [kWh]	50058560
U2 [kWh]	5271520
U3 [kWh]	57563680
U4 [kWh]	65476240
U5 [kWh]	19640640

Table 5. Material and energy inputs of the process

Total Cold energy [GWh]	-175.59
Total electricity energy [GWh]	0.22
Total heat energy [GWh]	168,88

Table 6. Total energy transfer in the process

DME [t/year]	116089.22
Water [t/year]	49397.90

Table 7. Material output of the process

### 3.11.2 Results and discussion

The study has been realized with the software Simapro using the method *CML-IA baseline V3.05*. The data base used is Ecoinvent. FIGURE 13 shows all the impact categories for the production of 1kg of DME. To normalized them, each of those impacts has been divided by the corresponding impact generated by an average European resident per year. As can be seen in FIGURE 13, the four main impact categories are marine aquatic ecotoxicity, abiotic depletion, fresh water aquatic ecotoxicity and global warming. It can also be observed that there are three contributions for each impact: methanol production, electricity and heat consumption among which the methanol production is by far the main in almost all the impact categories. This is confirmed in FIGURE 14. That means that the main environmental impact in DME production is methanol production due to the raw material extraction.

A comparison between the LCA project results and the Ecoinvent data base is presented in FIGURE 15.

As can be observed, there is no big difference between the impacts intensity in both cases apart for the photochemical oxidation where the project’s value is quite the half of that of the database. Those differences may be due to the use of another version of CML or simply another method, like Recipe 2008.

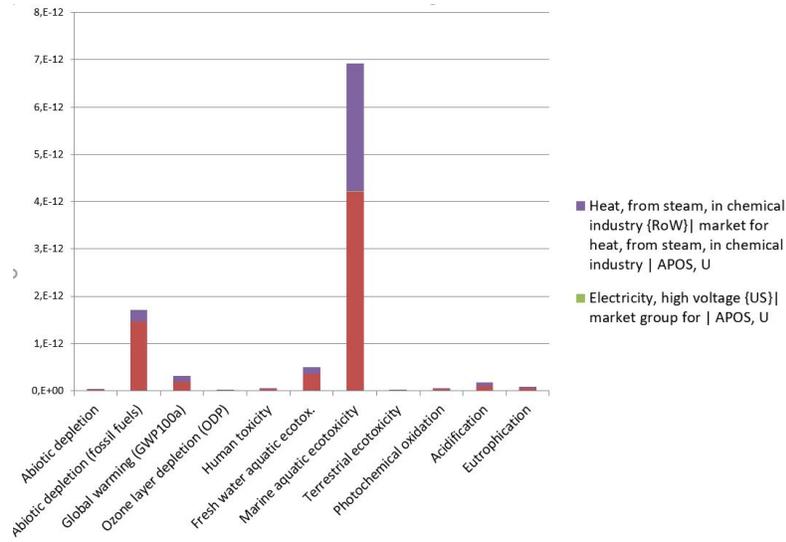


Figure 13. Standardization of the total impact by impact of a standard European inhabitant per year

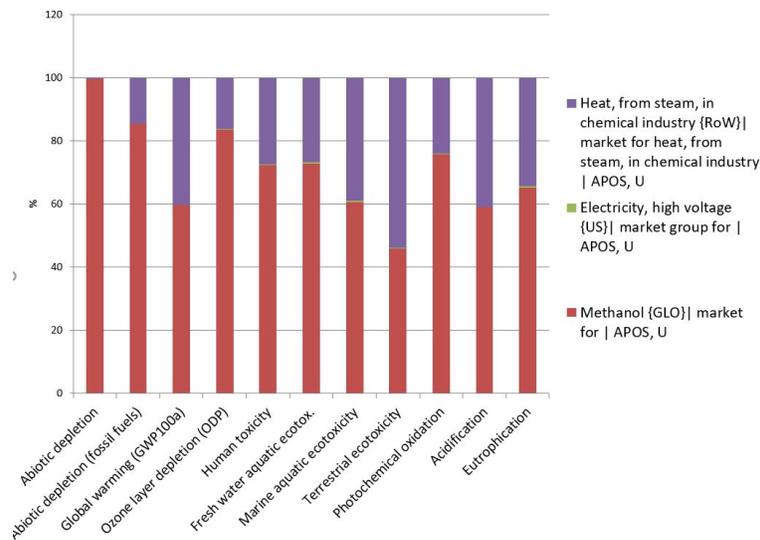


Figure 14. Contribution of methanol, electricity and hot steam on the different impacts

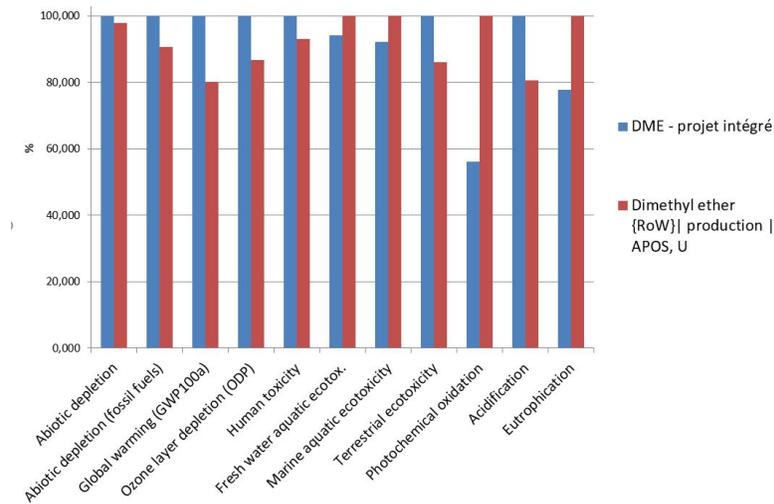


Figure 15. Comparison of the impact of the integrated project values and data base values

## 4. Confronting integrated project results with literature data

### 4.1 Comparison of Aspen and mass balance results

In this section, a brief comparison between the first mole balance and the last stream table is made. As seen in TABLE 10 (APPENDIX 1), a production of 315.02 kmol/h of DME is obtained. In the first mole balance, the production was 313.57 kmol/h. Consequently, the results are quite similar. However, during the 8000 h, the final mole balance gives a 115,660 tons/y with a purity of 99.6% while the first was made to obtain 100,000 tons/y for a purity of 99.5%. So, in the final process, better results are obtained since 15,660 tons more are produced with a higher purity. This difference is due to the initial number of hours considered in the first semester's calculations (6957 hours) which is different from the number of hours considered currently (8000 hours).

### 4.2 Comparison with literature data

In order to validate the process modeled for the integrated project, a comparison with literature is performed. The idea is to realize two types of comparison: the first one with another computing simulation and the second with real DME production plant data.

The study proposed by *Bai Z. et al.* [17] allows to perform these two types of comparison. Indeed, in this study, the results of a simulation built on PRO/II platform that models the dimethyl ether synthesis in a fixed-bed reactor are compared to data of a real DME factory. The initial simulation models a one million tons per year (8000 hours) DME production plant. The validation of the model proposed by *Bai Z. et al.* was performed by comparing their simulation results with available data from an industrial plant with a capacity plant of 200,000 tons per year. The results of this study show a good agreement between the predicted values and the actual ones. Consequently, if results of the integrated project are closed to these of the simulation performed by *Bai Z. et al.*, one can conclude that the integrated project simulation describes quite well a real DME production plant.

The integrated project simulation and these carried out by *Bai Z. et al.* share common points:

- DME is produced through dehydration of methanol over  $\gamma - \text{Al}_2\text{O}_3$  catalyst in an adiabatic fixed-bed reactor.
- Both simulation include two distillation columns and a methanol recycled stream.
- The DME distillation column parameters of the two simulations are similar. In the simulation performed by *Bai Z. et al.*, the number of theoretical stages and the DME production purity are respectively equal to 22 and 99.9 mol % while the same parameters in the our simulation are equal to 20 and 99.6 mol % respectively.
- Inlet reactor operating conditions are quite the same: 260°C and 12 bar for the simulation of *Bai Z. et al.* and 296.85 °C and 15 bar for our process.

Despite these similarities, several points differ between these two simulations:

- The reactor outlet conversion reached 80% in the simulation proposed by *Bai Z. et al.* while ours is equal to 66.38%
- The DME yields are different: *Bai Z. et al.* obtained a DME yield of 98% while our simulation leads to a value of 93.1%.
- Inlet flux compositions are different. In our process, the feed contains methanol and water but also ethanol.

Moreover, because the DME plant capacities are different between these two simulations (one million ton/y versus 116 kton/y for our process), a comparison regarding fluxes are impossible. Thus, one can conclude that similarities between these two simulations are encouraging regarding the reliability of our process but insufficient to validate it properly.

## 5. Technical alternatives within the indirect route

### 5.1 Other catalyst

#### 5.1.1 Improvement of $\text{Al}_2\text{O}_3$

The catalyst  $\gamma - \text{Al}_2\text{O}_3$  is probably the most known and efficient catalyst for DME synthesis. It is low cost, has a high selectivity, good lifetime and high mechanical resistance [18]. But it still has some drawbacks: byproducts, low hydrothermal activity, etc. Scientists search how to improve this alumina catalyst. *Jian Sul et al.* [18] have embedded some silica to this catalyst which enhance the catalytic performances. Indeed, it shows higher methanol conversion thanks to a bigger surface area. Moreover, this catalyst exhibits better activity and no byproduct in the DME compared to  $\gamma - \text{Al}_2\text{O}_3$ .

Another way to improve the  $\gamma - \text{Al}_2\text{O}_3$  was found by *Khom-in et al.* [19]. They mixed the gamma form with 20 wt% of the  $\xi$  phase. This increase the surface acidity of alumina which leads to good stability and better DME yield of 86%.

#### 5.1.2 Zeolite

Instead of using alumina, zeolite catalyst can lead to DME formation by dehydration of methanol. Indeed, *Khandan et al.* [20] or *Vishwanathan et al.* [21] have shown that H-ZSM-5 (Zeolite Socony Mobil-5) has good catalytic performances for this reaction. The interesting point of this catalyst is its high stability in presence of water. However, hydrocarbons are formed at 270°C or higher temperature with this zeolite [22]. It is due to the fact that acidic zeolite has generally strong acid sites while DME synthesis is favorable in presence of weak or moderate acidic site. To adjust the acidity of the zeolite, elements are embedded to the zeolite. A known process to dilute the strong acid sites is the modification of the zeolite by  $\text{Na}^+$ . This sodium-modified HZSM-5 shows better activity,

selectivity and stability over a wide range of temperature (230-340°C) [18].

Moreover, the impregnation on H-ZSM-5 of others elements such as Zr, Zn, Al, Mg in order to improve the properties of the catalyst was studied [20]. Also, a comparison with an impregnation with Na<sup>+</sup> was made. The reaction conditions were a temperature of 523 K and a pressure of 20 bar. All the conversion and selectivity obtained are found in TABLE 8:

Catalyst	Conversion	Selectivity
HZSM-5	78	68
Mg-HZSM-5	81	85
Zn-HZSM-5	85	92
Al-HZSM-5	91	95
Zr-HZSM-5	94	99
Na-HZSM-5	82	85

**Table 8.** Conversion and selectivity for zeolite embedded with other elements

As seen in this table, the Zr-modified-H-ZSM-5 gives the best conversion and is the best catalyst. It was also demonstrated that impregnation of the elements rises the stability of the zeolite.

## 5.2 Process intensification

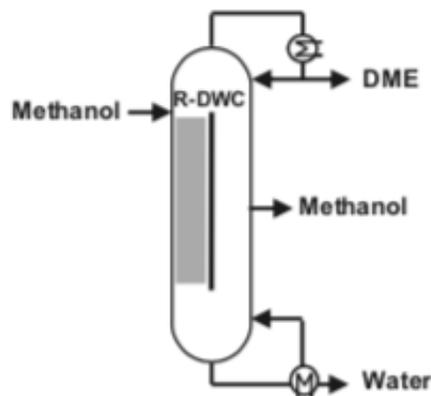
Process intensification can be defined as any chemical engineering development that aims to obtain a cleaner, safer, cheaper and more energy-efficient process. Process intensification gives great attention to improve distillation technologies. Indeed, conventional distillation separations are characterized by a large energy consumption and a high capital investment.

Conventionally, high purity DME is produced through a methanol dehydration process that implies a fixed-bed reactor followed by a direct sequence of two distillation columns (see FIGURE 3). Anton A. Kiss *et al.* [23] compare this conventional DME production process with a process based on a reactive dividing-wall column (R-DWC). R-DWC unit is a combination of two technologies: a reactive distillation process where reaction and distillation are integrated in a single unit and a dividing-wall column which allows the separation of three components. R-DWC unit is schematized in FIGURE 16.

One can see that the process intensification proposed by Anton A. Kiss *et al.* decreases the number of units from three to one for the reaction-separation part.

Anton A. Kiss *et al.* demonstrate, through Aspen simulations, that the process based on R-DWC leads to a significant energy savings of 11%, a 12% reduced CO<sub>2</sub> emissions and a decrease of total investment, total operating and total annual costs of respectively 12%, 55% and 46%. TABLE 9 gives some key performance indicators for both studied processes. In both simulations, DME production capacity is fixed at 103.65 kg/h and a purity of 99.99 wt% is obtained.

Anton A. Kiss *et al.* study demonstrates that the innovative R-DWC process allows the production of high purity



**Figure 16.** Simplified DME production process based on R-DWC [23]

DME (99.99 wt%) with better performances than the conventional process. As a result, this process can be considered as a candidate for DME production both in new plants and in revamped industrial plants.

## 6. Direct synthesis method

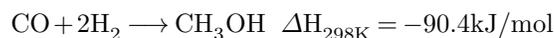
### 6.1 Conventional process

In the last years, a new method to produce DME was found. It consists in a STD method (synthetic gas to dimethyl ether) in which the syngas is converted in DME in one step. The flowsheet of this process can be found in FIGURE 17.

The operational units are those generally used for the purification and separation of the DME process. It allows to separate CH<sub>4</sub>, CO, N<sub>2</sub> and H<sub>2</sub> and recovering methanol through absorption, flash and distillation. It enables to obtain a DME product with high purity. Another interesting feature of this process is the consumption of methanol for DME production which shifts the methanol equilibrium toward a greater methanol conversion [6].

In this synthesis, H<sub>2</sub>, CO and CO<sub>2</sub> are used to produce dimethyl ether in four reactions :

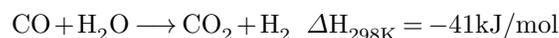
- Methanol synthesis from CO



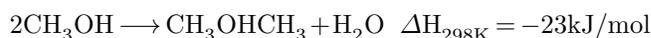
- Methanol synthesis from CO<sub>2</sub>



- Water gas shift reaction (WGS)

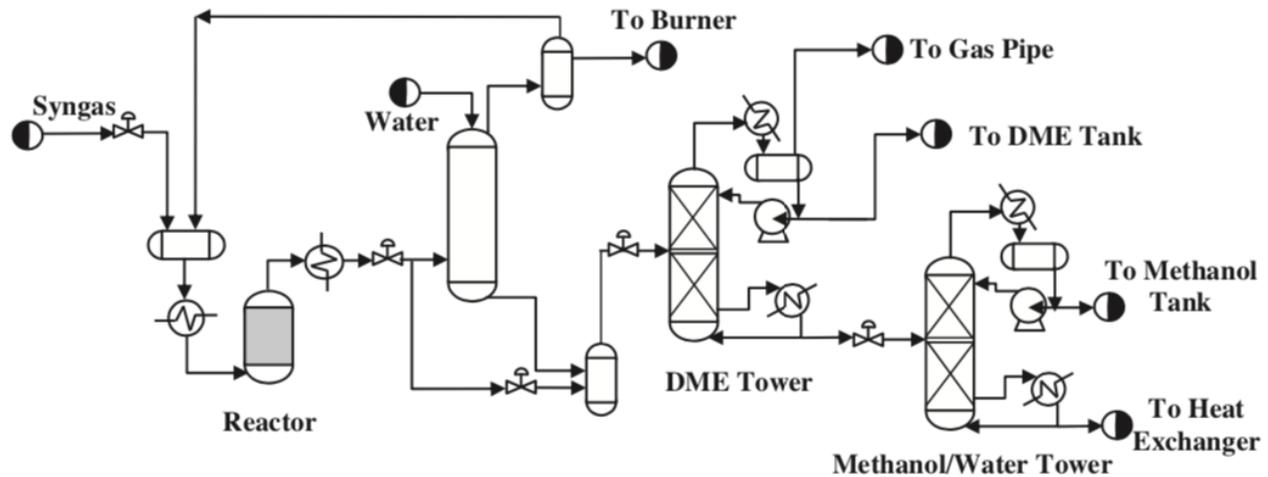


- Methanol dehydration



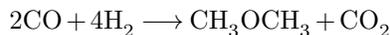
Key performance indicators	Conventional process	R-DWC process
Total investment costs	\$126,075	\$96,531
Total operating costs	\$31,233	\$13,988
Total annual costs	\$43,840	\$23,641
Specific energy requirements (kWh/tonDME)	640.5	566.4
CO <sub>2</sub> emissions (kgCO <sub>2</sub> /h ton DME)	89.57	79.20

**Table 9.** Comparison of conventional vs alternative R-DWC DME processes for a capacity plant of 103.65 kg/h. [23]

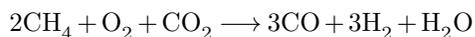


**Figure 17.** Flowsheet of the direct process [6]

The overall equation can be written as following, the first taking into account the WGS reaction and the second without it:



This reaction is highly exothermic which means that a control of the temperature is necessary. For each equation, the maximum equilibrium conversion is reached when the ratio H<sub>2</sub>/CO corresponds to the stoichiometric value. CO<sub>2</sub> is the main by-product of this process. Therefore, it will be re-used in the methane reforming unit to recover CO and H<sub>2</sub> thanks to the equation:



Due to the fact that the STD process takes into account the formation of methanol, the catalyst has to contain bifunctional sites for the synthesis and dehydration of methanol [24]. For now, the most known catalyst is CuO – ZnO – Al<sub>2</sub>O<sub>3</sub> (CZA) for methanol synthesis and WGS (water gas shift) where Cu corresponds to the active phase. The Cu in its metallic form allows to achieve high selectivity of methanol synthesis [24, 25]. The ZnO part promotes the Cu dispersion and activity. This component acts as a geometrical spacer for Cu particles which enhance surface area. However, scientists observe that

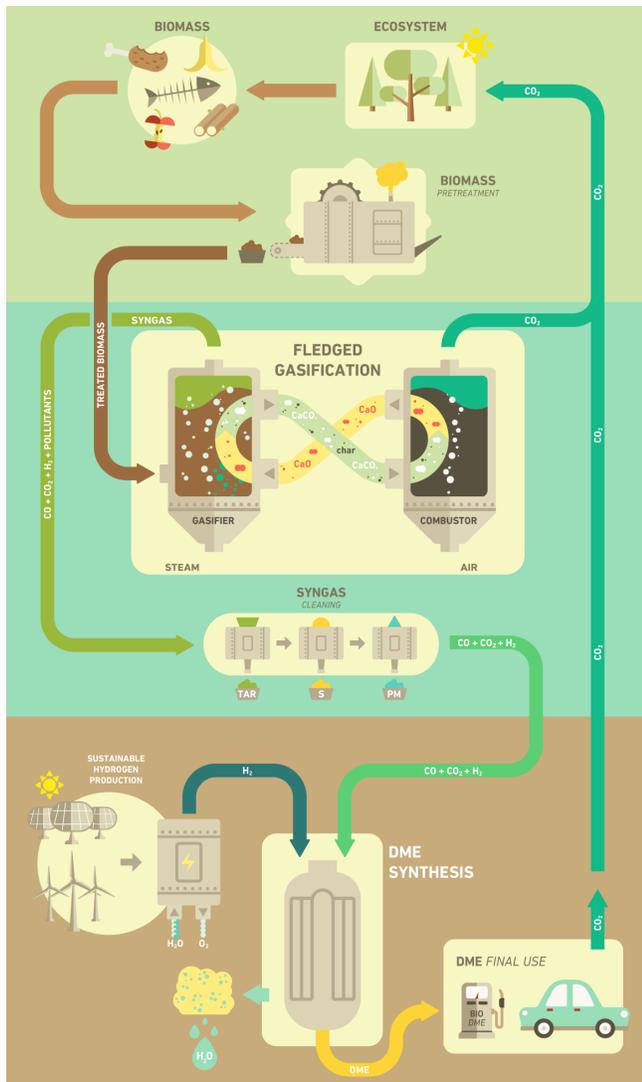
excess of ZnO has a negative effect on the activity. An addition of a M<sup>3+</sup> into the CuO-ZnO-based catalyst has for purpose to increase both surface area and copper dispersion, which in the case of CZA is Al<sup>3+</sup> [6]. This catalyst can be obtained by co-precipitation or sol-gel method. It can be used under working conditions with a temperature of approximately 250°C and a pressure up to 50-100 bar [26].

Once the methanol synthesis is done, the dehydration takes place over a solid acid catalyst such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or HZSM-5. A study made by *Abu-Dahrieh et al.* [22] has proven that the most suitable ratio CZA/solid acid catalyst is 1:1 for CZA/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 3:1 for CZA/HZSM-5.

## 6.2 Biomass to DME: FLEDGED Project

The FLEDGED project aims to develop a large-scale and efficient bio-fuel production process from biomass. This project is funded by the European Union's Horizon 2020 Research and Innovation Program under Grant Agreement n°727600. Due to its physical properties and its clean burning, DME can be envisaged as the most promising bio-alternative to traditional fuels. The project target is to reach of over 60% efficiency of biomass to DME. The acronym FLEDGED stands for FLExible Dimethyl ether production from biomass Gasification with sorption-enhanced processes. The process is summarized in figure 18 and explained in the following paragraphs.

First, biomass is treated through shredding and grinding in order to reduce its size and its moisture. Then, the treated



**Figure 18.** Biomass to DME process - FLEDGED project [27]

biomass is fed into the gasifier and converted into syngas. The gasification is indirect (heat is provided from a air-blown combustor) and CaO is used as bed-material in a dual fluidized bed system. This system allows the production of a N<sub>2</sub>-free syngas with no need of pure oxygen. In addition, the in-situ removal of CO<sub>2</sub> by the conversion of CaO into CaO<sub>3</sub> allows adjusting syngas composition to reach specifications of the downstream process.

Once the syngas is produced, it is purified before entering into the DME reactor. The typical direct method synthesis of DME is enhanced here with an in-situ water adsorption. The fixed-bed reactor is filled with catalyst and water sorbent. While the conversion of syngas to DME occurs, the produced water is removed through adsorption and, consequently, the equilibrium is shifted to higher DME yield. This sorption enhanced DME synthesis shows a high flexibility on feed gas composition. This property allows the FLEDGED process

to support a Power-to-Liquid process: additional hydrogen produced from renewable energies can be provided to the plant and boosts the DME production.

## Conclusion

Dimethyl ether and his production processes have been investigated. The main actor (producer and consumer) on the DME market is Asia thanks to China since there DME is widely used as a fuel. Indeed, it has advantages over traditional fuels such as less pollutant emissions during its combustion.

To produce dimethyl ether two main synthesis methods are used.

The first one, the indirect route, is the one used in the process designed in this project. A DME production process whose feedstock contains mainly methanol but also some percentages of water and ethanol was modelled and integrated from an energy point of view using Aspen Plus software. A process meeting the required purity and quantity of DME per year could be obtained. Moreover, based on the calculated costs, it appears that the company would be in profit after six years, including the year of construction of the plant. From an environmental point of view, the LCA highlighted that the step of this process with the greatest impact is the extraction of the raw materials used to produce methanol. To complete the study of this process, the results obtained were compared with those found in the literature. Although the results appear to be quite consistent, they could not be fully validated. Lastly, technical alternatives and process intensification for this first synthesis route have been presented.

The second method is the direct route that transforms synthetic gas into DME. The conventional process as well as a process using biomass to produce the synthetic gas have been discussed.

To go even further in this work, it could be interesting to study the process with the first column separating methanol from ethanol, mentioned in the introduction. This additional unit would indeed impact the production as well as the costs. In the same way, the improvements presented in section “Technical alternatives within the indirect route”, could be integrated in the designed process to see if more profits could be made.

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## Appendix 1: Stream Tables

Stream number	1	1B	1C	1D	1E	2
Temperature (°C)	24.85	25.96	101.77	109.7	145	146.47
Pressure (bar)	1	15	15	15	15	15
Molar vapor fraction	0	0	0	0	0	0
Mole flow (kmol/h)	687.88	687.88	687.88	687.88	687.88	1023.88
<b>Component flowrates (kmol/h)</b>						
Methanol	674.12	674.12	674.12	674.12	674.12	991.37
Water	10.12	10.12	10.12	10.12	10.12	13.49
Dimethyl ether	0	0	0	0	0	1.53
Ethanol	3.64	3.64	3.64	3.64	3.64	5.08
Diethyl ether	0	0	0	0	0	12.41
Ethylene	0	0	0	0	0	$1.18 \times 10^{-8}$
Stream number	3	4	5	5B	5C	5D
Temperature (°C)	155	296.85	389.83	342.35	311.36	138
Pressure (bar)	15	15	15	15	15	15
Molar vapor fraction	1	1	1	1	1	0.57
Mole flow (kmol/h)	1023.88	1023.88	1027.37	1027.37	1027.37	1027.37
<b>Component flowrates (kmol/h)</b>						
Methanol	991.37	991.37	333.30	333.30	333.30	333.30
Water	13.49	13.49	346.04	346.04	346.04	346.04
Dimethyl ether	1.53	1.53	330.58	330.58	330.58	330.58
Ethanol	5.08	5.08	1.49	1.49	1.49	1.49
Diethyl ether	12.41	12.41	12.47	12.47	12.47	12.47
Ethylene	$1.18 \times 10^{-8}$	$1.18 \times 10^{-8}$	3.49	3.49	3.49	3.49
Stream number	6	7	8	9	9B	9C
Temperature (°C)	110.15	20.65	116.75	106.34	106.98	145
Pressure (bar)	6	6	6	6	15	15
Molar vapor fraction	0.66	0	0	0	0	0.03
Mole flow (kmol/h)	1027.37	315.02	694.86	336	336	336
<b>Component flowrates (kmol/h)</b>						
Methanol	333.30	$4.17 \times 10^{-3}$	333.36	317.25	317.25	317.25
Water	346.04	$6.43 \times 10^{-8}$	346.07	3.37	3.37	3.37
Dimethyl ether	330.58	313.82	1.53	1.53	1.53	1.53
Ethanol	1.49	$9.28 \times 10^{-10}$	1.49	1.44	1.44	1.44
Diethyl ether	12.47	0.05	12.41	12.41	12.41	12.41
Ethylene	3.49	1.14	$1.18 \times 10^{-8}$	$1.18 \times 10^{-8}$	$1.18 \times 10^{-8}$	$1.18 \times 10^{-8}$
Stream number	10	11	12	S1		
Temperature (°C)	150.84	128.93	50	20.65		
Pressure (bar)	6	6	6	6		
Molar vapor fraction	0	0	0	1		
Mole flow (kmol/h)	358.87	358.87	358.87	17.57		
<b>Component flowrates (kmol/h)</b>						
Methanol	16.12	16.12	16.12	$1.51 \times 10^{-5}$		
Water	342.51	342.51	342.51	$2.25 \times 10^{-11}$		
Dimethyl ether	$7 \times 10^{-7}$	$7 \times 10^{-7}$	$7 \times 10^{-7}$	15.22		
Ethanol	0.046	0.046	0.046	$5.28 \times 10^{-13}$		
Diethyl ether	$3.5 \times 10^{-7}$	$3.5 \times 10^{-7}$	$3.5 \times 10^{-7}$	$2.56 \times 10^{-4}$		
Ethylene	$1.9 \times 10^{-22}$	$1.9 \times 10^{-22}$	$1.9 \times 10^{-22}$	2.35		

Table 10. Stream Table

Stream number	QCOND1	QCOND2	QCOND3
Initial temperature (°C)	116.81	116.81	116.81
Final temperature (°C)	106.34	106.34	106.34
Heat duty (kW)	7863.22	6257.32	1605.90

**Table 11.** Heat Stream Table

Stream number	STEAM1	STEAM2	STEAM3	STEAM4	
Associated heat exchanger	U4	U4	U5	U5	
Temperature (°C)	400	179.36	400	258.83	
Pressure (bar)	46	46	46	46	
Molar vapor fraction	1	0	1	0.58	
Water mass flow (kg/h)	12000	12000	9000	9000	
Stream number	WATER1	WATER2	WATER3	WATER4	WATER5
Associated heat exchanger	U1	U1	U2	U2/U3	U3
Temperature (°C)	25	133.60	25	64.15	133.60
Pressure (bar)	3	3	3	3	3
Molar vapor fraction	0	0	0	0	0.68
Water mass flow (kg/h)	72061.1	72061.1	14412.2	14412.2	14412.2

**Table 12.** Utility Summary Table

## Appendix 2: Major Equipment Summary

Heat exchanger	Area ( $m^2$ )	Heat duty (kW)	Maximum pressure rating (bar)
HX1	3.64	616	15
HX2	4.90	993.51	15
HX3	7.09	202.80	15
E-203	71.5	1605.90	15
U1	226.94	6257.32	3
U2	18.55	658.94	6
U3	290.69	7195.46	15
U4	100.20	8184.53	46
U5	140.14	2455.08	46

**Table 13.** Heat Exchangers Summary Table

Pump	Net work required (kW)	Inlet pressure (bar)	Outlet pressure (bar)	Efficiency
PUMP1	8.39	6	15	0.49
PUMP2	19.18	1	15	0.56

**Table 14.** Pumps Summary Table

Valve	Inlet pressure (bar)	Outlet pressure (bar)
V-1	15	6

**Table 15.** Valve Summary Table

Reactor	Type	Min T ( $^{\circ}C$ )	Max T ( $^{\circ}C$ )	Length (m)	Diameter (m)	Volume ( $m^3$ )
R-201	Adiabatic	296.85	389.83	8.92	1.48	15.35

**Table 16.** Reactor Summary Table

Column	D-201	D-202
Number of stages	12	20
Reflux ratio	3.48	1.6
Condenser duty (kW)	7836.69	7863.22
Reboiler duty (kW)	2370	8100
Volume ( $m^3$ )	12.33	17.92

**Table 17.** Columns Summary Table

Mixer	Outlet temperature ( $^{\circ}C$ )	Outlet pressure (bar)
MIXER	146.47	15

**Table 18.** Mixer Summary Table

Split	Split fraction
QCOND2	0.80
QCOND3	0.20

**Table 19.** Split Summary Table