Process modeling and economic analysis of ethanol synthesis via CO_2 hydrogenation

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Abstract:

The Carbon Capture and Utilization (CCU) concept is an alternative to the Carbon Capture and Storage (CCS). Carbon available in the form of CO_2 could be reutilised through a power to fuel concept i.e. elevated pressure synthesis of CO_2 with H_2 into a liquid fuel, such methanol and ethanol. Methanol and ethanol are recently discussed as products of synthesis.

In this study, two energy systems that reuse the captured CO_2 from fossil fuel plant transforming it into ethanol are investigated. The first is based on the CO_2 conversion to CO through the reverse water gas shift (rWGS) reactor followed by the mixed alcohol synthesis reactor and the second one on the intermediate DME synthesis. The mass and energy analysis of these two concepts is presented aiming to evaluate the performance in terms of power consumptions and productivity yields. The process simulation, that was performed with ASPEN Plus[TM], reveal that the second (novel) concept for ethanol synthesis via DME has a higher efficiency because of lower heat and power demands for its effective operation. From the economic analysis of the corresponding systems, it is shown that the second novel scheme results to lower ethanol production cost than the conventional through the rWGS but the high cost for H_2 production through water electrolysis keeps it far for competitive levels. The use of cheap electricity in conjunction with high capacity factor is of high importance for further development of the power-to-fuel concept.

Keywords:
Carbon utilisation, CCU, ethanol, power to fuel, electrolysis.

1   Introduction

The control of the Greenhouse Gas (GHG) emissions is one of the most challenging environmental issues that should be faced in the 21st century. According to IEA Blue Map Scenario for reducing CO_2 emissions, the Carbon Capture and Storage (CCS) is considered among the major measures that should be addressed in large scale worldwide **[1, 2]**. However, several obstacles such as high capital and operational cost, the several social and technical issues that should be addressed for the CO_2 safe storage in conjunction to the low carbon pricing policy, hinder the adoption of this option for CO_2 footprint mitigation.

A more feasible option to mitigate CO_2 emissions is to transform it into valuable compounds, like fuel organic and inorganic chemicals, namely as 'the CO_2 capture and utilization (CCU) concept'. The majority of CO_2 use in industry is for urea production, which accounts for more

than half of the global annual usage [3]. Alternatively, CO_2 is utilized also physically in various applications such as refrigerant medium, in fire extinguishers and in the petroleum and NG industry for Enhanced Oil Recovery (EOR) and Enhanced Gas Recovery (EGR), respectively [2, 4]. The methods for CO_2 transformation can be sorted in six categories [3, 5]: chemical reduction (i.e. Boudouard), electrochemical reduction [6], photochemical reduction (i.e. artificial photosynthesis), thermochemical conversion (i.e. dry reforming and hydrogenation), biological (i.e. photosynthesis, anaerobic conversion)[7] and inorganic transformation. In order the CCU concept to have effective impact on the drastic reduction of the CO_2 emissions, the quantities of end-products derived from CO_2 transformation should cover the market demand. The selection of the final products should be correlated to global demands and consumptions of them. Thus, this study focuses on synthesis of transportation fuels from CO_2.

Since the H_2/CO_2 ratio for CO_2 hydrogenation towards hydrocarbons synthesis should be four (4) for methane and three (3) for methanol synthesis, the required amounts of hydrogen are very large. There are three routes for non-fossil derived hydrogen production: water electrolysis, biomass conversion and solar conversion [8, 9]. In the present study, the hydrogen is considered to be derived from electrolysis, since this is the most mature and well-established technology even in industrial scale [10] and also it is not relied on carbon-contained source like biomass. Electrolysis is based on the water splitting into H_2 and O_2, the energy for this reaction is given in the form of electricity derived from Renewable Energy Source (RES) i.e. photovoltaic panels (PV), wind farms hydropower and geothermal plants.

Methanol is considered as one of the most valuable chemicals with a series of uses in various sectors (power, transport, steel, chemical industry) either as fuel or as block for the synthesis of other chemicals (dimethyl ether, formaldehyde, methyl tert-butyl ether, acetic acid, gasoline, etc). Apart from methanol, ethanol is gaining the interest the last decades not only as an alternative fuel [11, 12] but also a valuable chemical block for numerous products synthesis [13]. In order the CCU concept to become the most appropriate option for CO_2 mitigation in a global scale, the synthesis of several chemical products should be included in a generalized road map. Ethanol is considered as a perfect additive into petrol, contributing to the increase of octane number and the reduction of CO and PM emissions. Furthermore, ethanol has an important advantage over methanol for application as transportation fuel because it is less toxic and dangerous, permitting higher blending ratios with conventional gasoline [14, 15]. However, the alternative ethanol fuel is bio-based and is mainly produced from sugar/starch crops through fermentation. There are also few studies [16-18] that have investigated the technical and economical prospects for CO_2 derived ethanol synthesis.

The scope of this study is the investigation of a new process scheme for the valorization of CO_2 towards the production of ethanol through DME synthesis. The alternative ethanol and the intermediate product (DME) from this process can be used either as transportation fuels or as the basis for the synthesis of other chemicals. The ASPEN Plus^{TM} process specifications and the approach for the modeling of the fuel synthesis unit are described in the following paragraphs in detail. The comparison with the conventional technology based on the reverse water gas shift (rWGS) reaction is made in terms of efficiency by performing the thermodynamic analysis and in terms of economic feasibility, determining the minimum ethanol production cost so that the proposed concept can be profitable.

2 **Concept description**

The concept for transportation fuels through CO_2 hydrogenation is shown in **Figure 1**. Carbon dioxide is separated and purified from the flue gas of a power intensive industry such as power sector or cement plant. The required hydrogen for the CO_2 hydrogenation is derived from water electrolysis that is accomplished with electricity derived either from renewable energy sources or from the grid. The process configuration for the CO_2 transformation into fuels and the final product separation and purification depends on the product type (methanol or ethanol). Since the CO_2 hydrogenation is accomplished in high pressure (>40 bar) both the inlet gases should be compressed before they are delivered to the CO_2 Utilization Unit (CUU).
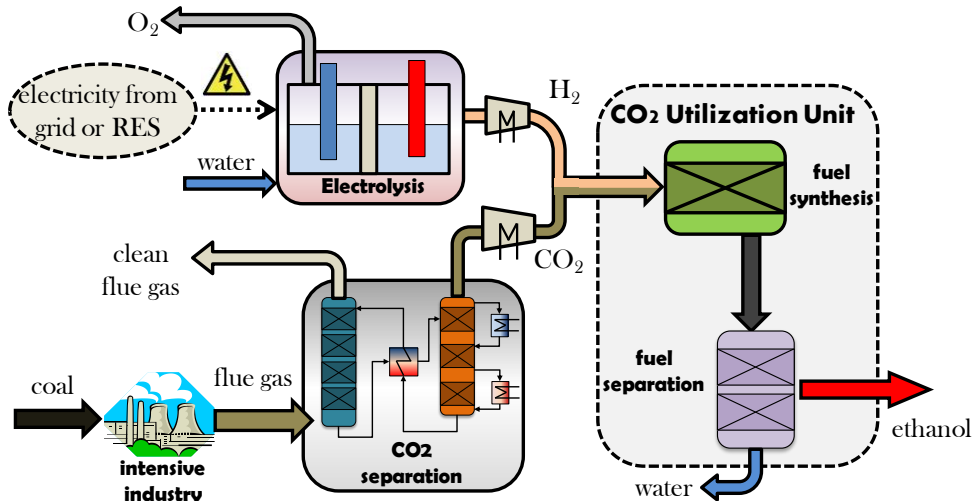

Figure 1. Conceptual design of the proposed avionics production from CO_2

2.1 **Feedstock gases**

The input gases that are required for the alternative ethanol synthesis are carbon dioxide (CO_2) and hydrogen (H_2).

Pure CO_2 from combustion gases of a power plant or other intensive carbon emission industry (e.g. cement plant). The Carbon Capture and Storage concept has attracted a lot of attention the past decade. A great development has been gained on each of the main CO_2 separation techniques, even though no concept has reached to a commercial level yet. Among the several CO_2 caption options, amine scrubbing (MEA) and oxyfuel technology are considered the most competitive and ready to apply technologies for the first generation of applications in industrial scale. The chemical absorption technique with amine scrubbing is the most mature technology with higher Technology Readiness Level and has already been tested and implemented in large scale applications. Therefore, it is selected for this study as the CO_2 capture technology. The delivered CO_2 stream bares the same specification with storage specification: oxygen should absent from the pure CO_2 stream to avoid ignition after reaction with the H_2 in the reactor. The specific heat demands for amine regeneration are 4.17 MJ_{th}/kg_{CO2} and the electric power consumption 0.021 kWh/kg_{CO2} [19].

In water electrolysis, water is split into O_2 and H_2 by means of electrical power. This option for H2 production has the lowest efficiency (35-42%) and the highest H_2 production cost (for large scale 20-25 $/GJ_{H2}$) among the other technological options but, it is considered as the best option for sustainable and clean hydrogen production [20, 21] There are three main electrolysis options

(alkaline electrolysis, polymer electrolyte membranes and high-temperature electrolysis). Alkaline (KOH) electrolysis is the best available since it is quite mature up to large scale H_2 production [22]. Moreover, it has been tested successfully for discontinuous operation, and its load can be altered easily by adapting the current density [23]. Therefore KOH electrolysis is selected as the most suitable technique for the examined concept in this study. For the analysis in this study, it is assumed that highly pure (>99.9%) H_2 and O_2 gaseous streams are produced in the electrolyzer, the operating conditions of which are 80 ^{o}C/30 bar, which are typical for large scale commercial alkaline electrolyzers [23-25]. The specific power consumption is set 4.34 kWh/Nm^3 based on [23]. Assuming that the rest of power demands in the electrolysis unit is 10% of the consumptions for water electrolysis and hydrogen production [24], the overall electrical consumptions are 55.56 kWh/kg$_{H2}$.

2.2 Ethanol synthesis from CO_2

Concerning the CO_2 fixation step towards the production of valuable chemicals, the catalytic hydrogenation for ethanol synthesis is examined. The scope of this analysis is to present novel process configurations for ethanol production and to investigate how these schemes can improve the whole plant performance. As quoted in the introduction, a central plan for CO_2 fixation towards to the drastic mitigation of GHG emissions should not rely on methanol production, exclusively, but it should include the production of other valuable chemical products. One of them is ethanol. In this section, two schemes for ethanol synthesis are presented, the first is the "traditional" route based on the reverse water gas shift reaction and the second scheme –the "novel" one - is based on the intermediate synthesis of DME.

2.2.1 Ethanol synthesis based on reverse WGS (rWGS)

The direct reaction of ethanol synthesis through CO_2 hydrogenation is the reverse reforming:

$$2CO_2 + 6H_2 \Leftrightarrow C_2H_5OH + 3H_2O \tag{R1}$$

In practice, the direct ethanol synthesis suffers from very low selectivity to C_{2+} alcohols and low conversion rates at even high pressures [16, 18, 26]. Hence the thermochemical route that is adopted is in two steps through reverse water gas shift (rWGS) followed by the CO hydrogenation:

$$CO_2 + H_2 \Leftrightarrow CO + H_2O \tag{R2}$$

$$2CO + 4H_2 \Leftrightarrow C_2H_5OH + H_2O \tag{R3}$$

However, the effective CO_2 conversion into CO is achieved in high temperatures (in 575°C, a CO_2 conversion around 48% can be achieved) due to the strong endothermic nature of the rWGS, increasing the demands for a high temperature heat source, which is achieved through the combustion of a portion of the recycling gas (tail gas), as it shown in **Figure 2**. After the rWGS reactor, the produced H_2O is removed through condensation after gas cooling at 30°C. The gas is compressed at 80bar and fed the Mixed Alcohol Synthesis (MAS) reactor, where CO is catalytically hydrogenated at 325°C. The methodology for a modified FT catalyst MAS reactor and the process configuration for alcohols separation have already been described in previous studies [27, 28].
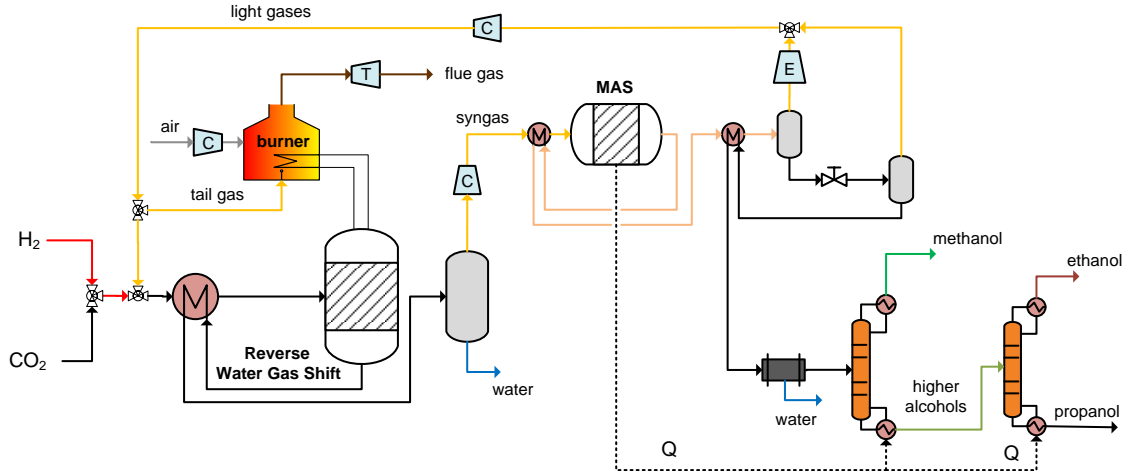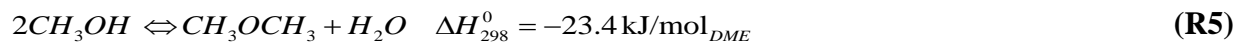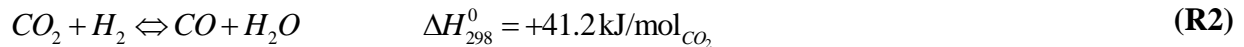
**Figure 2**. Process flowsheet of the rWGS-FT concept

2.2.2 Ethanol synthesis from DME

The novel thermochemical route for ethanol synthesis from CO_2 through DME that is proposed in this study consists of a series of two reaction stages. The first stage is the DME synthesis from CO_2 and H_2. Even though the conventional method for commercial DME synthesis from syngas (including both CO and CO_2) is in two steps 1) methanol synthesis and 2) methanol dehydration, it have been shown that the one-step process based on bifunctional catalysts is more thermodynamically and economically favorable **[29-32]**. The main reactions that take place in the DME synthesis reactor are (**(R4)**, (**R2)** and (**(R5)**. The first and the third are catalyzed by a methanol synthesis catalyst such as $Cu/ZnO/Al_2O_3$, while the second reaction by an acidic catalyst such HZSM-5 **[32]**.

$$CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O \qquad \Delta H_{298}^0 = -49.5\,\mathrm{kJ/mol}_{CO_2} \tag{R4}$$

$$CO_2 + H_2 \Leftrightarrow CO + H_2O \qquad \Delta H_{298}^0 = +41.2\,\mathrm{kJ/mol}_{CO_2} \tag{R2}$$

$$2CH_3OH \Leftrightarrow CH_3OCH_3 + H_2O \quad \Delta H_{298}^0 = -23.4\,\mathrm{kJ/mol}_{DME} \tag{R5}$$

This process is kinetically rate depended and conducts in the range of 220–300 ∘C and 30–60 bar. The methodology for the kinetic rate calculation is adopted from the study of Lu et al. **[32]** and the parameters are summarized in the following **Table 1**.

The second stage of the proposed concept for alcohols synthesis is the DME transformation into C_2H_5OH. The alcohols (methanol and ethanol) production from methyl ether is conducted in two consecutive steps **[33-35]**. The first is the DME carbonylation where methyl acetate (MA) is formed in the presence of H-Mordenite (H-MOR) zeolite:

$$CH_3OCH_3 + CO \Leftrightarrow CH_3COOCH_3 \tag{R6}$$
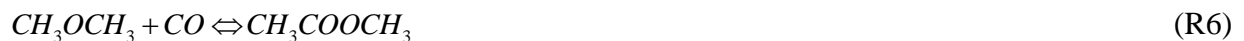
The next one is the produced ester hydrogenation over the Cu/ZnO catalyst.

$$CH_3COOCH_3 + 2H_2 \Leftrightarrow CH_3OH + CH_3CH_2OH \tag{R7}$$

Table 1. Kinetic rate calculation for DME synthesis [32]

parameter [1]	reaction (R4)	reaction (R2)	reaction (R5)

rate r_i (kmol/kg$_{cat}$/s)	$r_1 = k_1 \dfrac{p_{CO_2} p_{H_2}\left(1 - \dfrac{1}{K_{eq,1}} \dfrac{p_{H_2O} p_{CH_3OH}}{p_{CO_2} p_{H_2}^3}\right)}{\left(1 + K_{CO_2} p_{CO_2} + K_{CO} p_{CO} + \sqrt{K_{H_2} p_{H_2}}\right)^3}$	$r_2 = k_2 \left(\dfrac{p_{CH_3OH}^2}{p_{H_2O}} - \dfrac{p_{DME}}{K_{eq,2}}\right)$	$r_3 = k_3 \dfrac{p_{H_2O} - \dfrac{1}{K_{eq,3}} \dfrac{p_{CO_2} p_{H_2}}{p_{CO}}}{1 + K_{CO_2} p_{CO_2} + K_{CO} p_{CO} + \sqrt{K_{H_2} p_{H_2}}}$
exponential factor k_i	$k_1 = 35.45 \exp\left(\dfrac{-1.7069 \cdot 10^4}{RT}\right)$	$k_2 = 8.2894 \cdot 10^4 \exp\left(\dfrac{-5.2940 \cdot 10^4}{RT}\right)$	$k_3 = 7.3976 \cdot 10^4 \exp\left(\dfrac{-2.0436 \cdot 10^4}{RT}\right)$
equilibrium constant $lnK_{eq,i}$	$\ln K_{eq,1} = \dfrac{4213}{T} - 5.752 \ln T - 1.707 \cdot 10^{-3} T + 2.682 \cdot 10^{-6} T^2 - 7.232 \cdot 10^{-10} T^3 + 17.6$	$\ln K_{eq,2} = \dfrac{4019}{T} - 3.707 \ln T - 2.783 \cdot 10^{-3} T + 3.8 \cdot 10^{-7} T^2 - 6.561 \cdot 10^4 T^{-3} - 26.64$	$\ln K_{eq,3} = \dfrac{2167}{T} - 0.5194 \log T - 1.037 \cdot 10^{-3} T - 2.331 \cdot 10^{-7} T^2 - 1.2777$
K_{CO2}		$K_{CO_2} = 1.02 \cdot 10^{-7} \exp\left(\dfrac{6.7400 \cdot 10^4}{RT}\right)$	
K_{CO}		$K_{CO} = 7.99 \cdot 10^{-7} \exp\left(\dfrac{5.8100 \cdot 10^4}{RT}\right)$	
K_{H2}		$K_{H_2} = 0.249 \exp\left(\dfrac{3.4394 \cdot 10^4}{RT}\right)$	

[1] partial pressure p_i in bar, temperature T in K and R=8.314 J/molK

The reaction process is accomplished in a dual bed reactor sequentially, at 15 bar and 220 °C. Apart from the produced alcohols and the unreacted DME and MA, CO_2 and ethyl acetate (EA) are also found in the reactor exit **[33, 34]**. After the products separation, DME, MA and EA reenter to the reactor, whereas the CH_3OH and CO_2 are sent at the DME synthesis unit. The process configuration for the ethanol separation and purification is similar to the conventional CO_2 to ethanol plant.
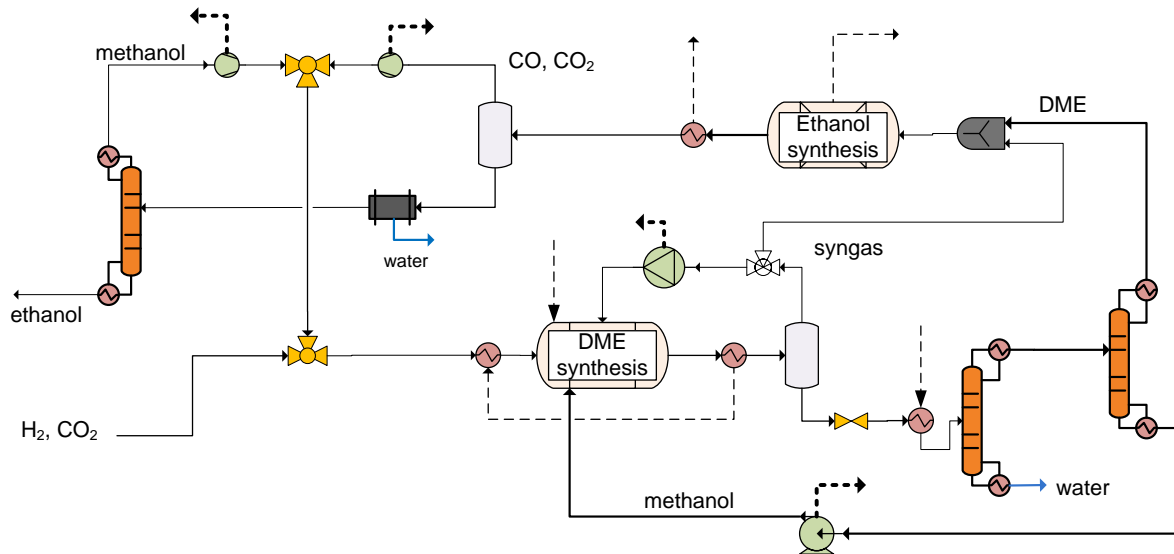

Figure 3. Process configuration of the CO_2 to Ethanol plant through DME

3 **Cost analysis**

One of the most important aspects of the economic analysis is the determination of the H_2 cost. The selection of the power supplier for the electrolysis operation, the hydrogen management prior utilization, the electrolysis technology are decisive parameters for the estimation of the hydrogen production and delivery cost [23, 25, 36]. However, since the detailed estimation of the hydrogen production cost is out of the scope of this study, it is assumed equal to 3.0€/kg.

The cost for CO_2 capture with the amine scrubbing port-combustion technology is set at 43.8 €/tn$_{CO2}$ [37]. In addition, the location of the CO_2 capture unit with respect to the CO_2 utilization unit influences the cost for CO_2 transportation. In case that the two units are in the same place, the cost of CO_2 equals to the cost for CO_2 separation. Otherwise, a specific cost 9.23 €/tn for CO_2 transportation is assumed [38] when a pipeline network is applied. From the same study, it is concluded that the specific cost for CO_2 storage in liquid form 4.46 to 13.86 €/tn CO_2. Hence, in this study, the total cost for CO_2 transport and constant when the CO_2 is conducted far away from the CO_2 capture plant is set 20 €/tn following the assumption made by Barbato et al. in [36].

The Total Capital Investment (TCI) estimation is performed according to Peters & Timmerhaus methodology [39] and is based on a series of intermediate cost types, the first of which is the Total Purchased Equipment cost (TPEC) for each case. The equipment cost of each component is estimated based on similar equipment costs from the literature according to the following equation:

$$C_i = C_0 \cdot \left(\frac{S_i}{S_o}\right)^f$$

Equation 1

Furthermore, having the Total Purchased Equipment Cost (TPEC) estimated, the next step is the Total Installed Cost (TIC) calculation. This is accomplished by multiplying each equipment cost with an installation factor n, specified for each component (see Table 2).

Table 2. Equipment cost estimation

Equipment List	Scaling parameter	Reference erected cost, C_o (M€)	Reference size S_o	Scale factor f	installation factor n	reference year	Ref.
rWGS reactor	feed gas (t/h)	0.4720	210	0.8	2.47	2010	[40]
DME reactor	kmol/s feed gas	15.855	2.91	0.65	1.52	2007	[41]
ethanol reactor[1]	feed gas (lb/h)	49.600	729095	0.65	2.47	2005	[42]
heat exchanger	heat duty (MW$_{th}$)	39.26	355	1	1.49	2007	[43]
distillation unit	methanol flow rate (t/h)	16.58	6.75	0.7	1.52	2006	[44]
compressor	power (MW$_e$)	12.08	10	0.67	1.72	2006	[45]
cooling system	Q rejected (MW$_{th}$)	49.600	470	0.67	1.49	2007	[46]
booster	power (MW$_e$)	14.770	47.61	0.67	2.47	2011	[47, 48]
alcohols separation	liquid feed (kg/s)	7.207	8.836	0.67	2.47	2005	[49]
wastewater treatment	kg/hr water input	20.353	393100	1.05	2.47	2010	[50]
gas turbine	power output (MW$_e$)	73.2	266	0.75	1.27	2007	[41]
flash tank	gas feed (kg/s)	installation cost (in M€) = 2.47·983.2·10^{-6}·(feed gas in kg/s)$^{0.8}$				2000	[51]
boiler	boiler capacity (lb/hr)	online equipment cost estimation					[52]

[1] the same methodology for both ethanol reactors is followed.

The parameters for the operational cost calculation such as O&M and insurance are considered as a portion of the Fixed Capital Investment (FCI).

Table 3. Economic assumptions

|	
exchange rate	0.755 €/$
discount rate	10%
recovery period	25 years
Capital Recovery Factor	0.11
year basis	2012
Operating and Maintenance (O&M)	5% FCI
Insurance	2% FCI

4 Results and Discussion

4.1 Process Simulation results

In order to assess the performance of each CO_2 Utilization Unit, the CUU efficiency is introduced and defined as:

$$\eta_{CUU} = \frac{\dot{m}_{CH_3OH} \cdot LHV_{CH_3OH}}{\dot{m}_{H_2inlet} \cdot LHV_{H_2} + \sum P_{cons}}$$

Equation 2

The energy flow at the two ethanol plants is illustrated by the corresponding Sankey diagrams in **Figure 4**. The heat streams in the DME scheme (Figure 4b) that are used for the coverage of the heat demands in various process come from the useful heat that is generated in the boiler.
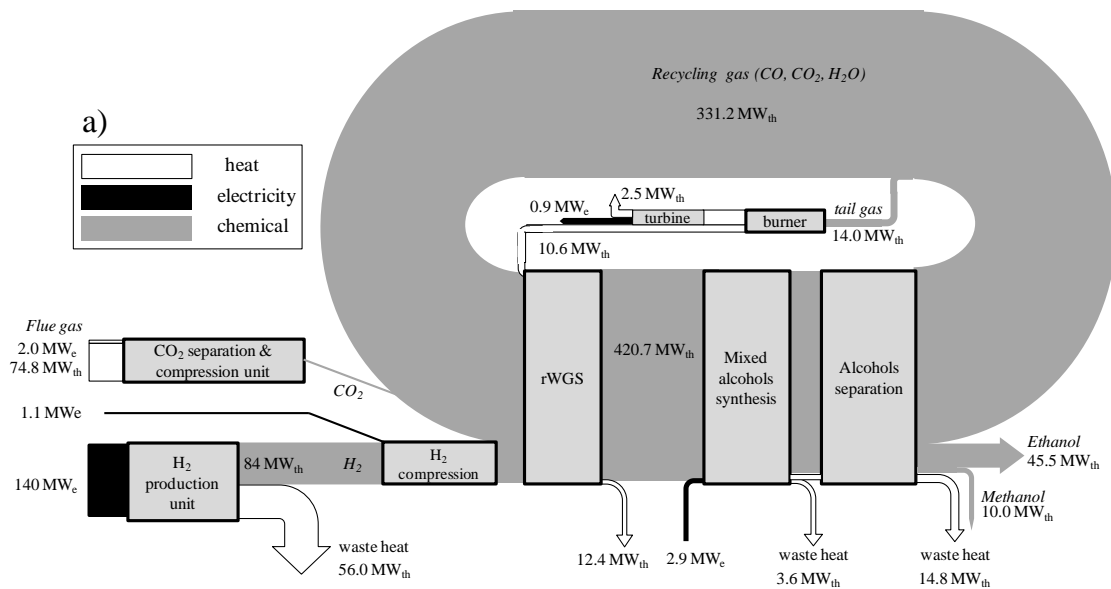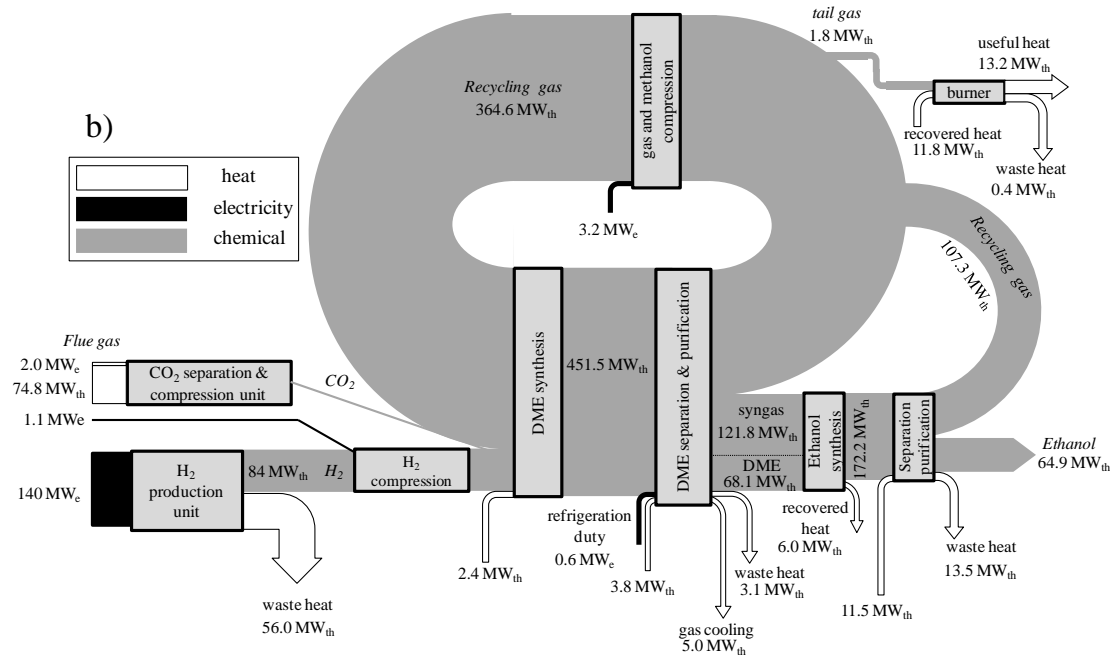
Figure 4. Energy flow diagram of the CO_2 to Ethanol Plant through a) reverse Water Gas Shift and b) DME synthesis

The main mass and energy balance simulation results are shown in **Table 4**. The DME annual production refers to the DME that is produced at the first reactor and undergoes to transformation into ethanol into the second reactor. Since the DME stream is purified, it could be considered as the final product in case that the ethanol is not the desired product. Due to the nature of the MAS catalyst, high selectivity rates for the ethanol and higher alcohols synthesis cannot be achieved. In this light, methanol is considered as by-product. Alternatively, methanol can be reformed in high temperature under oxy conditions and reenter the mixed alcohol reactor, resulting to 100% selectivity in C2+ alcohols **[27]**. However, this option is not adopted in this analysis. On the other hand, the produced methanol in the ethanol synthesis reactor can be separated and returned to the first reactor for DME synthesis. Similar to the ethanol cases, large amounts of heat is required for products separation in both processes. Most of the heat requirements are covered by the cooling of the hot gases exiting the reactors. Even though the demands for heat along the whole process in the first scheme are more, the flow rate of the tail gas that is combusted is greater, due to the strong endothermic nature of the reverse water gas shift reaction. On the contrary, only 0.5% of the recycling gas at the DME reactor is extracted in order to be burnt. As a result, the carbon utilization in the second case is much greater than the "conventional" way.

Regarding the performance of the two process schemes, the Ethanol plant based on DME has greater CUU thermal efficiency (i.e. the chemical products heat input to the total energy input). This is mainly attributed to the milder reactions that take place along the process resulting to lower heat demands, despite the higher power consumptions due to gas recycling and compression. The total exergy efficiency for the both systems is 41.9% for the first case (rWGS) and 49.3% for the second one (DME based). It is clear that the synthesis of higher alcohols has smaller performance in comparison to the methanol case as it is illustrated by the comparison of the corresponding exergy efficiencies.

Table 4. Main simulation results from the Power-to-Ethanol cases

	EtOH from rWGS	EtOH from DME
DME annual production	-	72036
ethanol annual production (t/y)	32777	61983
methanol annual production (t/y)	12357	-
propanol annual production (t/y)	10079	-
CO_2 conversion (%)	49.5	56.5
CO_2 utilization (%)	68.7 (81.1)[1]	98.0
total heat requirements (MW_{th})	13.78	13.18
tail gas heating value (MW_{th})	14.03	1.82
rejected heat (MW_{th})	27.38	21.81
total power requirements (MW_e)	2.05	4.18
CUU efficiency (% LHV basis)	63.2	70.3

[1] the value in the parenthesis refers to the carbon in both methanol and higher alcohols

4.2 **Economic analysis**

As far as the economic analysis is concerned, **Figure 5** presents the ethanol cost breakdown for the two cases. The oxygen utilization is not taken into account in this analysis. The same qualitative conclusions with the methanol case are extracted: The hydrogen production cost, and more specifically the electricity for H_2 production is the most important parameters that influence the ethanol production cost. On the other hand, similar to the methanol case, the other component for the ethanol synthesis (CO_2) has a small contribution (only 6.6 to 7.0%) to the economic scale of the investment as the specific cost of the delivered CO_2 stream is 108 €/tn of ethanol (rWGS based) and 139.2 €/tn of ethanol (DME based). The specific cost of the CUU (both the capital and operational part) for the rWGS based and DME based scheme is 376.1 and 389.2 €/tn of ethanol, respectively.
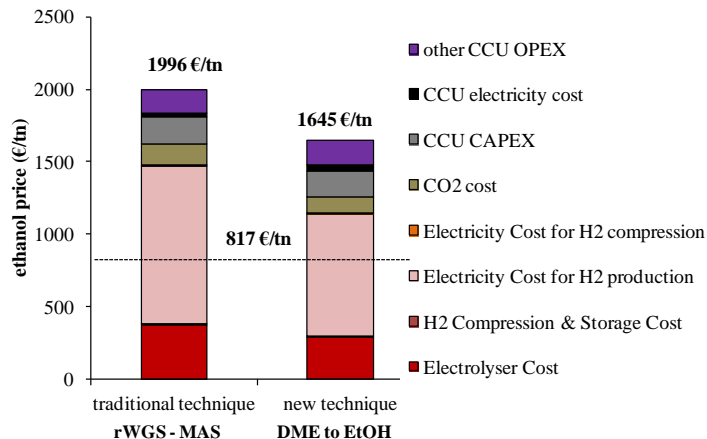

Figure 5. Ethanol production cost breakdown for the two CO_2-to-Ethanol schemes

Comparing the two process schemes, the proposed scheme for ethanol production via DME synthesis leads to lower production cost than the rWGS based scheme. The estimated production cost in the former scheme is 2.01 times greater than the current ethanol price whereas in the later scheme it is 2.44.

In case that the produced oxygen can be considered as a by-product and is sold, the minimum ethanol price in the rWGS case is 1.27 €/l whereas in the DME based case is 1.11 €/l. Taking into account that the cost of cellulosic ethanol, which is derived from lignocellulosic biomass

fermentation is currently around to 0.70 €/l, more effort should be paid in order the CO_2 based options for alternative ethanol production can compete the bio-based routes.

5 Conclusions

In this study two process schemes were investigated in terms of efficiency and cost towards the production of ethanol through CO_2 hydrogenation. The novel scheme through DME has higher thermal efficiency because of lower heating demands, and thus, the ethanol production cost is lower than this of the rWGS case. The production cost of the ethanol from CO_2 is 2-2.5 times higher than the corresponding conventional prices. A considerable effort is needed in order the CO_2 derived fuels to reach a competitive level in the global market. For that reason, the drop in electricity prices in the future and the adoption of costly-effective process configuration schemes are necessary.

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