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Techno-economic and exergy analysis of polygeneration plant for power and DME production with the integration of chemical looping CO₂/H₂O splitting / Uddin, Azhar; Ferrero, Domenico; Santarelli, Massimo. - In: ENERGY CONVERSION AND MANAGEMENT. - ISSN 1879-2227. - ELETTRONICO. - 186:(2019), pp. 200-219. [10.1016/j.enconman.2019.02.043]

Availability:

This version is available at: 11583/2726896 since: 2021-02-14T09:36:04Z

Publisher:

Elsevier

Published

DOI:10.1016/j.enconman.2019.02.043

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<http://dx.doi.org/10.1016/j.enconman.2019.02.043>

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1

2 **Techno-economic and exergy analysis of polygeneration plant for power and DME production**
3 **with the integration of chemical looping CO₂/H₂O splitting**

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15 **Abstract**

16 In this paper, we present a novel polygeneration plant with carbon capture for the combined
17 power and dimethyl ether (DME) production. The plant layout integrates a chemical looping
18 CO₂/H₂O splitting (CL) unit producing syngas (CO and H₂) for the DME synthesis using the
19 exhaust gases of an oxyfuel power cycle. The primary power is generated by oxy-combustion of
20 syngas generated by the reduction of the metal oxide in the reduction unit of the CL redox cycle
21 with incoming natural gas. The oxyfuel power plant also generates steam for combined power
22 production with two streams Rankine cycles. The aim of the present work is to assess the process on
23 the basis of energy and exergetic efficiency and economic performance of the integrated CL unit for
24 combined power and DME production. The integration proposed resulted in a production of 103
25 MW_e and 185.6 ton/day (2.15 kg/s) of DME. The corresponding energy and exergetic efficiency
26 was 50.2% and 45%, respectively. A discounted cash flow analysis was performed to evaluate the
27 profitability of the process. With a carbon credit of \$80/tonne, the plant would be able to meet the
28 current electricity with carbon capture and DME prices of \$50/MWh and \$18/GJ respectively. The
29 economic analysis provided information on the main economic drivers associated with the high
30 capital investment in the process plant with individual sub-systems. The analysis highlighted the
31 strong potential of integrating chemical looping CO₂/H₂O splitting for syngas production into
32 polygeneration systems to increase the overall efficiency while reducing the cost of carbon capture.

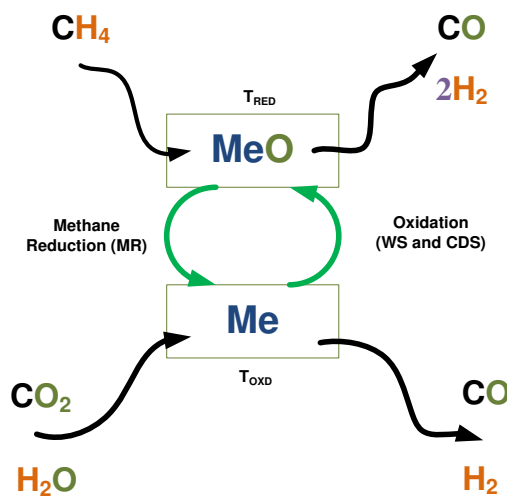
33 **Keywords:** CO₂/H₂O splitting, Chemical looping, Polygeneration, Oxyfuel combustion, Dimethyl-
34 ether (DME), carbon capture.

35 1. Introduction

36 CO₂ emissions from the energy sector – mainly from the combustion of fossil fuels – comprise
37 the largest fraction of the global anthropogenic GHG emissions, representing 58% of the total
38 emissions, as of 2014 [1]. The quest to meet the never-ending energy demand and the rise of
39 emissions is leading to the search for innovative technologies and non-petroleum based alternative
40 fuels which would help in restricting the global warming to 1.5°C above the pre-industrial
41 temperatures (new target set by the recent report by Intergovernmental Panel on Climate Change
42 (IPCC), 2018) [2]. Among the multiple pathways proposed for the reduction of anthropogenic
43 emissions of CO₂, Carbon capture and utilization (CCU) to convert captured CO₂ into valuable
44 products have recently gained much focus as an alternative to Carbon Capture and Storage (CCS)
45 [3–5]. CCU is not only complementary to CCS in some respects but also provides multi-product
46 outputs through the recycling and reuse of the captured CO₂ in several synthesis processes [6–9].
47 Carbon capture in power plants comes with huge energy penalty and loss of efficiency. For
48 example, in oxyfuel natural gas combined cycle (NGCC) power plants, Air separation unit (ASU),
49 used to produce pure oxygen for combustion results in the decrease the efficiency of the
50 conventional NGCC by as much as ~13% [10]. Multiple studies have been proposed to gain this
51 loss of efficiency by alternate methods like the use of ion transport membranes (ITM) for oxygen
52 separation instead of ASU [11] or recycling exhaust flue gas to run a redox cycle with a metal oxide
53 [12]. Polygeneration systems, which can combine efficiently multiple utility outputs (e.g., electrical
54 power, chemicals, fuels etc.) from one or more input in a single system, provide an interesting
55 option for CCU [13]. Besides the potential to gain significant efficiency and local use of the
56 captured CO₂, suitable integration and synergy between different processes also ensure higher
57 flexibility of operation. This would allow varying between the share of products according to their
58 value, for example, related to fluctuating market prices [14]. Multiple configurations of
59 polygeneration systems integrated with CO₂ capture processes have been reported in the literature.
60 Li et al. [15] modelled a polygeneration plant with CO₂ capture for production of power and
61 synthetic natural gas, the proposed arrangement achieving a lower life-cycle energy use and GHG
62 emission with respect to the ultra-supercritical coal power plant. Bose et al. [16] studied a cost-
63 effective production of urea and power combined with CCS using coal gasification. Jana et al [17]
64 reported the improved sustainability through life cycle assessment for a rice-straw based power,
65 ethanol, heating and cooling polygeneration power plant. Huang et al [18] highlighted both
66 energetic and economic benefit of a coal based polygeneration system for power and methanol
67 production as opposed to single coal-to-methanol or coal-to-power systems. Salkuyeh [19] proposed
68 a novel methanol, DME and power production plant from the combined use of coal and natural gas
69 via chemical looping combustion that not allowed complete carbon captured at improved efficiency.

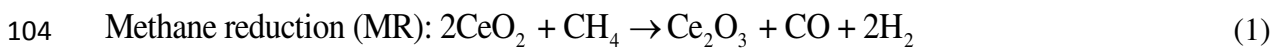
70 Most polygeneration systems designed or proposed till date have employed coal as the fuel
71 [13]. However, oxyfuel combustion using gaseous fuels like natural gas and biomethane has been
72 shown to be the most promising among the low emission technologies (LETs) [12]. Above such,
73 innovative methods for the use of natural gas are being proposed to improve upon the efficiency of
74 natural gas combined cycle power plants, which can reach an efficiency of as high as 57% [20].
75 One such innovative technology is the chemical looping CO₂/H₂O splitting cycle using methane
76 reduction, to produce CO and H₂ [12]. This indeed forms an interesting alternative to the solar

77 thermochemical redox cycle, which has gained attention for CO₂/H₂O splitting to produce syngas
 78 (CO/H₂) utilizing the successful demonstration of water splitting by oxygen carriers [21–24]. For the
 79 solar-thermochemical redox cycle, the metal oxide (also called as oxygen carrier (OC)) undergoes
 80 endothermic thermal reduction (TR) step, thus requiring a very concentrated heat, usually provided
 81 by solar energy under a very high vacuum pressure [25,26]. In the second step, the reduced oxygen
 82 carrier undergoes oxidation by the incoming CO₂/H₂O producing CO/H₂, thereby ensuring a
 83 continuous cycle. The second step is exothermic in nature and operates at near atmospheric
 84 pressures and lower temperature than the thermal reduction creating a temperature and pressure
 85 swing between the two steps. Fuel reduction with methane, however, results in the reduction step to
 86 operate at near atmospheric conditions, thus, avoiding pressure swing operation. Furthermore, it
 87 lowers the reduction temperature, preventing a large temperature swing between the two-steps. An
 88 added advantage is gained from the production of syngas in both the steps of redox cycle
 89 [12,27,28]. Chemical looping (CL) cycle driven by methane reduction (which can be replaced by
 90 bio-methane in future), has an added benefit of being able to operate round the clock, unlike solar
 91 driven cycles that are constrained by the fluctuation of the solar energy source. A basic schematic of
 92 the methane-driven chemical looping CO₂/H₂O splitting cycle is shown in Figure 1.



93
 94 Figure 1. A representative schematic of chemical looping syngas production through methane reduction and
 95 corresponding splitting of water and carbon dioxide.

96 Multiple metal oxide redox pairs have been studied for the CL application [25,26,29]. Among
 97 the materials, cerium (IV) oxide (CeO₂) is considered to be one of the most promising for the
 98 present application due to its strong ability to undergo cyclic redox reactions while retaining its
 99 chemical and structural properties together with high resilience to mechanical stress and
 100 agglomeration resistant [30]. Ceria reduction by methane has been investigated by Warren and
 101 Scheffe [31]. Results indicate that CeO₂ undergoes complete reduction to Ce₂O₃ above 900°C.
 102 Accordingly, the CeO₂/Ce₂O₃ redox pair with reduction of CeO₂ in the presence of methane, and
 103 subsequent oxidation with CO₂/H₂O can be described in terms of the following equations (1-3).





107 By optimally combining the ratio of water and CO_2 in the inlet gas mixture to the oxidation
108 reactor and the temperature of reaction, the desired composition of syngas can be obtained, to be
109 subsequently utilized for production of chemicals (H_2/CO : 1.79) methanol [32,33], (H_2/CO : 2.1) jet
110 fuels [34] and naphtha [34–36], (H_2/CO : 1.76) kerosene and gasoil [36] etc.) through industrial
111 processes.

112 Dimethyl Ether (DME) is one of the most attractive candidates as a synthetic fuel due to its
113 similarity with diesel. Even though DME has a lower LHV than conventional diesel and its use
114 requires pressurization to maintain it in a liquid state at ambient conditions, its physical properties
115 and chemical structure make it a very interesting fuel. Low NO_x , limited hydrocarbon (HC) and
116 almost no SO_x and particulate emissions during the combustion [37,38], are added advantages of its
117 use. However, challenges including the need for re-design of the injector and fuel pump systems,
118 compatibility of sealant materials are current limitations to the complete replacement of diesel by
119 DME in conventional compression ignition engines [37]. In this regard, blending of DME with
120 conventional automotive fuels have been advocated as an important strategy to improve both
121 applicability and economic viability of DME in the short term [37,39]. Furthermore, the unique
122 physico-chemical properties of DME would allow its use as a raw material for the synthesis of
123 aromatics, gasoline, olefins and other chemicals besides direct use as an alternative fuel or a
124 substitute to conventional refrigerants [40]. It is to highlight that DME also gained attention in recent
125 times due to its physicochemical properties are similar to liquid petroleum gas (LPG) giving the
126 chance to retrofit the LPG based automobiles [41]. However, being a synthetic fuel, the price of
127 DME would be constrained by the cost of feedstock, including its transportation, in the present case,
128 natural gas [42]. As per long term future predictions, both diesel and natural gas prices have been
129 projected to rise at an equal steady rate [43,44]. This, even though would allow the relative
130 economic competitiveness of DME with respect to diesel, would increase its cost nevertheless in
131 future. In this regard, research and development for sourcing methane from biomass as biomethane
132 could potentially improve both environmental and economic volatility associated with DME
133 synthesis.

134 DME synthesis is generally classified as i) two-step process (indirect) which uses
135 hydrogenation to produce methanol and then dehydration to DME ii) the second method is one-step
136 (direct) process reported to be more efficient which uses bi-functional catalysts. Both the pathways
137 are commercially viable technology and invested by companies such as Haldor Topsoe, Korea Gas
138 Corporation, Air products, JFE Holdings, Toyo, MGC, Lurgi and Udhe [45,46]. Synthesis of DME
139 using syngas (CO and H_2) from $\text{CO}_2/\text{H}_2\text{O}$ splitting can, therefore, present an interesting pathway for
140 the production of clean fuels using an unconventional process [47,48]. Interestingly, the production
141 of DME by the single step process has been shown to significantly improve the overall process
142 efficiency with respect to both methanol production or the indirect DME synthesis process,
143 providing additional economic impetus to its commercial application [49].

144 Alternative methods to produce syngas by the chemical looping processes has been reported
145 such as chemical looping reforming (CLR), autothermal reforming and chemical looping partial
146 oxidation of methane (CLPOM) [50,51]. CLR and autothermal reforming usually operate at a lower

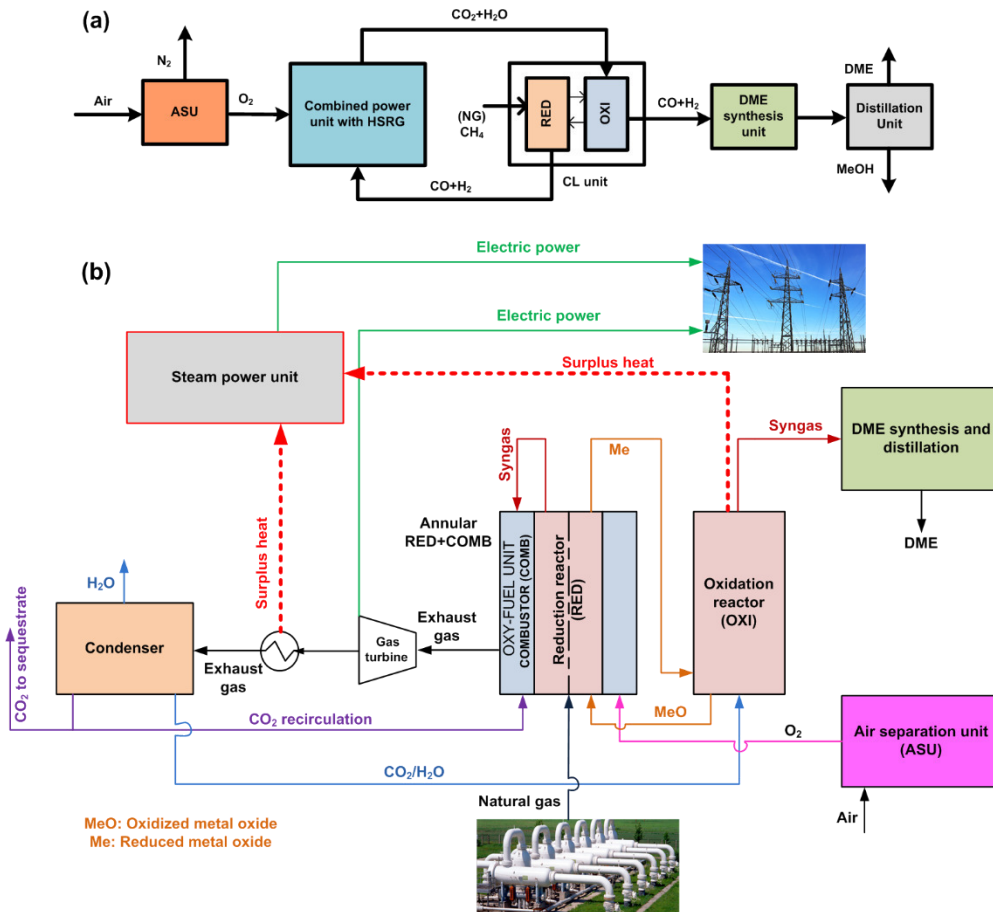
147 temperature of 800-900°C that produces H₂/CO ratio of 2.8-4.8 and 1.8-4.0 respectively with a
148 higher concentration of CO₂/H₂O at the outlet stream. While syngas production by CLPOM needs a
149 temperature above 1300°C with H₂/CO of 1.7-1.8 and also has lower H₂O/CO₂ in the product [52].
150 This makes CLR more suitable for Fischer-Tropsch synthesis for methanol or hydrogen production.
151 However, a novel process of generation of syngas from the exhaust stream and re-use within the
152 power plant for producing additional power has been shown to be a viable alternative to improve
153 the efficiency with 100% carbon capture [12]. Indeed, within a polygeneration scheme, the use of
154 syngas for synthetic fuel production becomes an imperative option. Hankin and Shah [49] in an
155 study explored the process of DME and methanol synthesis from CO₂ and H₂O. Syngas is produced
156 by water electrolysis and solid oxide electrolysis for CO where all the processes such as DME,
157 methanol synthesis, electrochemical electrolysis and solid oxide electrolysis for CO are investigated
158 by assumption of chemical equilibrium. Salkuyeh and Adam II [19] proposed a polygeneration
159 scheme which combines the coal gasification, natural gas reforming by chemical looping processes
160 such as gasification and combustion to produce power, methanol, and DME. The system was tested
161 with iron oxide and nickel oxide oxygen carrier for chemical looping processes with different gains
162 based on the operability of the system. The path for syngas production as feedstock DME was
163 investigated.

164 However, till date, as per the knowledge of the authors, no polygeneration system which
165 integrates the chemical looping CO₂/H₂O splitting (CL) with fuel reduction step and DME and
166 power production have been studied for utility-scale. In this work, an oxyfuel natural gas combined
167 cycle power plant integrated with CL CO₂/H₂O splitting and DME production has been proposed
168 (OXYF-CL-PFG) with a detailed techno-economic, exergetic and environmental assessment. The
169 exergetic study was carried out for the proposed OXYF-CL-PFG layout to identify the sources of
170 irreversibility, with which the proposed layout could be improved and optimized. The analysis
171 includes power production, fuel production, and power consumption, exergy analysis, economic
172 estimation along with the net present value (NPV) with different carbon credit scenarios, as well as
173 efficiency and percentage of carbon captured and recycled.

174 2. Process and plant description

175 The proposed polygeneration scheme is an oxyfuel natural gas fed combined cycle power plant
176 integrated with a chemical looping CO₂/H₂O splitting unit (CL) for power and DME production
177 (OXYF-CL-PFG) shown in Figure 2. To maintain the simplicity of analysis, the gas pre-treatment
178 including sulphur removal has been assumed to have occurred upstream [53] The clean natural gas
179 is sent to the chemical looping (CO₂/H₂O) splitting unit where it is converted into a hydrogen-rich
180 syngas by the simultaneous reduction of ceria. The produced syngas is sent to an oxyfuel unit where
181 it is combusted with pure oxygen from an ASU. The hot combustion products, primarily comprising
182 H₂O and CO₂ are firstly expanded in a gas turbine and then sent in a heat recovery steam generation
183 unit (HRSG). Here, the surplus heat is exploited to produce superheated steam for power production
184 in a bottoming steam cycle. Finally, a water condenser partially separates carbon dioxide and water.
185 The large part of the separated CO₂ can be sequestered for storage or used in other processes, while
186 another fraction together with steam is sent to the chemical looping CO₂/H₂O (CL) unit. In the CL
187 unit, both H₂O and CO₂ are dissociated to H₂ and CO in an oxidation reactor by the reduced ceria
188 from the reduction reactor. The produced syngas from the oxidation reactor is used for DME

189 synthesis. The diluted DME, resulting thus, is cleaned in a distillation unit (or clean-up unit),
 190 additionally producing a secondary fuel stream of methanol. In the following sub-sections, the
 191 methodology adopted for the presented work, along with more details on each unit and their
 192 integration are described.



193

194 Figure 2: General concept of integration of oxy-fueled power unit with chemical looping (CO_2/H_2O) splitting unit and
 195 DME production process (a) block diagram (b) process flow diagram

196 2.1 Simulation Methodology

197 The polygeneration plant has been modelled by combining mass and energy balance equations.
 198 As per the detailed plant layout proposed in Figure 3. Simulations were performed using the
 199 commercial software Aspen Plus v8.8. The characteristic components of the system are the
 200 integrated combustor of the oxyfuel unit and the reduction reactor of the CL unit and oxidation
 201 reactor, the DME synthesis reactor, the DME distillation columns, and the ASU apart from the
 202 standard components of the plant, such as heat exchangers, pumps, compressors, and turbines. The
 203 entire modelling was performed with the assumption of chemical equilibrium with the exception of
 204 the DME reactor, for which a kinetic approach has been used. Therefore, RGIBBS reactor blocks
 205 were used for modelling the oxidation and reduction reactors of the CL unit, as well as the
 206 combustor of the oxyfuel unit. The distillation unit and air separation columns were modelled using
 207 the RADFRAC column. The DME reactor was simulated with an RPLUG reactor using the
 208 Langmuir-Hinshelwood Hougen-Watson (LHHW) kinetic model. During the simulation of this

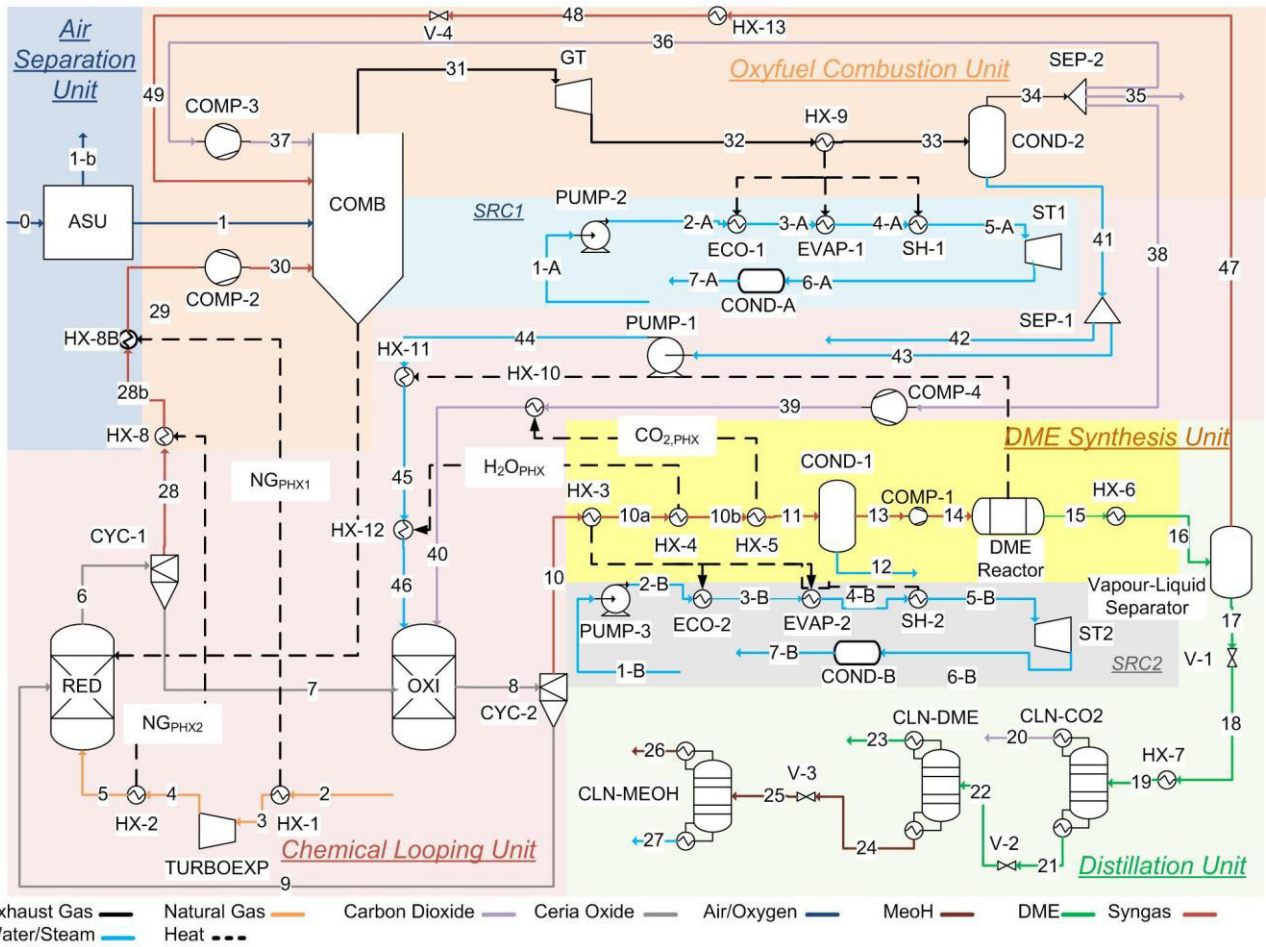
209 component, the Soave-Redlich-Kwong (SRK) EOS model was utilized, which is usually applied to
 210 binary components [54]. Graaf et al. [55] demonstrated that the chemical equilibrium of the
 211 methanol reaction and water gas shift (WGS) reaction can be well described at high-pressure by
 212 using the SRK-EOS model. More details on the modelling approaches followed for the main
 213 components of the plant are given in section 2.1-3.

214 The material streams used in the model involve conventional and solid components. The Peng-
 215 Robinson-Boston-Mathias (PR-BM) property method was used for conventional components, as
 216 this approach was recommended for hydrocarbon processing applications such as gas processing,
 217 refinery, and petrochemical processes [56–58]. This method uses the Peng-Robinson cubic equation
 218 of state combined with the Boston-Mathias alpha function for all the thermodynamic properties
 219 [57]. The oxygen carriers ($\text{CeO}_2/\text{Ce}_2\text{O}_3$) used for the chemical looping simulation were
 220 implemented as conventional pure solid components. For this type of streams, the Barin equation
 221 was used [59,60]. The main hypotheses used in the modelling phase are summarized in Table 1.
 222 CLN-CO₂, CLN-DME, and CLN-MeOH are the columns used in the distillation unit.

223 Table 1. Main assumptions and hypothesis used in the process simulation.

Natural gas	Composition (std.vol%): 93.1% CH ₄ , 3.2% C ₂ H ₆ , 1.6% N ₂ , 1.1% C ₃ H ₈ , 1.0% CO ₂ ; LHV=47.1 MJ/kg [61];	
Oxidation and reduction reactors	Model: RGIBBS, no heat losses; 10°C drop for ceria recirculation from OXI to RED was assumed in order to assess heat losses; Model: RGIBBS;	
Combustor	Model: RGIBBS; $\Delta P=0.2$ bar, no heat losses;	
Compressors, pumps and turbines	$\eta_{\text{is,comp}}=0.9$, $\eta_{\text{mech,comp}}=0.98$, $\eta_{\text{is,pump}}=0.9$, $\eta_{\text{driver,pump}}=0.90$, $\eta_{\text{is,turb}}=0.9$, $\eta_{\text{mech,turb}}=0.98$;	
Oxygen carrier	Solid ceria: $\text{CeO}_2/\text{Ce}_2\text{O}_3$, diameter=100 μm ; Temperature drop of 20°C during ceria recycling from OXI to RED;	
DME reactor	Model: RPLUG multi-tube reactor, Operation: T=250°C P=50 bar;	
Heat exchangers	$\Delta T_{\text{min}}=10^\circ\text{C}$;	
Distillation unit	Model: RADFRAC, Reboiler type: Kettle.	
CLN-CO ₂	CLN-DME	CLN-MeOH
P=10 bar	P=9 bar	P=2 bar

224



226 Figure 3. Detailed polygeneration plant layout OXYF-CL-PFG.

227 **2.2 Polygeneration plant units**

228 **2.2.1 Chemical looping CO₂/H₂O splitting unit (CL unit)**

229 The chemical looping unit consists of two interconnected reduction reactor (RED) and the
 230 oxidation reactor (OXI) operating at 2 bar with the circulating oxygen carrier pair (CeO₂/Ce₂O₃).
 231 The pre-cleaned natural gas, at a grid pressure of 70 bars (stream 2) [62] is heated up at 290°C
 232 and expanded to 2 bar via the turbo-expander (TURBOEXP). Table 1 lists the composition of natural
 233 gas at the inlet to the plant (without H₂S). The preheating is necessary to prevent an outlet
 234 temperature of the natural gas (stream 4) from the turbo-expander lower than 0°C. After the
 235 expansion of the natural gas, it is heated to 890°C (stream 5) and fed to the RED. For the
 236 endothermic reduction reaction, external heat is mandatory to maintain the reaction temperature.
 237 Ceria reduction by methane occurs above 900°C to achieve full conversion to CO and H₂ as well as
 238 a reduction to Ce₂O₃ [31]. From the thermodynamic studies, it was found that 40 to 60% excess
 239 flow of methane is required to ensure complete conversion of OC below 950°C. It was also found
 240 that the most suitable methane to ceria flow ratio (CH₄/CeO₂) for the reduction reactor was 0.7
 241 instead of the stoichiometric ratio of 0.5. Here CeO₂ (stream 9), at an inlet temperature of 1312°C
 242 as a result of the exothermic oxidation reaction, is completely reduced with natural gas, producing a
 243 syngas in a 2:1 H₂/CO ratio (reaction 1) and unreacted natural gas [12]. As for the external heat
 244 source to sustain the reaction in the RED, it has been proposed to use a part of the heat generated in

245 the oxyfuel combustion chamber. To this end, a reduction reactor thermally integrated with the
246 oxyfuel combustion chamber was proposed utilizing an annular combustion chamber design already
247 analyzed by Khan and Shamim [63] (see Figure 2 (b)). The hot syngas (stream 6) produced in RED
248 exits it at 900°C and is separated from the solid (stream 7) by a cyclone (CYC-1), cooled and sent
249 to the oxyfuel unit. The reduced ceria is fed, without an intermediate heat recovery, into the OXI
250 where it is then oxidized (reactions 2 and 3) by a gas mixture coming from the oxyfuel unit. The gas
251 mixture of 60% H₂O and 40% CO₂ (stream 40 and 46) is necessary to ensure an H₂:CO ratio of 1:1,
252 ideal for DME production, as described in section 3. It is observed that in order to achieve a full
253 oxidation of Ce₂O₃, a 60% excess of the gas mixture is required. Before the oxidation, both water
254 and carbon dioxide is compressed at the operating pressure of OXI (2 bar), respectively with a
255 pump (PUMP-1) and a compressor (COMP-4), and heated up at 500°C. Since the reactions in the
256 oxidation reactor are exothermic and the reactor itself is set as adiabatic, the outlet temperature of
257 the reactor goes to 1322°C. The hot syngas produced is separated from the oxidized ceria by the
258 cyclone separator (CYC-2), cooled down (stream 10, 10a, 10b, 11) and sent to the DME unit, while
259 the solid stream is re-circulated back for a new reduction cycle (stream 9).

260 2.2.2 Air separation unit (ASU)

261 The ASU consists of a cryogenic distillation unit able to produce 99.99% pure O₂. The
262 schematic of the ASU layout is shown in Figure 4. The air is separated into two thermally
263 interconnected distillation columns, HP-COL and LP-COL, which work at 5 and 1.2 bar
264 respectively [64–66]. The overall refrigeration is driven by the expansion from high pressure (30
265 bar) of the compressed air (stream 6-C and 7-C, which become 14-C and 16-C respectively, after
266 cooling down in HX-2C) through the VALVE-2 and the TURBOEXP-2C. The inlet air (1-C) is
267 compressed at 6.3 bars by the compressor COMP-1C and separated in two streams (4-C and 8-C)
268 by the splitter SPLIT-1C. The stream 8-C is cooled down (becoming 9-C in the figure) in the
269 exchanger HX-2C by the cold products (stream 19-C) of the LP-COL and then is sent to the HP-
270 COL. The HP-COL is a 40 stages distillation column which produces N₂-rich gaseous (stream 12-
271 C) from the top and an O₂-rich liquid stream (stream 10-C) from the bottom. The latter stream is
272 further cooled down through Joule-Thomson effect in the valve VALVE 1-C and fed in the 56 stage
273 low-pressure column. The low-temperature air streams 15-C and 17-C, together with the rich-in O₂
274 liquid stream 11-C, provide the necessary refrigeration in the LP-COL to obtain pure N₂ (stream 20-
275 C) from the top and from the bottom condenser the pure O₂ (stream 18-C) is produced. The latter is
276 pumped by the PUMP-1C at the operational condition of the combustor (26 bar) in the oxyfuel unit
277 and heated in the HX-2C to 80°C. The stream data is listed in Table S1 of the supplementary data
278 file.

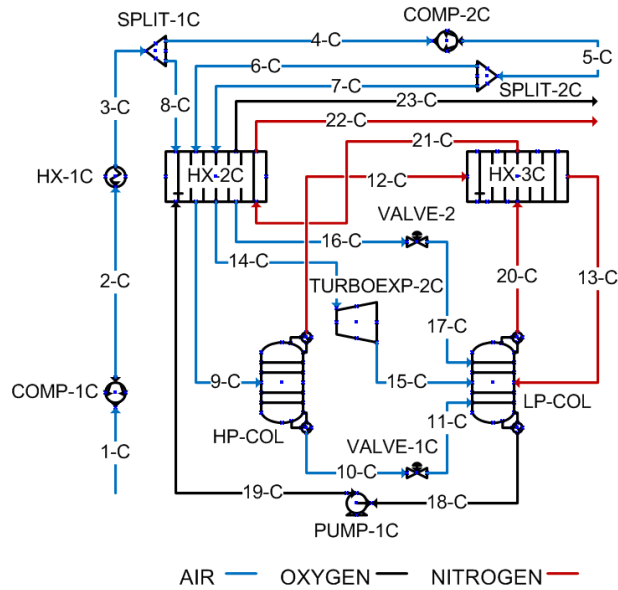


Figure 4. Detailed layout of the air separation unit

279
280
281

282 2.2.3 *Oxyfuel combustion unit*

283 In this unit, combustion of syngas is performed with oxygen instead of air. This eliminates the
284 presence of nitrogen in the exhaust gases that would have affected the subsequent CO₂ separation
285 process. Another advantage is a substantial reduction in thermal NO_x due to the absence of nitrogen
286 [67].

287 The primary unit of the oxyfuel unit is the combustor (COMB), where the syngas from the
288 reduction (stream 30) and the non-condensable gases from the clean-up unit (stream 49, mainly CO₂
289 with CO and H₂) are burnt with a 5% excess oxygen stream derived from the ASU (stream 1). The
290 temperature control within the COMB is maintained by recycling a part of the captured CO₂
291 (Stream 36). The recirculation ratio was set so as to achieve a combustor outlet gas temperature of
292 1377°C in agreement to the limits of the turbine inlet temperature of commercial gas turbines as
293 stated and selected from literature [14,68–70]) while simultaneously providing the required heat
294 sustain the ceria reduction reaction in the RED. The CO₂ and syngas streams entering the COMB
295 are compressed to 26 bar with two two-stage compressors (COMP-2 and COMP-3). The flue gas
296 exiting the combustion chamber is firstly expanded in a two-stage gas turbine GT (26 bar to 5 bar
297 and 5 bar to 1.05 bar) and then sent to the heat recovery steam generator (HX-9) for the generation
298 of steam for the steam power cycle SRC1. More details on the steam power cycle are given in
299 section 2.2.4. Finally, the CO₂ from the exhaust gas is separated from the water in a condenser
300 (COND-2), generating highly pure CO₂ stream that is split into three parts. One part is recirculated
301 to the combustor (stream 36), one is sent for sequestration or other applications (stream 35) and the
302 last part (stream 38) is sent to the oxidation reactor for dissociation (OXI).

303 2.2.4 *Steam power cycle*

304 Two steam Rankine cycles (SRC1 and SRC2) are included in the system layout. The extra heat
305 available within the polygeneration system is exploited to produce steam by heat recovery steam
306 generators (HRSGs), which expands in steam turbines to generate power. The turbines and the

307 HRSGs were modelled as simple units, without reheating or multi-pressure systems. In fact, as the
 308 primary objective of the present study is to understand the benefits deriving from polygeneration by
 309 integration of a chemical looping unit in a conventional oxyfuel plant, the optimization of the
 310 system was not further considered. The SRC1 uses the heat of the flue gases from the oxyfuel unit
 311 (stream 32) to produce super-heated steam (125582 kg/h) at 150 bar and 550°C (stream 5A),
 312 generating an electrical power of around 44 MW while expanding in the turbine (ST1). The SRC2
 313 uses the extra heat from the chemical looping unit to produce a smaller flow of steam (8305 kg/h) at
 314 the same condition as that of stream 5A (stream 5B), generating 3 MW in ST2. The reason for the
 315 choice of two HRSGs connected to two different steam cycles is to ensure flexible operation by
 316 minimizing the influence of DME and power production over each other.

317 2.2.5 DME synthesis unit

318 In this unit, the syngas produced in the oxidation reactor (stream 10) is converted into liquid
 319 fuel within the catalytic reactor. Before the syngas is fed to the DME reactor, it undergoes
 320 condensation (COND-1) to completely remove H₂O at atmospheric pressure. The operating
 321 conditions of the DME reactor have been selected from the work of Pozzo et al. [71] fixing the
 322 pressure at 50 bar and the temperature at 250 °C. In order to reach the operating pressure of the
 323 reactor, the dried syngas (stream 13) is compressed by a three-stage compressor at 50 bar (COMP-
 324 1). The DME reactor is a fixed bed reactor which is kept at the constant temperature of 250°C by a
 325 water-jacket cooler used for saturated steam generation at 2 bar (stream 44) for the oxidation (OXI)
 326 reactor.

327 The DME reactor was considered as a multi-tube fixed bed reactor. Each tube contains the dual
 328 catalyst (physically mixed) with a bed voidage of 0.45. The total density of the catalyst particles is
 329 an average of the density of the two catalysts, Cu/ZnO/Al₂O₃, and γ -Al₂O₃, used in the 1:2 optimal
 330 ratio. The parameters used for the DME reactor are listed in Table 2.

331 Table 2 Fixed parameters for DME reactor design.

N° tubes	Diamater [m]	Bed voidage	density Cu/ZnO/Al ₂ O ₃ [kg/m ³]	density γ - Al ₂ O ₃ [kg/m ³]	ρ average [kg/m ³]	Temperature (°C)	Pressure (bar)
5000	0.02	0.45	1200	1470	1380	250	50

332

333 2.2.6 DME distillation unit

334 The produced DME contains significant impurities, requiring a separation or distillation unit to
 335 obtain pure dimethyl ether. The distillation plant comprises a cooling and a gas-liquid separation
 336 unit. The cooling unit, represented in the layout by a vapour-liquid separator (VLS), is used to
 337 produce chilled streams at -40°C resulting in a liquid stream of DME with dissolved CO₂ and
 338 MeOH (stream 17) and a gas stream of incondensable gases, namely, H₂, CO, undissolved CO₂ and
 339 traces of other diluents (steam 47). The gas stream is re-circulated into the oxyfuel unit and burnt,
 340 while the liquid stream is further processed in the gas-liquid separation unit. The gas separation unit
 341 is composed of three different distillation columns: CLN-CO₂, CLN-DME, and CLN-MEOH (Table
 342 3). The first one is used to separate the dissolved CO₂, the second to produce a pure 99% DME and
 343 the last one to separate the methanol from the water. Thus, an additional fuel as methanol is

344 generated as a by-product of DME distillation. A valve and a heat exchanger are placed before each
 345 column in order to adjust the pressure to the optimal value and to have 50% of vapor in the inlet
 346 stream [71]. The number of stages used in the distillation columns was estimated by increasing
 347 them until a certain change in composition was detected.

348 Table 3 Distillation unit operation parameters.

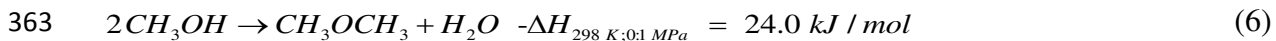
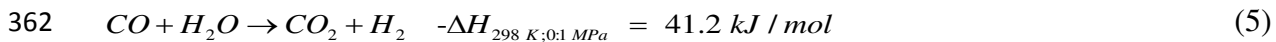
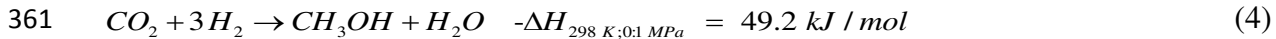
Column	T _{REB} [°C]	Q _{REB} [MW]	T _{cond} [°C]	Q _{cond} [MW]	Number of stages	Feed-in stage	Purity of the product [%]
CLN-CO ₂	45.87	1.12	-40.83	-0.64	25	10	-
CLN-DME	150.99	0.93	42.57	-0.55	30	24	99.1
CLN-MeOH	101.53	0.03	66.36	-0.05	24	18	94.1

349

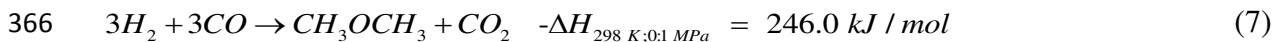
350 3. Synthesis of DME

351 3.1 Reaction scheme

352 DME production can be realized in two steps (methanol and DME are produced in two different
 353 reactors) or in a single step adopting a dual catalyst. The disadvantage of the two-step process is
 354 that syngas conversion to methanol is significantly limited by equilibrium and thermodynamic
 355 constraints [72]. The conversion of methanol to DME in the single step process shifts the
 356 equilibrium toward more methanol production. Consequently, the direct DME synthesis is
 357 thermodynamically and economically preferable than the two steps process [73–75] and hence
 358 selected in the present study. The overall process can be described by three main reactions: the
 359 syngas conversion to methanol (reaction (4)), water gas shift (reaction (5)) and methanol
 360 dehydration to DME (reaction (6)).



364 The overall reaction to synthesize the syngas to DME route is represented by the combination
 365 of reactions (4), (5) and (6) into reaction (7):



367 The overall reaction is exothermic and generates two molecules of products from six molecules
 368 of reactants. Hence, according to the Le Châtelier principle [76], conversion is favored working at
 369 high pressure and low temperature.

370 3.2 Reaction kinetics

371

372 The DME reactor was simulated in Aspen Plus with an RPLUG reactor combined with a
 373 Langmuir-Hinshelwood Hougen-Watson (LHHW) kinetic model based on three simultaneous
 374 reactions (Eqs.4,5,6). Bi-functional catalyst Cu/ZnO/Al₂O₃:γ-Al₂O₃ with a loading ratio of 1:2 has
 375 been selected from the literature, with the Cu/ZnO/Al₂O₃ active for the methanol synthesis, while

376 the γ -Al₂O₃ component catalyzes the methanol dehydration [72] among the other presented in the
 377 literature the selected is most investigated [77]. The details of the catalyst properties are reported in
 378 Table 2. The kinetic model adopted in the present simulations has been extensive used in the
 379 literature [14,71,78–80]. The rate expression for CO₂ hydrogenation, RWGS, methanol dehydration
 380 is given by equations (8-10) [72,81,82].

$$381 \quad r_{CO_2 \text{ hydrogenation}} = \frac{k_1 (p_{H_2} \cdot p_{CO_2}) \left[1 - \left(\frac{1}{K_{eq,1}} \right) \frac{p_{CH_3OH} \cdot p_{H_2O}}{p_{CO_2} p_{H_2}^3} \right]}{\left(1 + k_2 \frac{p_{H_2O}}{p_{H_2}} + \sqrt{k_3 \cdot p_{H_2}} + k_4 \cdot p_{H_2O} \right)^3} \quad (8)$$

$$382 \quad r_{RWGS} = \frac{k_5 \cdot p_{CO_2} \left[1 - \frac{1}{K_{eq,2}} \frac{p_{CO} \cdot p_{H_2O}}{p_{CO_2} \cdot p_{H_2}} \right]}{1 + k_2 \frac{p_{H_2O}}{p_{H_2}} + \sqrt{k_3 \cdot p_{H_2}} + k_4 \cdot p_{H_2O}} \quad (9)$$

$$383 \quad r_{MeOH \text{ dehydration}} = \frac{k_6 \cdot K_{CH_3OH}^2 \left[[\Pi]_{CH_3OH}^2 - \left(\Pi_{H_2O} \cdot \frac{\Pi_{DME}}{K_{eq,3}} \right) \right]}{\left(1 + 2 \sqrt{K_{CH_3OH} \cdot \Pi_{CH_3OH}} + K_{H_2O} \cdot \Pi_{H_2O} \right)^4} \quad (10)$$

384 Reaction rates of equation (8-10) are expressed in kmol/kg_{cat} s, p is the partial pressure of the
 385 gases in Pa and Π the concentration expressed in kmol/m³. The equilibrium constant (K_i) and
 386 constant rate (k_i) values used to determine the reaction rates are shown in Table 4.

387 Table 4. Kinetic parameters used in DME synthesis.

	Pre	unit	B	unit
k_1	1.07×10^{-13}	(kmol/(kg·sPa ²))	36,696	(J/mol)
k_2	3450	-	0	(J/mol)
$k_3^{0.5}$	1.578×10^{-3}	Pa ^{-0.5}	17,197	(J/mol)
k_4	6.62×10^{-16}	Pa ⁻¹	124,119	(J/mol)
k_5	122	(kmol/(kg s Pa))	-94,765	(J/mol)
k_6	1.486×10^{11}	(kmol/(kg s))	-143,666	(J/mol)
K_{CH_3OH}	5.39×10^{-4}	m ³ /kmol	70,560.92	(J/mol)
K_{H_2O}	8.47×10^{-2}	m ³ /kmol	42,151.98	(J/mol)

388

389 These parameters refer to the Arrhenius equation shown by equation (11).

390 $k_i = (\text{Pre})_i \times \exp\left(\frac{B_i}{RT}\right)$ (11)

391 where B represents either the activation energy or the reaction enthalpy or a combination of both
 392 [81] as in LHHW kinetic mechanism the rate constants are represented as combination of rate
 393 constants and equilibrium constants. The following expressions were used to determine the
 394 equilibrium constants [55,81,83].

395 $\log_{10} K_{eq,1} = \frac{3066}{T} - 10.592$ (12)

396 $\log_{10} (1 / K_{eq,2}) = -\frac{2073}{T} + 2.029$ (13)

397 $\ln K_{eq,3} = \frac{3220}{T} - 1.7$ (14)

398 The model was used to perform a sensitivity analysis of methanol and DME yield using the
 399 equations (15) and (16) varying the composition of the inlet stream, H₂:CO ratio, and the amount of
 400 the diluent H₂O and CO₂.

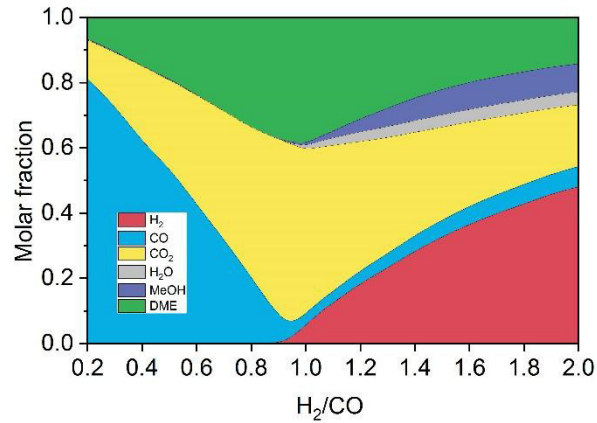
401 $DME_{yield} = \frac{DME_{out}}{(CO + CO_2)_{in}}$ (15)

402 $MeOH_{yield} = \frac{MeOH_{out}}{(CO + CO_2)_{in}}$ (16)

403 Where DME_{out} and MeOH_{out} are the DME and methanol molar flow at the outlet of the reactor
 404 (stream 15) and CO and CO₂ the molar flow at the inlet (stream 14).

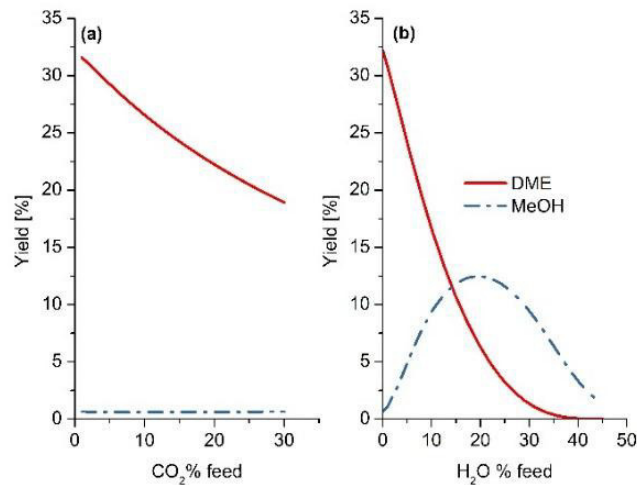
405 As shown in Figure 5 the highest DME yield is obtained by feeding a syngas with an H₂/CO =1
 406 with a positive effect of having the main byproduct of the reaction as CO₂ which can be easily
 407 separated from the DME and MeOH in the separation unit which is verified from the results
 408 reported by Ogawa et al [41] . At H₂/CO=1, the DME yield was 38.6% and MeOH yield was 0.8%
 409 which are similar to the results reported by Pozzo et al [71]. It is observed that with increasing the
 410 CO₂ content at the inlet feed, the DME yield decreases. This is attributed mainly to two factors.
 411 Firstly, the methanol synthesis is retarded with the increase of CO₂ content [84] as CO₂ molecules
 412 are absorbed by the methanol catalyst by occupying the active sites quicker than CO and H₂,
 413 affecting the MeOH production and consequently also the DME synthesis [85] as shown in Figure
 414 6(a). Secondly, with a high CO₂ concentration in the feed of the DME reactor, the beneficial effect
 415 of the water gas shift reaction would get decreased. The water formed is removed by WGS
 416 producing hydrogen which kinetically advances the methanol production. Therefore, the higher CO₂
 417 favors the reverse-water gas shift that reduces the hydrogen content and produces more water. The
 418 effect of higher water content at the inlet is even worse than CO₂ and it can be seen in Figure 6(b).
 419 The high water percentage shifts the methanol dehydration towards the reactants, increasing the

420 MeOH yield while reducing the DME yield. With a water percentage higher than 20%, also
 421 methanol production is penalized. In addition, the water tends to deposit near the catalyst
 422 accelerating the catalyst degradation [41]. Therefore, to increase the DME production it is necessary
 423 to have at the inlet of the DME reactor a syngas composed by an equimolar H₂-CO mixture, reduce
 424 the CO₂ percentage (molar fraction) in the 0-5% range and remove as much as possible the water
 425 content.



426

427 Figure 5: Influence of the H₂/CO ratio on the equilibrium synthesis of DME at T=250°C and p=50 bar.



428

429 Figure 6: a) Influence of the CO₂ and b) H₂O on the equilibrium synthesis of DME at T=250°C and p=50 bar.

430 4. Results

431 4.1 Effect of operating conditions

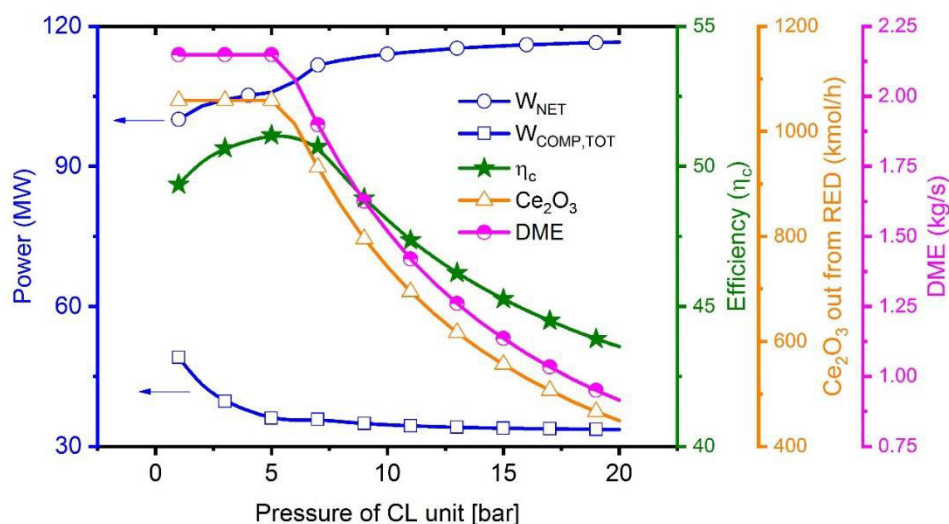
432 A sensitivity analysis of the most influential parameters – namely: the operating pressure of the
 433 chemical looping CO₂/H₂O splitting unit, outlet temperature of reduction reactor, CO₂/H₂O
 434 composition in the oxidation reactor of the CL unit, and turbine inlet temperature – was performed
 435 to maximize the global efficiency of the plant (Eq. 17) and the DME production.

436
$$\eta_c = \frac{\dot{m}_{DME} \cdot LHV_{DME} + \dot{m}_{MEOH} \cdot LHV_{MEOH} + W_{NET}}{\dot{m}_{NG} \cdot LHV_{NG}} \quad (17)$$

437 where: \dot{m}_{DME} , \dot{m}_{MeOH} represent the DME and MeOH streams produced (kg/s), while LHV_{DME} ,
 438 LHV_{MeOH} , and LHV_{NG} are the lower heating value (MJ/kg) of DME, MeOH and natural gas
 439 respectively, and W_{NET} is the net power (MW) produced inside the plant with \dot{m}_{NG} being the natural
 440 gas stream feed into the plant (kg/s).

441 4.1.1 Chemical looping ($\text{CO}_2/\text{H}_2\text{O}$) splitting (CL) unit pressure

442 Figure 7 shows the effect of varying the pressure of the chemical looping unit, where both
 443 oxidation and reduction reactors work at the same pressure. With the increase of pressure of the CL
 444 unit, an efficiency gain is observed from 49.4% at 1 bar to 51.1% at 5 bar. This can be attributed to
 445 the fact that a significant saving of the auxiliary power compression ($W_{\text{COMP,tot}}$ in Figure 7) is
 446 obtained by reducing the pressure ratio of syngas compression. However, with a further increment
 447 of the pressure, the efficiency decreases, dropping down to 43.6% with 20 bar of pressure. Based on
 448 the Le Châtelier principle, it can be understood that the reaction in the RED reactor is not
 449 thermodynamically favored at high pressure since the reduction reaction has three moles of
 450 reactants and four moles of products. In fact, it can be seen that over 5 bar the amount of reduced
 451 ceria (Ce_2O_3 line in Figure 7) at the outlet of the reactor decreases. This results in a lower syngas
 452 production from the OXI reactor, as less reduced ceria is available, subsequently, the DME
 453 production drops effecting the overall plant efficiency. DME production drops after 5 bar pressure
 454 and it does not vary between 1 to 5 bar while the W_{NET} increases very slowly from 100 to 105 MW.
 455 The CL unit pressure can be fixed to 2 bar as the benefit of working at higher pressure is offset by
 456 the power required to maintain pressure drop while working with solids.



457

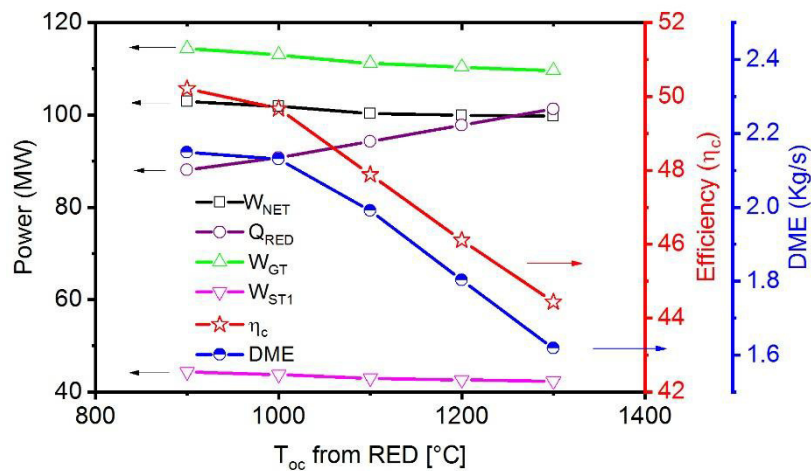
458 Figure 7 Influence of chemical looping unit pressure on efficiency η_c , W_{NET} , Ce_2O_3 outlet from RED and $W_{\text{COMP,tot}}$
 459 ($=W_{\text{COMP-1}}+ W_{\text{COMP-2}}+ W_{\text{COMP-3}}$).

460 4.1.2 Outlet temperature of the RED reactor

461 Another fundamental parameter is the outlet temperature of the OC from the RED. It is found
 462 that below 900°C there is no complete metal oxide conversion, similar to the results observed by
 463 Warren and Scheffe [31]. Therefore, all the analysis were performed considering reduction
 464 temperature above 900°C . A higher OC temperature at the outlet of the reactor, inherently demands

465 more heat supply. Since this heat is derived from the heat of combustion, to have higher RED
 466 temperature, less CO₂ needs to be recirculated to the combustion chamber. This, even though results
 467 in a corresponding drop in the power spent for recycling CO₂, also implies a lower mass flow
 468 through the GT, producing less power, as shown in Figure 8. Such would then lower the power
 469 produced by the ST1 as well, notwithstanding the higher temperature of the GT outlet, and hence
 470 decreasing the net power output. In addition, a higher outlet temperature of RED also restricts the
 471 effective operation of the OXI. In fact, since both the CO₂ and H₂O splitting reactions are
 472 exothermic, by principle, this requires the reactions to take place at a lower temperature. Moreover,
 473 the water-splitting reaction has a higher exothermicity than CO₂ splitting with Ce₂O₃; thus, a higher
 474 temperature would result in a slower reaction rate for H₂O splitting, resulting in a CO-rich syngas.
 475 This effect is evident in Figure 8, in which a significant drop in the DME production can be seen
 476 beyond 1000°C (from 2.15 kg/s for 900°C to 2.13 kg/s at 1000°C and to 1.99 kg/s at 1100°C) due to
 477 a deviation from the ideal H₂-CO ratio and higher concentration of CO₂ in the produced syngas
 478 stream (Figure 9).

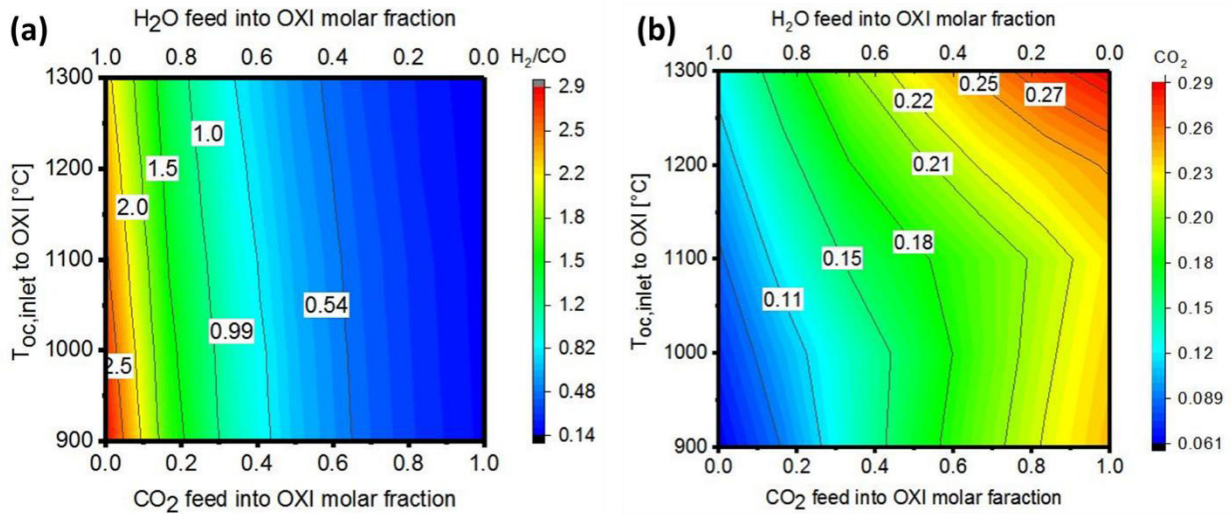
479 DME is one of the primary products of the proposed polygeneration system, a decrease in the
 480 DME production has a dramatic impact on the plant efficiency, as clearly observed in Figure 8
 481 where the drop in the DME yield drives the trend of the decrease in the overall plant efficiency. To
 482 be more specific, a relative drop of 10.5% in efficiency is observed between 1000°C and 1300°C,
 483 corresponding to an in DME production of 24% and a relative net power output drop of 2%.



484
 485 Figure 8 Influence of the metal oxide outlet temperature of RED on efficiency (η_c), W_{NET} , W_{ST1} , W_{GT} , Q_{RED} , and DME
 486 production

487 Figure 9 shows the effect of the metal oxide inlet temperature to the OXI on the H₂/CO ratio in the
 488 syngas and on the CO₂ content in the syngas after water removal. As mentioned before, water
 489 splitting is favored at a lower temperature compared to CO₂ splitting due to the higher
 490 exothermicity of the reaction. Hence, in order to have the ideal H₂/CO = 1 for DME production, it is
 491 necessary to send an increasingly H₂O rich mixture with the higher temperature to the OXI. In fact,
 492 with the increase of the OC temperature, the water splitting is further penalized and consequently, a
 493 higher H₂O content ranging from 60% to 74% for OC temperature from 900-1300°C. In addition, as
 494 already explained in section 2.2.5, the dilution of syngas with CO₂ has to be avoided in order to
 495 enhance DME production. As shown in Figure 9(b), even if it might be possible to produce the ideal
 496 composition of syngas (i.e., 1:1 H₂/CO ratio) for any metal oxide temperature inlet, the CO₂ content

497 increases at higher temperatures. For this reason, it is suitable to work with lower ceria inlet
 498 temperature (900-1000°C) to avoid CO₂ dilution.

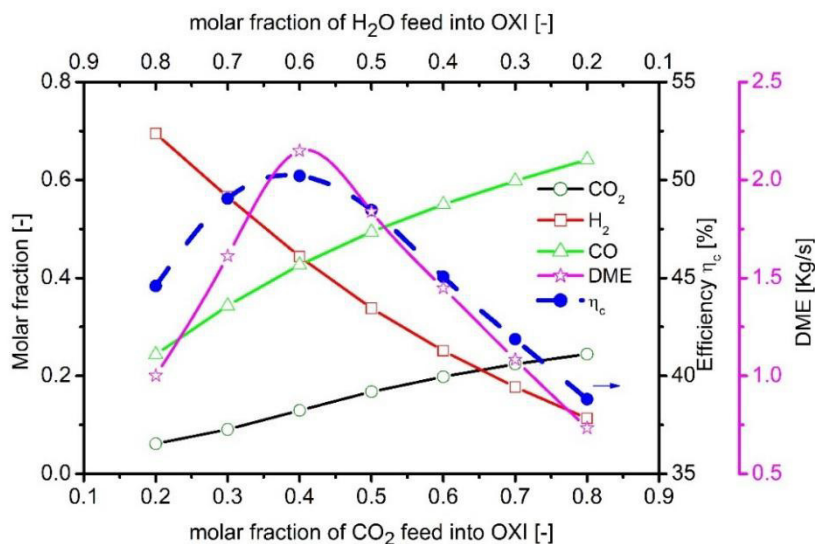


499

500 Figure 9 Effect of the gas mixture composition fed into OXI on a) final syngas H₂/CO ratio, b) CO₂ content (molar
 501 fraction) in the syngas after water removal.

502 *4.1.3 Composition of inlet gas mixture to the OXI*

503 Figure 10 describes the effect of the variation of the gas mixture composition at the inlet of the
 504 OXI on plant performance. The maximum efficiency of 50% is achieved with an OXI inlet mixture
 505 of 60% of H₂O and 40% CO₂. In such a condition, the OXI outlet gas has the equimolar H₂:CO
 506 ratio (i.e., H₂ and CO curves intersect) which reflects the maximum DME production. Similar
 507 claims has been presented by Ohno et al [86].

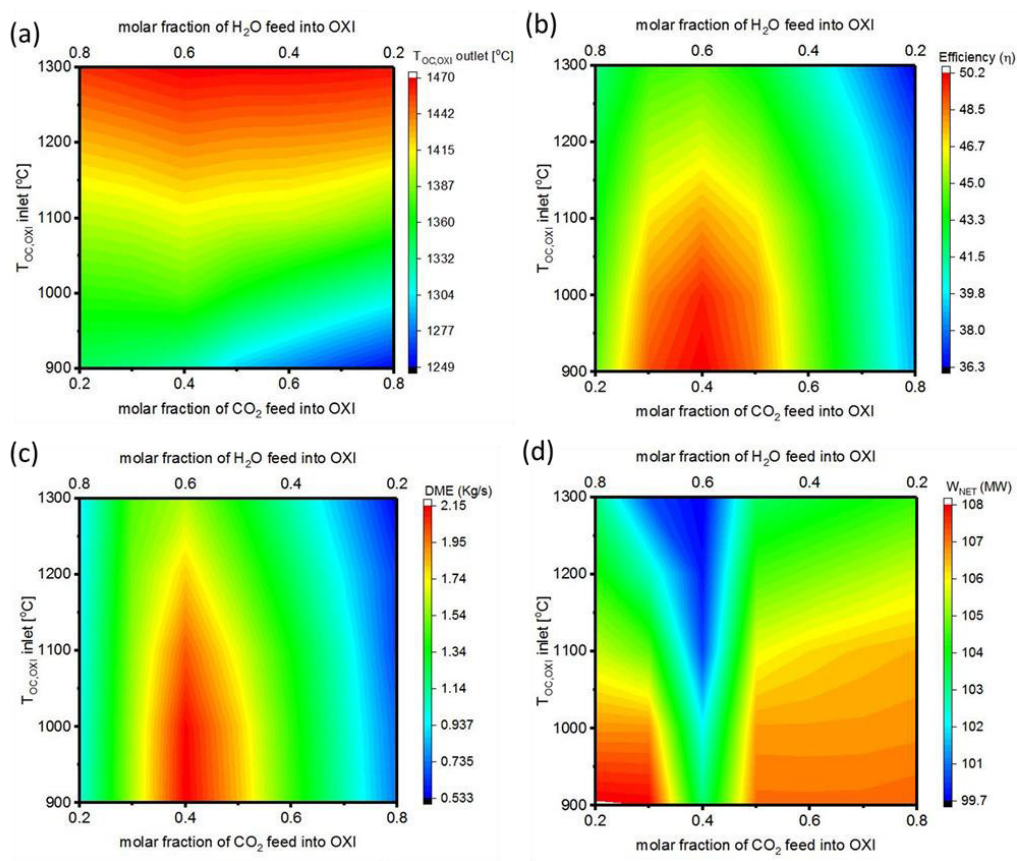


508

509 Figure10 Influence of the gas mixture composition at the inlet of the OXI reactor on the plant performance by
 510 considering a metal oxide outlet temperature from the RED equal to 900°C.

511 Increasing the water content in the feed to OXI reactor increases outlet metal oxide temperature
 512 (Figure 11(a)) as water splitting is more exothermic than CO₂ splitting reaction. In the proposed

513 OXYF-CL-PFG plant layout, the oxidized ceria is recirculated back to the reduction reactor without
 514 intermediate heat recuperation. Hence, a higher temperature of oxidized ceria at the outlet of OXI
 515 results in a higher inlet temperature of OC to the RED which thereby reduces the heat requirement
 516 for the reduction reaction. Due to inlet higher temperature of OC to the RED reactor, the heat
 517 requirement from the combustion chamber reduces and therefore, the recirculation of CO₂ to the
 518 combustion chamber to maintain the temperature of the outlet would be increased. With this, the
 519 power output from the gas turbine (GT) increases as higher flow expands which increases the net
 520 power production, as seen in Figure 11(d). As stated earlier, this can be possible with the higher
 521 H₂O concentration in the feed of OXI which increases the H₂/CO ratio more than unity leading to
 522 the drop in DME production and overall efficiency (see Figure 11(b) and (c)). Therefore, an ideal
 523 H₂/CO ratio feed to DME reactor, even though leads to lower overall net power, however, ensures
 524 the highest efficiency of the polygeneration unit, as can be understood from Figure 11(d). In the
 525 case of a non-ideal H₂/CO ratio being fed to the DME reactor, it leads to a lower conversion with
 526 unreacted syngas in the product stream. Even though after distillation, this is recycled to the
 527 combustor increasing the power, but reduces the DME production and thus, the overall efficiency of
 528 the plant.

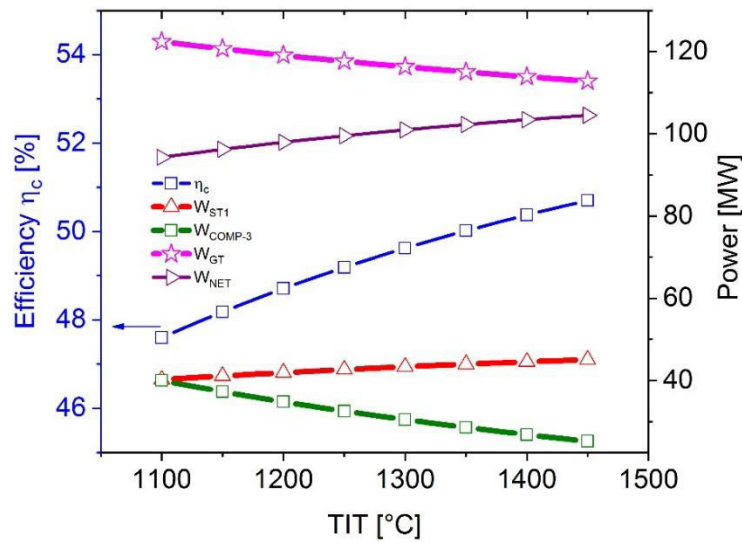


529
 530 Figure 11 Effect of the gas mixture inlet composition and metal oxide inlet temperature ($T_{OC,OXI}$ inlet) on (a) the
 531 temperature of the metal oxide outlet, (b) plant efficiency, (c) DME production, and (d) net power.

532 *4.1.4 Gas turbine inlet temperature*

533 Finally, the impact of the gas turbine inlet temperature (TIT) was analyzed. It can be said from
 534 Figure 12 that with an increase of TIT the efficiency and net power produced are positively
 535 influenced. Nevertheless, the output from the GT drops, which is the result of a lower recirculation

536 of CO₂ to the combustor, needed to ensure a higher combustor exit temperature and consequently a
 537 higher TIT. This also causes a lower gas volume to be expanded within the GT, resulting in a lower
 538 power output, even though a partial compensation of the lost work is obtained by the lower
 539 compression work for the recirculated CO₂ in COMP-2. The power produced by the steam turbine
 540 ST1 increases slightly due to a higher exhaust temperature from the GT, overcoming the lower
 541 overall gas flow rate. For a TIT of 1100°C, the efficiency of 47.6% was obtained, which increases
 542 to 50.7% for a TIT of 1450°C.



543

544 Figure 12 Effect of the gas turbine inlet temperature TIT on the efficiency of the plant (η), power produced by the steam turbine
 545 (W_{ST1}), by the gas turbine GT (W_{GT}) and the power absorbed by the COMP-3 (W_{COMP-3})

546 4.2 Plant performance

547 Based on the sensitivity analysis the following operating parameters were chosen:

- 548 – chemical looping operation pressure of 2 bar;
- 549 – 40% CO₂ and 60% H₂O in the gas mixture feed to the oxidation reactor with an excess of
 550 60% with respect to the stoichiometry as per the Ce₂O₃ inlet to OXI;
- 551 – reduction reactor outlet temperature 900°C;
- 552 – TIT of 1377°C.

553 The plant performance based on the listed parameters is summarized in Table 5. Overall, the
 554 plant produces 102.90 MW_e, 185.6 ton/day (2.15 kg/s) of DME and 2.59 ton/day (0.03 kg/s) of
 555 methanol with a total efficiency of 50.21% and a DME yield of 24.9% (as per equation (8)). The
 556 highest power consumption is represented by the COMP-3 for the recycle of the CO₂ followed by
 557 the compression work in the ASU which accounts for 17% and 11.5% of the gross power generated
 558 respectively. Table 6 lists the composition and main thermodynamics parameters of major streams.

559 The inlet stream to the DME reactor (stream 14) has the ideal H₂/CO =1 ratio, while the CO₂
 560 content is 13%. However, it can be seen in Figure 11(b), that the minimum CO₂ percentage which
 561 can be achieved from the oxidation reactor is near 6%, even though not producing the equimolar
 562 mixture of H₂/CO. Therefore, the actual plant configuration allows producing a syngas with a
 563 composition which diverges from the ideal H₂/CO ratio of syngas. A solution might be to propose

564 two distinct oxidation reactors, one for the CO₂ splitting and another for the water-splitting.
 565 However, this will lead to two different oxidized metal oxide temperatures, complicating the system
 566 design dynamics and operations.

567 An encouraging result is that the proposed oxyfuel-NGCC cycle with the chemical looping and
 568 DME unit permits to cut the efficiency penalty of CCS. In particular, compared with results from
 569 literature [87], it is possible to achieve a gain of 4 percentage points with respect to a stand-alone
 570 Oxyfuel-NGCC process¹.

571 To evaluate the overall plant performance with regards to CO₂ savings, besides calculating the
 572 overall CO₂ avoided, the plant carbon efficiency, C_{eff} provides an alternative measure as per the
 573 following equation (18) [78,88,89].

$$574 \quad C_{eff} = \frac{\dot{m}_{C,DME} + \dot{m}_{C,MeOH}}{\dot{m}_{C,NG}}, \quad (18)$$

575 where $\dot{m}_{C,DME}$ and $\dot{m}_{C,NG}$ are respectively the mass flow of carbon contained in the product
 576 (DME) and the primary reactant (inlet NG stream) respectively. $\dot{m}_{C,MeOH}$, denoting the mass flow of
 577 carbon in methanol contributes an minor fraction to the overall carbon efficiency of the
 578 polygeneration system as well.

579 The total CO₂ produced in polygeneration plant is 3.36 million tons per year out of which 3.4%
 580 is converted to the DME (CO_{2,DME}) with an overall plant carbon efficiency of 22.25% (Table7). The
 581 recirculation streams of CO₂ (CO_{2,REC}) in the combustor accounts for the 85% produced CO₂ from
 582 the exhaust (2.86 million tons per year), while the one sent into OXI for dissociation is 6.54%. In
 583 addition, a polygeneration scheme ensures the ability to produce DME within the same system, thus
 584 cutting emissions from stand-alone DME production. Conventional DME production via a stand-
 585 alone steam methane reforming process results in an equivalent CO₂ emission of 51.1 kgCO₂/GJ of
 586 DME [53]. Therefore, an equivalent of an additional 85.65 kilotonne of CO₂ was saved by the
 587 polygeneration scheme accounting of total 589.15 kilotonne of CO₂ avoided annually. More
 588 detailed share of carbon capture and utilization is listed in table S2 in supplementary file. As for the
 589 carbon efficiency, the CL unit pressure and increase in CO₂ content to the OXI form the most
 590 negative impacts, as can be observed from Table 7. This can be concluded from the decrease in
 591 DME production, indicating the contribution of different operating conditions to the overall optimal
 592 operation of the polygeneration plant.

593 Table 5 Plant results with selected parameters.

NG feed	25.2 ton/h
W_{GROSS}	167.61 MW
W_{NET}	102.90 MW
η_c	50.21%
W_{COMP-1}	3.76 MW
W_{COMP-2}	10.67 MW

¹ considering 0.09 kWh/Nm³ energy requirement for CO₂ compression [113].

$W_{\text{COMP-3}}$	28.29 MW
W_{ASU}	19.34 MW
W_{GT}	114.42 MW
W_{ST1}	44.30 MW
W_{ST2}	2.96 MW
W_{TURBEXP}	4.37 MW
\dot{m}_{DME}	185.6 ton/day (2.15 kg/s)
\dot{m}_{MeOH}	2.59 ton/day (0.03 kg/s)
$\text{CO}_{2,\text{REC}}$	85%
$\text{CO}_{2,\text{DME}}$	3.4%

594

595 Table 6. Thermodynamics properties and composition of selected streams.

Stream	28	10	14	15	17	20	31	37	38	43	47	7	9
T (°C)	900	1322	200	250	46	43	1377	80	40	40	-41	900	1322
P (bar)	2	2	5	50	10	9	26	26	1	1	10	2	2
Mole flow (kmol/s)	1	0.47	0.34	0.15	0.05	0.04	3.67	2.44	0.19	0.28	0.09	0.59	0.29
Molar fraction													
H ₂	0.57	0.32	0.44	0.04	0	0	0	0	0	0	0.01	0	0
H ₂ O	0	0.28	0	0.01	0.03	0	0.22	0	0	0.99	0	0	0
CO ₂	0	0.09	0.13	0.6	0	0	0.77	0.99	0.99	0	0.96	0	0
CO	0.29	0.30	0.43	0.03	0	0	0	0.01	0	0	0.03	0	0
CH ₄	0.12	0	0	0	0	0	0	0	0	0	0	0	0
other gases*	0.02	0.01	0	0	0	0	0	0	0.005	0.01	0	0	0
MeOH	0	0	0	0.01	0.02	0.01	0	0	0	0	0	0	0
DME	0	0	0	0.31	0.95	0.99	0	0	0	0	0	0	0
CeO ₂	0	0	0	0	0	0	0	0	0	0	0	1	0
Ce ₂ O ₃	0	0	0	0	0	0	0	0	0	0	0	0	1

596 *other gases include N₂ and other trace gases of natural gas

597

598 Table 7. Overall plant carbon efficiency for specific plant operating parameters.

Plant Operation Conditions	CL Unit Pressure [bar]	Toc from RED [°C]	H ₂ O%:CO ₂ % feed to OXI	Gas Turbine TIT [°C]	Carbon Efficiency (C_{eff}) [%]
Ideal	2	900	40:60	1377	22.25%
High CL Unit Pressure	20	900	40:60	1377	9.48%
High Toc from RED	2	1300	40:60	1377	16.70%
High CO ₂ % in OXI gas Feed	2	900	80:20	1377	7.60%
High H ₂ O % in OXI gas Feed	2	900	20:80	1377	10.40%
High Gas Turbine TIT	2	900	40:60	1450	22.25%

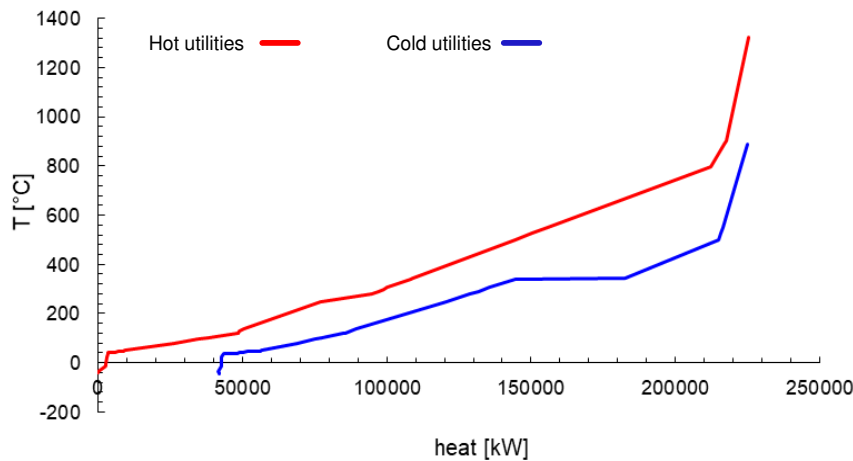
599

600 5. Pinch analysis

601 The thermal integration of the proposed polygeneration plant was performed using the pinch
602 point analysis [90]. The highest temperature of 1322°C corresponds to the oxidation reactor outlet,

603 while the lowest of -40°C is the DME condensation temperature. Figure 13 shows the hot and cold
 604 composite curve indicating a good thermal integration between cold and hot utilities, without the
 605 use of an external heat source. Therefore, the scope for a further increment in the efficiency of the
 606 power plant through optimized heat integration is limited. Starting from the hotter utilities, the
 607 profile can be interpreted as follow:

- 608 – The cold utility curve from 50°C to 550°C represents the steam generation (stream 2A-5A
 609 and 2B-5B) driven by the exhaust gas from GT (stream 32) and the hot syngas from the
 610 oxidation (stream 10). It also represents the $\text{CO}_2\text{-H}_2\text{O}$ preheating before the dissociation
 611 (stream 39 and 45) driven by stream 10a and 10b (hot syngas) in the HX-5 and HX-10 (for
 612 CO_2 preheating) and HX-4 and HX-12 (for H_2O preheating);
- 613 – The steep part of the curves, from 550° to 900°C for the cold utilities, represents the of
 614 natural gas preheating before the reduction in RED (stream 5) taking place in the heat
 615 exchangers (HX-1 and HX-8B) and (HX-2 and HX-8);
- 616 – The part of the curves near and below zero is mostly related to the distillation unit and the
 617 condensation up to a temperature of -40°C of the DME;



618

619 Figure 13 Pinch point analysis with hot and cold composite curves

620

621 6. Exergy analysis

622 Exergy of a steady stream of matter is defined as the maximum amount of work obtainable
 623 when the stream is brought from its initial state to the dead state by processing during which the
 624 stream may interact only with the environment [91]. Exergy (E) can be divided into different
 625 components: kinetic exergy E_k , potential exergy E_{pot} , physical exergy E_{ph} and chemical exergy E_{ch} .

$$626 \quad E = E_k + E_{pot} + E_{ph} + E_{ch} \quad (19)$$

627 In the presented exergy analysis, the physical and chemical exergy are considered. The physical
 628 exergy is defined as the maximum work achievable from a system that from its initial state is

629 brought to the environmental state with only thermal and mechanical interaction with the
 630 environment. While the chemical exergy is the maximum work obtainable from a system that is
 631 brought from the environmental state to the dead state involving heat transfer and exchange of
 632 substances only with the environment. The two types of exergy are given by equation (20) and
 633 (21)[92]. In particular, for a mixture, the total chemical exergy $E_{ch,tot}$ is made by two contributes:
 634 the chemical exergy of the single i -th component $E_{0,i}$ and the work obtainable from a reversible
 635 isothermal expansion at T_0 from the partial pressure p_{00} of the i -th component and environment
 636 pressure p_0 .

$$637 \quad E_{ph} = \sum_i x_i \cdot \left[(h_i - h_{0,i}) - T_0 \cdot (s_i - s_{0,i}) \right] \quad (20)$$

$$638 \quad E_{ch,tot} = \sum_i x_i \cdot \left[E_{0,i} + \varphi \cdot R \cdot T_0 \ln \frac{p_0}{p_{00}} \right] \quad (21)$$

639 The exergy analysis is based on the second principle of thermodynamics, thus permits to
 640 evaluate the so-called ‘‘destroyed’’ exergy ($I_{destroyed}$). Destroyed exergy represents the real loss in
 641 the quality of energy that cannot be identified by means of a simple energy balance because the
 642 conservation of energy will always apply. The following equation represents an exergy balance of a
 643 general device in steady state condition:

$$644 \quad \sum_i (E_{out,i} - E_{in,i}) = \sum_i W_i + \sum_i Q_i \left(1 - \frac{T_0}{T_i} \right) + I_{destroyed} \quad (21)$$

645 In equation (21): i) the members at the left side represent the exergy contribution of the $E_{in,i}$ inlet
 646 and $E_{out,i}$ outlet mass flows, ii) W_i represents the absorbed/produced work by the device, iii) the
 647 second member at the right side is the contribution from the heat exchanged, which represents the
 648 work obtainable from the heat flux Q_i operating with a Carnot machine, and iv) $I_{destroyed}$ is the
 649 irreversibility generated.

650 In order to estimate the exergy efficiency (or efficiency of the second principle) of a system is
 651 necessary to define the resource exergy flow of the process (Fuel) and product of the process
 652 (Product). The exergy efficiency is shown by the following equation:

$$653 \quad \eta_{ex} = \frac{E_P}{E_F} \quad (23)$$

654 Where E_P represents the exergy of the product streams and E_F the exergy of the resource streams.
 655 However, the only exergy efficiency does not give a complete framework of the plant or subsystem.
 656 For this reason, an additional exergetic factor and other parameters were adopted [93]:

$$657 \quad - \text{Relative irreversibilities: } \chi_i = \frac{I_{i,destroyed}}{I_{tot,destroyed}} \quad (24)$$

658 – Fuel depletion rate: $\theta_i = \frac{I_{i,destroyed}}{E_{F,plant}}$ (25)

659 – Productivity lack: $\xi_i = \frac{I_{i,destroyed}}{E_{P,plant}}$ (26)

660 – Exergetic factor: $\psi_i = \frac{E_{F,i}}{E_{F,plant}}$ (27)

661 A reference state was selected for the analysis (Table 8). For the environmental state, a pressure
 662 (P_0) of 1 atm and a temperature (T_0) of 20°C were selected, while for the dead state the reference
 663 environment of Szargut [94] was chosen.

664 Table 8 Environment state and dead state data of chemical exergy.

Environmental state: $P_0=1$ atm $T_0=20^\circ\text{C}$											
Dead State											
Chemical exergy E_{ch} (kJ/mol)											
H ₂	CO	CO ₂	H ₂ O _{vap}	H ₂ O _{liq}	N ₂	CH ₄	O ₂	CeO ₂	Ce ₂ O ₃ [12]	DME[42]	MeOH[42]
236.09	275.1	19.20	9.181	0.87	0.696	853.36	3.837	33.8	384.7	1414.5	715.52

665

666 Since in the proposed layout there are several chemical reactions, which change the
 667 composition of the gaseous streams, the first step was to evaluate the reference chemical exergy of
 668 the multiple mixture streams using the dead state of the reference elements. The results are shown
 669 in Table 9.

670 Table 9. Specific chemical exergy of the gas mixture streams.

Stream	31	28	10	15	13	47
$e_{ch,i}$ [kJ/kg]	389	27110	7391	11287	11919	6225

671

672 The exergetic performance of the overall plant has been assessed by evaluating its exergetic
 673 efficiency (Eq. 28) and the total irreversibility generated (Eq. 29). As can be clearly observed pinch
 674 analysis, due to both electricity and heat self-sufficiency of the system, the input fuel, namely
 675 natural gas, contributes entirely to the net exergy input to the system (i.e., it is 100% of the total
 676 exergy input). The products are the total DME, MeOH and the net power produced by the plant.

677 $\eta_{ex} = \frac{\dot{m}_{DME} \cdot E_{DME} + \dot{m}_{MEOH} \cdot E_{MEOH} + W_{NET}}{\dot{m}_{CH_4} \cdot E_{NG}}$ (28)

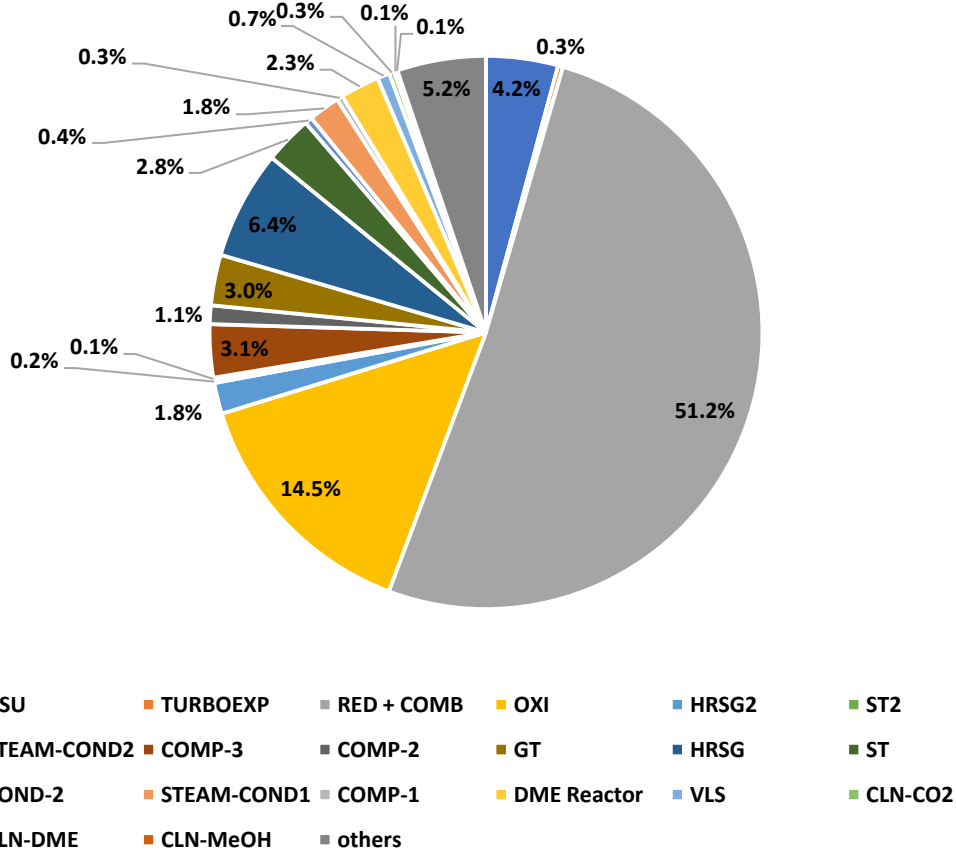
678 $I_{tot, destroyed} = \dot{m}_{CH_4} \cdot E_{NG} - \dot{m}_{DME} \cdot E_{DME} - \dot{m}_{MEOH} \cdot E_{MEOH} - W_{NET}$ (29)

679 As expected, since the exergy efficiency is primarily influenced by to the fuel value of natural gas,
 680 DME, MeOH, and the net power produced, the exergy efficiency trend is specular to the

681 thermodynamic efficiency previously described. The energetic and exergetic efficiency with respect
682 to the pressure of CL unit and metal oxide inlet temperature to reduction reactor and turbine inlet
683 temperature is presented in Figure S1 and effect of the molar composition of CO₂ and H₂O in OXI
684 is presented in Figure S2 in supplementary file. Finally, also a detailed exergy analysis of the
685 components of the layout operating at the conditions described in section 4 was performed.
686 Chemical, physical and total exergy values of all streams are reported in Table S3 in supplementary
687 file.

688 The global exergy efficiency (η_{ex}) of the plant was obtained as 45.0%, five points lower than
689 the calculated first-law efficiency. The total irreversibilities generated are 202.72 MW with an
690 overall fuel depletion rate (θ) of 53.84%. All the components present an exergetic efficiency over
691 the 80%, with the exception of the ASU (55.9%), the two condensers for the steam cycle (32%) and
692 the CLN-MeOH (77%). However, the contribution of COND-A, COND-B, and ASU to the overall
693 efficiency is marginal since their relative irreversibilities χ_i do not exceed the 3.9% (see Table 10).

694 The exergy efficiency of the RED+COMB results in 88.1%. Although this value is not
695 extremely low, more than half of the 202.72 MW total irreversibilities are in this component (Figure
696 14). As shown in Table 10, the RED+COMB exergetic factor ψ results in 231.3%, so the
697 irreversibilities are not due to the efficiency but are mainly proportionally correlated to the high
698 exergy of the inlet streams. In fact, the exergy inlet of the RED+COMB ranks first among the
699 components (870 MW), the second being the turbo-expander inlet (378 MW). Moreover, it is worth
700 mentioning that, with the hypothesis of zero heat losses inside the combustor and reduction reactor,
701 the main contributor to the exergy losses are of the chemical form. In fact, the exergy efficiency of
702 the RED+COMB, considering only the chemical exergy of the inlet and outlet streams, results in
703 70%. The oxidation reactor is the second-ranked component for the relative irreversibilities
704 parameter (14.4%) even if the exergy efficiency (83.4%) results in to be lower than the one of the
705 RED+COMB. This is due to the lower exergy factor (50.7%).



706

707

Figure 5 Total irreversibilities distribution.

708

The other irreversibilities are mostly from the HRSRG1 of the steam ranking cycle (SRC1) (13.99 MW) and in the compression process (9.3 MW). The DME reactor jacketing for saturated steam production allows increasing the exergy efficiency of the component of 2.2%.

709

710

Table 10 Results from the exergetic analysis of the main components.

Componet	Exergy balance eq. ¹	I [MW]	$\eta_{ex,i}$ [%]	θ_i [%]	ψ_i [%]	ξ_i [%]
ASU	$E_0 + W_{ASU} = E_1 + E_{1b} + I_{ASU}$	8.53	55.91	2.26	5.14	5.03
TURBOEXP	$E_3 = W_{TURBOEXP} + I_{TURBOEXP}$	0.59	99.84	0.16	100.41	0.35
RED+COMB	$E_{9a} + E_5 + E_{30} + E_1 + E_{49} + E_{37} = E_{31} + E_{28} + E_7 + I_{RED+COMB}$	103.83	88.08	27.58	231.29	61.23
OXI	$E_7 + E_{46} + E_{40} = E_{10} + E_{9a} + I_{OXI}$	29.47	84.57	7.83	50.74	17.38
HRSRG2	$E_{10} + E_{2-B} = E_{10a} + E_{5-B} + I_{HRSRG-2}$	3.68	97.49	0.98	38.88	2.17
ST2	$E_{5-B} = E_{6-B} + W_{ST2} + I_{ST2}$	0.38	89.77	0.10	0.99	0.22
COND-B	$E_{6-B} = E_{7-B} + I_{COND-B}$	0.25	32.0	0.07	0.10	0.15
COMP-4	$E_{38} + W_{COMP-4} = E_{39} + I_{COMP-4}$	0.08	98.26	0.02	1.18	0.04
COMP-3	$E_{49} + W_{COMP-3} = E_{37} + I_{COMP-3}$	6.29	91.73	1.67	20.21	3.71
COMP-2	$E_{29} + W_{COMP-2} = E_{30} + I_{COMP-2}$	2.21	99.33	0.59	87.57	1.30
GT	$E_{31} = W_{GT} + E_{32} + I_{GT}$	6.00	97.57	1.59	65.57	3.54
HRSRG1	$E_{31} + E_{2-A} = E_{33} + E_{5-1} + I_{HRSRG-1}$	12.88	90.0	3.42	34.21	7.60
ST1	$E_{5-A} = E_{6-A} + W_{ST1} + I_{ST1}$	5.68	89.75	1.51	14.72	3.35
COND-2	$E_{33} = E_{34} + E_{41} + I_{COND-2}$	0.88	98.51	0.23	15.80	0.52

COND-A	$E_{6-1} = E_{7-A} + I_{COND-A}$	3.71	32.00	0.99	1.45	2.19
COMP-1	$E_{13} + W_{COMP-1} = E_{14} + I_{COMP-1}$	0.71	99.10	0.19	20.88	0.42
DME Reactor	$E_{14} + E_{44} = E_{15} + E_{45} + I_{DME reactor}$	4.64	94.05	1.23	20.73	2.74
VLS	$E_{15} = E_{47} + E_{17} + I_{VLS}$	1.45	97.99	0.39	19.16	0.86
CLN-CO ₂	$E_{19} + Q_{COND,CLN-CO_2}^* + Q_{RED,CLN-CO_2}^*$ $= E_{20} + E_{21} + I_{CLN-CO_2}$	0.60	99.15	0.16	18.56	0.35
CLN-DME	$E_{22} + Q_{COND,CLN-DME}^* + Q_{REB,CLN-DME}^*$ $= E_{22} + E_{23} + I_{REB-DME}$	0.30	99.56	0.08	17.90	0.18
CLN-MeOH	$E_{25} + Q_{COND,CLN-MeOH}^* + Q_{REB,CLN-MeOH}^*$ $= E_{22} + E_{23} + I_{REB-MeOH}$	0.15	77.39	0.04	0.18	0.09
NG _{PHX1}	$E_2 + E_{28} = E_3 + E_{28b} + I_{NG-PHX1}$	0.41	99.94	0.11	185.39	0.24
NG _{PHX2}	$E_4 + E_{28b} = E_5 + E_{29} + I_{NG-PHX2}$	1.59	99.78	0.42	188.17	0.94
CO ₂ PHX	$E_{10a} + E_{39} = E_{10b} + E_{40} + I_{CO_2-PHX}$	0.38	99.48	0.10	19.34	0.23
H ₂ O _{PHX}	$E_{10b} + E_{45} = E_{11} + E_{46} + I_{H_2O-PHX}$	3.26	95.63	0.87	19.80	1.92

712

713 ¹The left-side of the equation in the table represents the fuel of the component, while the right side
714 of the equation represents the product and the irreversibility of the component.

715 Q* represents the exergy obtainable using the heat of the selected stream

716

717 $Q_{COND,CLN-CO_2}^* = Q_{COND,CLN-CO_2} \times \left(1 - \frac{T_{COND,CLN-CO_2}}{T_0}\right);$

718 $Q_{REB,CLN-CO_2}^* = Q_{REB,CLN-CO_2} \times \left(1 - \frac{T_0}{T_{REB,CLN-CO_2}}\right);$

719 $Q_{COND,CLN-DME}^* = Q_{COND,CLN-DME} \times \left(1 - \frac{T_0}{T_{COND,CLN-DME}}\right);$

720 $Q_{REB,CLN-DME}^* = Q_{REB,CLN-DME} \times \left(1 - \frac{T_0}{T_{REB,CLN-DME}}\right);$

721 $Q_{COND,CLN-MeOH}^* = Q_{COND,CLN-MeOH} \times \left(1 - \frac{T_0}{T_{COND,CLN-MeOH}}\right);$

722 $Q_{REB,CLN-MeOH}^* = Q_{REB,CLN-MeOH} \times \left(1 - \frac{T_0}{T_{REB,CLN-MeOH}}\right);$

723

724 7. Economic analysis

725 An economic assessment was performed to calculate the capital cost of investment for the
726 construction of the proposed plant. The National Energy Technology Laboratory (NETL) guidelines
727 for techno-economic analysis for power plants was adopted [95,96]. This methodology defines
728 capital cost at five levels: bare erected cost (BEC), engineering, procurement, and construction cost
729 (EPCC), total project cost (TPC), total overnight cost (TOC) and total as-spent cost (TASC). In the
730 current study, the TOC was considered for the capital investment expenditure. The first four items
731 are “overnight cost” and are expressed in base-year US dollar that is the first year of capital
732 expenditure. The Bare Erected Cost (BEC) comprises the cost of the equipment, facilities and
733 infrastructure, and labor required for its installation. The equipment cost was estimated using the
734 scaling factor exponent M, as given by equation (30) [97] and details of which can be found in [12].

735 $C_{equ} = C_{equ,ref} (J/J_{ref})^M$ (30)

736 where C_{equ} and $C_{equ,ref}$ represent the equipment cost with a capacity of J and J_{ref} , respectively.

737 To assess further costs related to setting up of the polygeneration plant including installation
 738 and other direct and indirect costs related to the project development, a bottom-up approach
 739 following the methodology adopted in the CAESER project [98] was selected. All the estimated
 740 equipment costs (Table S5 in supplementary file) were converted to the year 2017 US dollar using
 741 the chemical engineering plant cost index (CEPCI, Table S6 in supplementary file).

$$742 \quad C_{\text{equ,actual}} = C_{\text{equ,ref}} \frac{\text{CEPCI 2017}}{\text{CEPCI at the time of original cost}} \quad (31)$$

743 The cost of the cooling tower system was included in the cost of the four condensers (COND-1,
 744 COND-2, SRC1, and SRC2 condenser). The overall cost was subdivided between the four
 745 components proportionally to the calculated rejected heat. The cost of the two condensers (COND-
 746 A and COND-B) of the two HRSG were included in the HRSG investment cost. The most
 747 expensive equipment is the ASU, followed by the GT. The RED+COMB unit accounts for 5.2% of
 748 the total expenditure. The individual contribution of the respective equipment to the total overnight
 749 cost is shown in Figure 15.

750 The bare erected cost (BEC) of each equipment was given summing all the installation costs
 751 (see Table S6 in the supplementary file for assumptions of CAPEX estimation) to the equipment
 752 cost is given by equation (32).

$$753 \quad \text{BEC} = C_{\text{equ,actual}} + \text{Installation Cost} \quad (32)$$

754 The engineering, procurement and construction cost (EPCC) comprises the BEC plus the costs
 755 of all services provided by the engineering, procurement and construction contractor (equation
 756 (33)). These items include detailed design, contractor permitting and project management costs.

$$757 \quad \text{EPCC} = \text{BEC} + \text{INDIRECT COST} \quad (33)$$

758 The total project cost (TPC) also includes the contingencies cost (equation (34))to account for
 759 unknown costs that are omitted or unheralded due to lack of complete project definition or
 760 uncertainties with the development status of a technology. In the present case, since the proposed
 761 plant is based on a novel technology arrangement, a high contingency cost of 30% was selected
 762 (Table S6 in supplementary file).

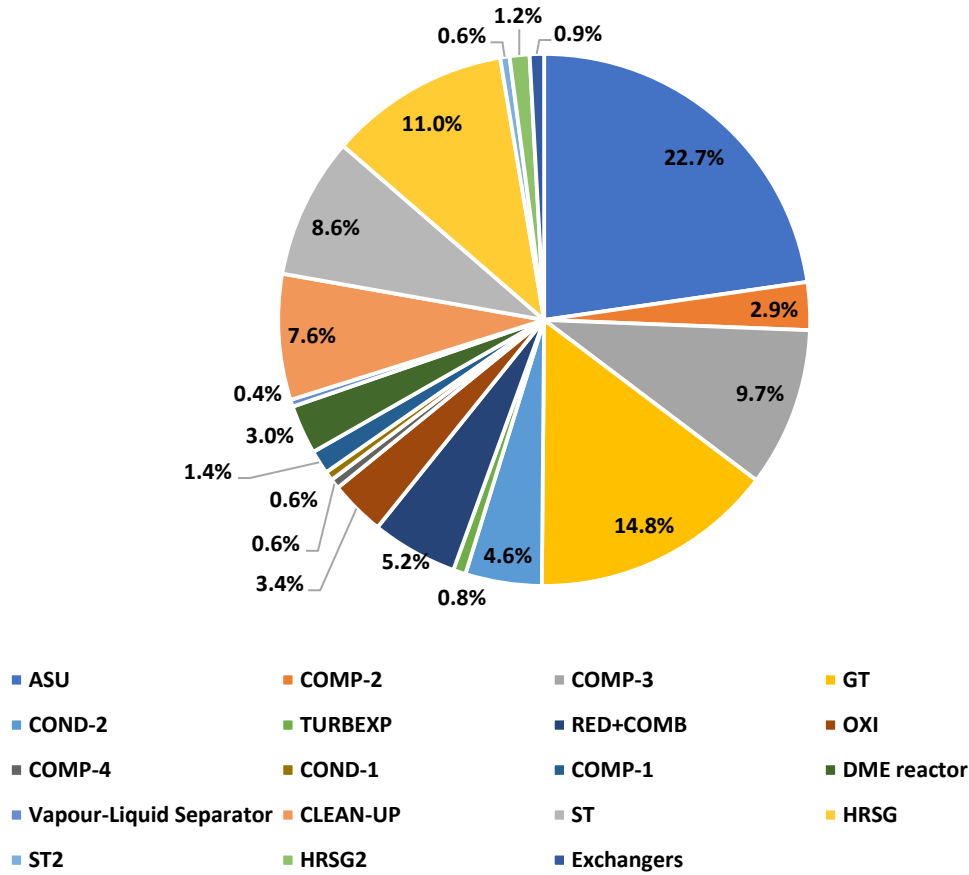
$$763 \quad \text{TPC} = \text{EPCC} + \text{CONTINGENCIES} \quad (34)$$

764 The total overnight cost (TOC) comprises the TPC plus other overnight costs (Table S4 in
 765 supplementary file), owner's cost included (i.e pre-production, inventory capital, land, financing), it
 766 was calculated as:

$$767 \quad \text{TOC} = \text{TPC} + \text{OWNER'S COST} \quad (35)$$

768 From the assumptions listed in Table S6 (in supplementary file), the total overnight cost (TOC)
 769 of the plant resulted in 537.45 \$million. Figure 15 represents the contribution to the total overnight

770 cost of the different equipment. The most expensive equipment resulted in the ASU, followed by
 771 the GT. The RED+COMB unit accounted for 5.2% of the total expenditure. For the economic
 772 analysis, all assumptions are listed in Table S7 and S8 in the supplementary file for OPEX
 773 estimations.

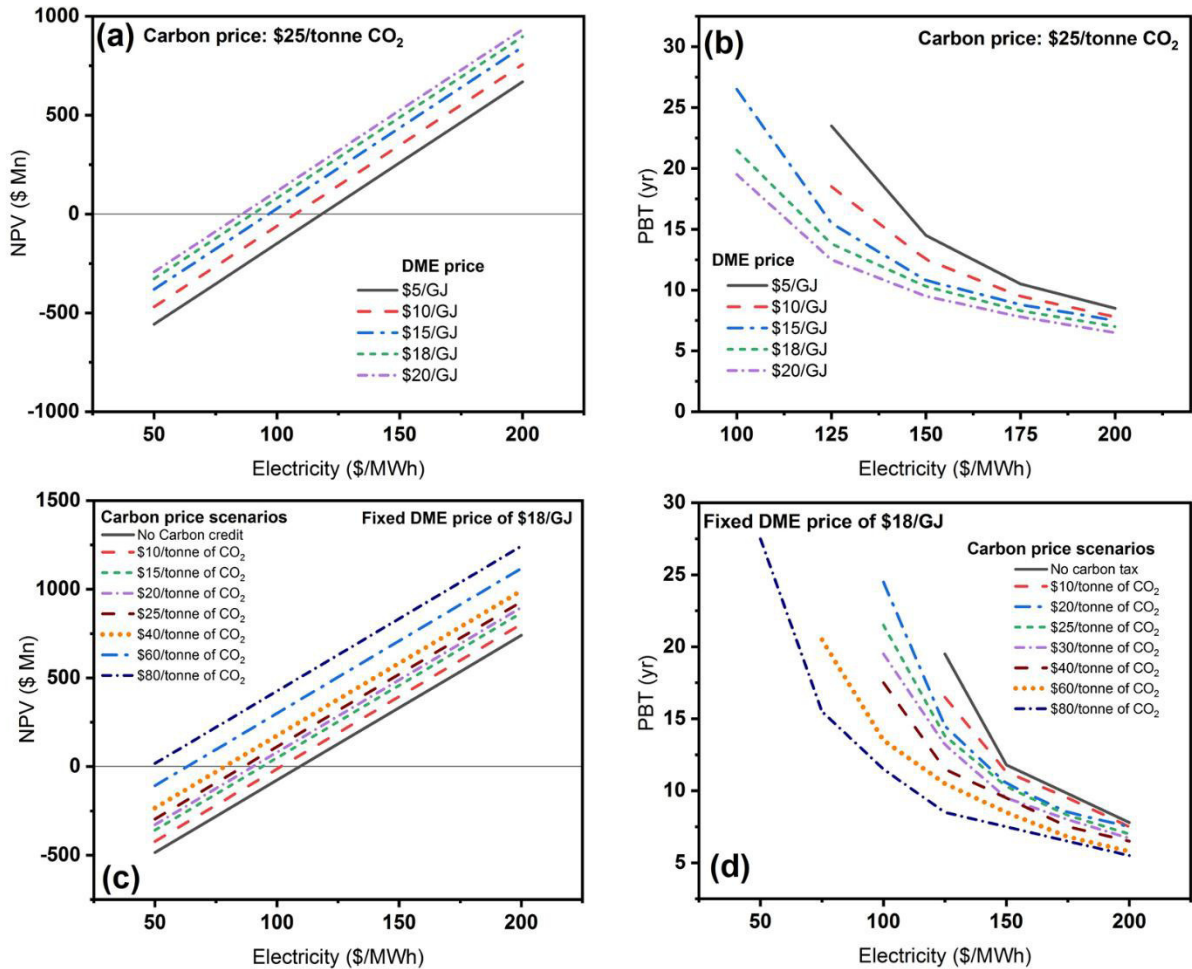


774
 775 Figure 15 Contribution of the components to the TOC.

776 Finally, to evaluate the profitability of the plant during its lifetime a discounted cash flow
 777 analysis (DCF) was adopted. DCF is based on the concept of the time value of money, all the future
 778 cash flows are estimated and discounted by a discounted factor (i) (Table S8 in supplementary file),
 779 obtaining their present value [99]. The sum of the all discounted cash flows, both positive
 780 (revenues) and negative (operation cost, Table S7 in supplementary file), gives the net present
 781 values (NPV) as shown by equation (36).

782
$$NPV = -TASC + \sum_{l=1}^t \frac{(\text{net cash flows})_l}{(1+i)^l} \quad (36)$$

783 A project is acceptable only if the NPV is positive. TASC is used to evaluate the total project
 784 cost instead of TOC, in order to asses both escalation and interest during construction (Table S7 in
 785 supplementary file) [95,96]. A sensitivity analysis was performed to evaluate the effect of the
 786 selling price of power and DME on the economic performance of the plant.



787

788 Figure 16 (a) and (c) Economic performance varying carbon credits and DME prices for different electricity prices (b)
 789 and (d) Payback period (PBT) varying DME and electricity price for different levels of carbon credit

790 It is observed that a payback period (PBT) of 20 years was obtained with the electricity and the
 791 selling price of DME of \$20/GJ and \$220/MWh respectively which is around 2.2 times the current
 792 whole sale electricity price without carbon credits considered

793 Figure 16 (a) and (b) represents the variation of electricity prices for different DME prices from
 794 \$5-20/GJ. It is observed that for the current reported carbon credit price of \$25/tonne of CO₂ [100]
 795 the NPV is positive if the electricity price of \$90/MWh (which is below current electricity price
 796 with CCS) with a payback period of 21.5 years. Nonetheless, a rapid increase in the CO₂ price
 797 between \$40 and \$80 per tonne is required to meet the agreements of Paris 2015 [101]. This trend
 798 can be observed in many countries where high carbon tax of over 55\$/tonne prevails including
 799 Switzerland, Finland, Sweden, Liechtenstein, Norway, Mexico, Chile and many others [101].
 800 Indeed, such rapid rise in the carbon price have already started to materialize, with further increase
 801 to be seen developed economies by 2030 [102–105]. Still many developing countries are struggling
 802 to adopt the carbon price and emission trading system making it difficult to match the carbon price
 803 difference. Therefore, the NPV values was varied for different scenarios of electricity and DME
 804 price based on the carbon credit variation from \$10-80/tonne of CO₂ [106]. Figure 16 (c) and (d)
 805 corresponds to the fixed current market DME price of \$18/GJ [53] and varying the carbon credits
 806 for electricity pricing. From Figure 16 (c) it can be said with the carbon price above \$40/tonne CO₂
 807 would have positive NPV that can be able to match with the current selling price of electricity is

808 above \$100/MWh with carbon capture [106–111] for the proposed polygeneration with a PBT of
809 17.5 years, with potential to drop further for higher carbon credit scenarios of \$60 and \$80/tonne of
810 CO₂ the payback period reduces by nearly 2/3 (11.5 years).

811 However, more strong carbon credit policies and a further development of technologies, such as
812 Oxyfuel combustion, air separation, and chemical looping, will make the proposed polygeneration
813 plant more competitive. By considering oxygen transport reactors that use ion transport membranes,
814 such as perovskites, for oxygen separation at high temperatures (i.e., above 700°C), high-purity
815 oxygen could be produced at a relatively lower price compared to ASU, thereby increasing the
816 efficiency and decreasing the equipment cost. At present, with this technology, it is possible to
817 produce 2000 tonne per day, which is sufficient for an oxyfuel plant of 110 MW capacity.
818 Therefore, with the adoption of the ion transport membrane technology that costs 31% less
819 compared to the ASU, consequently, the cost of DME and power production would decrease
820 tremendously and the overall efficiency of the plant would improve by 2-4% [112].

821 **8. Conclusion**

822

823 A novel natural gas feed polygeneration plant was proposed that integrates a chemical looping
824 CO₂/H₂O splitting unit with an oxyfuel combustion unit for the production of power, DME and
825 methanol. The results demonstrated the advantages of using a chemical looping CO₂/H₂O process in
826 a polygeneration plant to reduce the efficiency penalty due to the carbon capture. The analysis
827 revealed that the ideal H₂/CO ratio for a single step DME synthesis to be which can be obtained by
828 feeding H₂O/CO₂ ratio of 60/40%. The plant was able to produce 103 MWe and 185.6 ton/day (2.15
829 kg/s) of DME with an energetic and exergetic efficiency of 50.2% and 45.0%, respectively.
830 Compared to only power plant with carbon capture the present polygeneration revealed an
831 efficiency gain of 4%. Through an exergy analysis, the main contributors of exergy destruction
832 were identified: the combustor and reduction system resulted to contribute for 51.2% of the total
833 generated irreversibilities (221 MW). The capital investment was estimated to be \$534 million. The
834 overall CO₂ produced was 3.36 million tonne for 7446 hours (with a capacity factor of 0.85) of
835 annual operation of which approximately 3.4% is contributed by the DME production in a
836 polygeneration scheme accounting for 589.15 kilotonne of total CO₂ avoided annually. Economic
837 analysis revealed that around 23% of the total equipment costs is attributed by ASU and with the
838 use of more sophisticated technology for producing oxygen at less price would decrease the capital
839 investment. A discounted cash flow analysis revealed that the proposed plant would able to meet the
840 electricity and DME price of \$100/MWh an \$18/GJ with the carbon credit of \$40/tonne of CO₂,
841 which is projected to be the carbon credit by 2020. With stringent carbon pricing of \$80/tonne of
842 CO₂ the electricity price would drop below \$50/MWh.

843 **Author Contributions:**

844 A Farooqui and F Di Tomaso developed the model and performed simulations. A Farooqui, F Di
845 Tomaso, A Bose and D Ferrero written the manuscript in multiple iterations. J Llorca and M
846 Santarelli supervised the work and made the necessary modifications required in the manuscript.
847 The figures were made in multiple iterations by A Farooqui and Di Tomaso.

848 **Glossary:**

849	\dot{m}	Mass flow rate (kg/s)
850	LHV	Lower heating value (MJ/kg)
851	W_{NET}	Net power produced inside the plant (MW)
852	W_{ST1}	Power produced in steam turbine of SRC1 (MW)
853	W_{ST2}	Power produced in steam turbine of SRC2 (MW)
854	W_{GT}	Power produced in gas turbine (MW)
855	$W_{COMP,tot}$	Auxiliary compression power in compressors (MW)
856	W_{COMP-3}	Auxiliary compression power for recycling CO ₂ (MW)
857	CO _{2,DME}	CO ₂ embedded in DME (%)
858	CO _{2,REC}	CO ₂ recycled within the plant (%)
859	E	Total exergy (MW)
860	E_k	Kinetic exergy
861	E_{ph}	Physical exergy
862	E_{pot}	Potential exergy
863	E_{ch}	Chemical exergy
864	x	Mass fraction (-)
865	h	Mass enthalpy (kJ/kg)
866	s	Mass entropy (kJ/kg-K)
867	ϕ	Activity coefficient for the i-th component
868	R	Ideal gas constant (8.314 J/mol-K)
869	ρ	Density (kg/m ³)
870	p_{00}	Partial pressure of the i-th component (Pa)
871	W	Absorbed/produced work by the device (MW)
872	Q	Work obtained from heat flux (MW)
873	$I_{destroyed}$	Irreversibility generated (MW)
874	T	Temperature (°C)
875	η_{ex}	Exergy efficiency (-)
876	η_c	Energy efficiency (-)
877	Q^*	Exergy obtainable using the heat of the selected stream
878	C_{equ}	Equipment cost
879	$C_{equ,actual}$	Actual component cost
880	$C_{equ,ref}$	Reference component cost
881	M	Scaling factor (-)
882	l	Number of years (-)
883	i	Discounted factor (-)
884	P	Pressure (bar)
885	χ	Relative irreversibilities
886	θ	Fuel depletion rate (%)
887	ξ	Productivity lack (%)
888	ψ	Exergetic factor (%)
889	P_0	Pressure at environment state of 1 atm
890	T_0	Temperature at environment state of 20°C
891	E^0	Standard chemical exergy
892	ΔG^0	Gibbs free energy
893	e_{ch}	Specific chemical exergy (kJ/kg)
894	K_i	equilibrium constant (m ³ /kmol)
895	k_i	Arrhenius rate constant

896	r	reaction rate (kmol/kg _{cat} s)
897	Π	concentration expressed (kmol/m ³)
898	B	activation energy (J/mol)
899	Pre	pre-exponential factor
900	RGIBBS	GIBBS Reactor where the calculations are based on minimizing the Gibbs
901	energy	
902	OC	Oxygen Carrier
903	C_{eff}	Plant carbon efficiency
904		
905	Subscripts	
906	ph	physical
907	ch	chemical
908	vap	vapor state
909	liq	liquid state
910	COMP	compression work
911	TURBEXP	work by turbo expansion
912	0	environment state of 1 atm and 20°C
913	is	isentropic compressor
914	mech	mechanical
915	comp	compressor
916	turb	turbine
917	ex	exergy
918	in,i	contribution to inlet mass flows
919	out,i	contribution to outlet mass flows
920	tot	total or cumulative
921	i	i-th component in the mixture
922	COND	condenser
923	REB	reboiler
924	k	k-th component
925	P	product stream
926	F	resource stream
927	Acronyms	
928		
929	NG	Natural Gas
930	VLS	Vapor Liquid Separator
931	CLN	Column
932	SRC	Steam Rankine Cycles
933	MR	Methane Reduction
934	WS	Water Splitting
935	CDS	Carbon dioxide Splitting
936	DME	Dimethyl Ether
937	ASU	Air Separation Unit
938	TURBOEXP	Turbo Expander
939	RED	Reduction Reactor
940	OXI	Oxidation Reactor
941	LHHW	Langmuir-Hinshelwood Hougen-Watson
942	ST	Steam Turbine
943	GT	Gas Turbine

944	PHX	Preheater
945	TPC	Total Project Cost
946	BEC	Bare Erected Cost
947	EPCC	Engineering, Procurement, Construction Cost
948	TOC	Total Overnight cost
949	TASC	Total As-spent cost
950	TPC	Total Project cost
951	NETL	National Energy Technology Laboratories
952	CEPCI	Chemical Engineering Plant Cost Index
953	OPEX	Operational Expenditure
954	CAPEX	Capital Expenditure
955	DCF	Discounted Cash Flow
956	NPV	Net Present Value
957	HR	Heat Rate
958	CSP	Concentrating Solar Power
959	CCS	Carbon Capture and Sequestration
960	PBT	Payback period in years

961

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