

Sustainable DMC production from CO₂ and renewable ammonia and methanol

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Abstract

One of the main goals of the green chemistry is to develop sustainable and less hazardous chemical processes and products. Dimethyl carbonate (DMC) is attracting attention due to the wide variety of applications and the possibility of producing it from carbon dioxide. In this work, the DMC production process via urea has been optimized. Two main sections can be distinguished: the synthesis of urea and the production of DMC. An equation based approach is used to model the system. The DMC production from renewable ammonia/methanol/CO₂ presents a promising production cost, around 520 €/t. The production of urea alone has also been evaluated in this work. A sensitivity analysis is carried out showing the influence of the methanol price in the DMC cost and the ammonia price in the urea cost. A simplified sustainability index is used to evaluate the environmental performance of urea/DMC production.

Keywords: dimethyl carbonate, urea, process design, CO₂ utilization

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28 1. Introduction

29 One of the main goals of Green Chemistry is to design chemical products and processes with the aim of
30 reducing the use and/or avoiding the generation of hazardous substances to human health and also to the
31 environment [1]. The essentials of Green Chemistry are summarized in the widely known “Twelve
32 Principles of Green Chemistry” [2]. Some of these rules are the synthesis of less hazardous chemicals, the
33 use of renewable raw materials or the degradation of the chemicals when their use is over. In this context,
34 dimethyl carbonate (DMC) is attracting attention as one of the most interesting green chemical products
35 nowadays. The DMC is a safe reactant with low toxicity and bioaccumulation, it shows a fast
36 biodegradability and an excellent solubility in water [3]. The current consumption of DMC is about 90000
37 t/y [4]. Several applications for the DMC have been proposed. Organic carbonates have a good
38 performance as solvents due to the low viscosity and toxicity and a good solvency power, representing a
39 green alternative to halogenate solvents, ketones or acetate esters in several applications [4,5]. DMC is
40 also a good substitute for methyl-tert-butyl ether (MTBE) as oxygenated fuel additive [6] with a high octane
41 number [7]. Another growing application for DMC is as electrolyte in ion lithium batteries due to the rapid
42 expansion of this technology [7]. Finally, DMC is used as a reagent in methylation, carbonylation and
43 methoxycarbonylation reactions [4]. One of the most important reactions in which the DMC is involved is
44 the transesterification of phenyl acetate to generate diphenyl carbonate that is used as raw material in the
45 polycarbonate industry [5,8]. A review of the combination of DMC with different bio-substrates, as glycerol,
46 to produce high added value products is presented by Selva et al. [9].

47 Different production processes have been studied to produce DMC over time. According to the
48 classification provided by Kongpanna et al. [10], two main categories are identified: conventional
49 processes and CO₂ based processes. Within the first group, one of the early process to produce DMC
50 consists of its synthesis using phosgene and methanol. The main drawback of the process is the use of
51 phosgene, a very toxic reagent. This route has been discarded in the last years [7]. A novel route was
52 developed to avoid the use of phosgene in the synthesis of DMC: the oxidative carbonylation of methanol.
53 In this process, the feedstocks are methanol, carbon monoxide and oxygen and the reaction is catalysed
54 by CuCl or KCl. This process is the most widely extended nowadays to produce DMC [4,5]. Nevertheless,

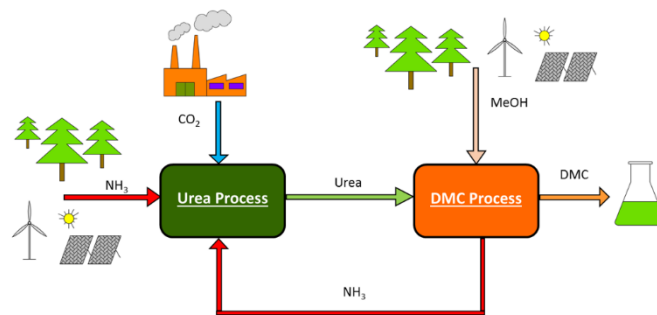
55 the most promising processes are those that use carbon dioxide as raw material. This alternative is
56 attracting attention because of the possibility of providing a new usage to the CO₂ captured [11]. Lately,
57 several bulk chemicals have been produced from renewable resources and CO₂ such as methane [12],
58 methanol [13] or dimethyl ether [14]. Different CO₂ to DMC processes have been proposed: direct
59 synthesis from CO₂ and methanol, synthesis from urea, synthesis from propylene carbonate (PC) and
60 synthesis from ethylene carbonate (EC). The direct synthesis from CO₂ and methanol is limited by the
61 reaction equilibrium and the activation of the CO₂ is difficult, therefore, further investigations are required
62 [7]. For instance, different materials to catalyse this reaction are being studied such as: Fe-Zr oxides [15]
63 or modified trifluoroacetic acid [16]. The electrochemical route is also investigated [17,18]. DMC from PC is
64 based on the transesterification of propylene carbonate and methanol [3]. PC, however, is obtained from
65 propylene oxide, that for the time being is produced from crude oil. The production of DMC from ethylene
66 carbonate is similar to the previous one. The last alternative is to synthesize DMC from urea. An
67 alcoholysis reaction between urea and methanol takes place [10]. A previous step is necessary in this
68 path: the synthesis of urea. The urea is produced from carbon dioxide and ammonia. One of the main
69 advantages of this process is that the raw materials can also be obtained in a sustainable way. The
70 ammonia, for instance, can be synthesized from water and air using renewable energy [19-21] as well as
71 biomass [22]. Methanol can also be produced from water and carbon dioxide [13], from biomass
72 gasification [23] or from biomass/waste digestion [24]. The CO₂ is obtained from carbon dioxide capture
73 [25] or biogas upgrading [26]. Therefore, the synthesis of DMC from urea and methanol is a promising
74 alternative where further investigation at process level is necessary.

75 In this work, a mathematical optimization approach for an integrated facility evaluating the synthesis of
76 DMC from ammonia, carbon dioxide and methanol is carried out. There are two main sections in the
77 process flowsheet: the synthesis of urea and the synthesis of DMC. In the urea synthesis stage, carbon
78 dioxide and ammonia react to synthesize urea. Then, urea and methanol react in two steps to produce
79 DMC. The synthesis of urea alone from sustainable ammonia is also studied. The processes are
80 evaluated in economic and environmental terms. The rest of the paper is organized as follows: Section 2
81 describes the process devoted to producing DMC from ammonia, carbon dioxide and methanol. Section 3

82 shows the approach to model the different units involved in the process flowsheet. Section 4 presents the
83 objective function, the solution procedure and the cost estimation procedure. Section 5 presents the
84 results. First, a summary of the main variables involved in the optimization procedure. Second, the
85 economic evaluation of the processes. In the third place, the sensitivity analysis of the feedstock prices
86 (methanol and ammonia). Finally, a simplified environmental analysis of the processes. Section 6 draws
87 some conclusions.

88 2. Process Description

89 In Figure 1, a schematic description of the entire process is shown. For the urea synthesis, a wide range
90 of processes has been proposed. Some of them are the Stamicarbon process with its different progresses,
91 the Snamprogetti process or the ACES process [27]. In this work, a CO₂ stripping process is selected
92 similar to the Stamicarbon process.



93

94 Figure 1: Simplified flowsheet for the entire process.

95 Carbon dioxide is fed to the stripper at 450K and the pressure selected in the urea reactor, see Figure 2.
96 For this reason, a compression step is used, followed by a heat exchanger to adjust the final temperature.
97 In the stripper, the ammonium carbamate from the reactor is converted to ammonia and carbon dioxide.
98 Heat is supplied to carry out this endothermic reaction. Besides, carbon dioxide and ammonia are
99 transferred, mainly, to the gas phase to be recycled to the urea reactor. The gas phase from the stripper is
100 mixed with the recycled gases from the medium pressure flash separation. These gases are fed to the
101 condenser where the formation of ammonium carbamate takes place removing the heat generated and
102 producing steam. The fraction of ammonia and carbon dioxide leaving the condenser reacts in the urea

103 reactor providing the heat necessary in this unit. The urea reactor transforms, essentially, ammonium
104 carbamate to urea. Complete transformation is not achieved. The stream leaving the urea reactor is sent
105 to the stripper.

106 The liquid from the stripping is expanded to a medium pressure (3-20 bar). Two phases are generated.
107 The gas phase is recompressed and recycled to the urea synthesis loop. The liquid phase, where urea
108 and water are the most significant components, is expanded again down to atmospheric pressure. The
109 gases are separated and sent out. The urea, with a minimum concentration of 90%w, is stored or sent to
110 the DMC synthesis section.

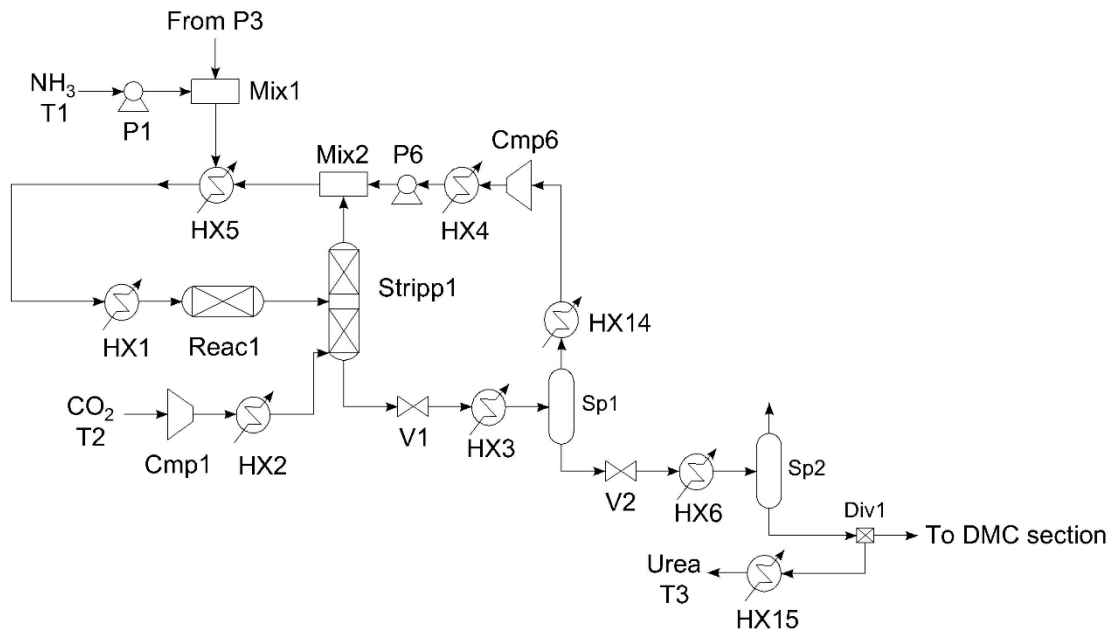
111 The urea is mixed with the stream from the mixer 3, see Figure 3, mostly methanol, to form the feed to the
112 first reactor for the synthesis of DMC. DMC is synthesized in two steps. The first one transforms urea and
113 methanol to methylcarbamate (MC). The second one converts MC to dimethyl carbonate (DMC). After
114 adjusting the pressure and the temperature, the stream is introduced in the first reactor. The reaction
115 takes place without catalyst and a conversion of 100% is reached [28]. Ammonia is separated in a
116 distillation column before introducing the stream to the second reactor due to the negative effects of this
117 chemical in the second reaction [28]. The ammonia is recycled to the urea synthesis loop. The bottom of
118 the distillation column is mixed with methanol from mixer 3 and a recycled stream to adjust the
119 methanol:MC ratio for the second reactor. Before the reactor, the stream is compressed and heated up.
120 The DMC is synthesized from methylcarbamate and methanol, generating also ammonia. A parallel
121 reaction takes place producing N-methyl methyl carbamate (NMMC). After this reactor, the different
122 products are separated in a sequence of distillation columns. First, the carbon dioxide and ammonia
123 generated are separated and recycled to the urea reaction section. The bottom product is sent to another
124 distillation column where the DMC is separated from other heavy components such as NMMC or MC. The
125 heavy components are recycled to the second reactor in the DMC section. A purge is allowed since the
126 NMMC is an impurity and can build-up in the process. The DMC is separated from methanol, mainly, using
127 a system of two columns due to the azeotrope present in the methanol-DMC system [29]. The bottom of
128 the last column is the final DMC that it is stored at ambient pressure and temperature. The methanol
129 streams from both condensers are recycled and mixed with the feed of methanol.

130 **3. Modelling issues**

131 Here, only a brief description of the modelling issues involved in the process is presented. Further details
132 are included in the supplementary material.

133 **3.1 Urea Section**

134 The following assumptions have been considered in the modelling of the urea synthesis loop. Although
135 ammonia and carbon dioxide are supercritical under the urea synthesis conditions, the vapour-liquid
136 equilibrium (VLE) is used to model the system with a supercritical phase and a liquid phase, containing a
137 suitable solvent [30-32]. The VLE has been modelled assuming the ideal behaviour where the fugacity and
138 the activity coefficient are equal to 1 (see supplementary material). A flowsheet of the urea section is
139 shown in Figure 2.

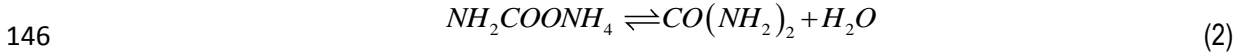
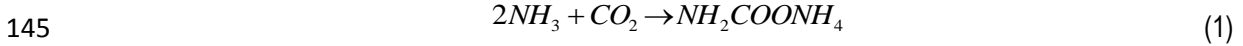


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141 Figure 2: Process flow diagram for urea synthesis section.

142 **3.1.1 Urea Reactor**

143 Urea is produced by the reaction of carbon dioxide and ammonia. Two reactions are involved in the
144 synthesis:



147 No biuret formation has been considered in the urea reactor. The first reaction is the production of
 148 ammonium carbamate from ammonia and carbon dioxide. This reaction is fast and exothermic (159 kJ/mol
 149 of carbamate). In the second one, ammonium carbamate is dehydrated to produce urea and water. This
 150 reaction is slow and endothermic (31.4 kJ/ mol of urea) [33]. The first reaction takes place between the
 151 carbamate condenser and the urea reactor. In the condenser, a large fraction of ammonia and carbon
 152 dioxide reacts and the heat produced is removed from the system generating steam. Only a small fraction
 153 of both reagents does not react to generate the heat necessary in the second reaction that takes place in
 154 the urea reactor itself [27]. For modelling purposes, the first reaction has a conversion of 100% with the
 155 only limitation of heat removal [30]. For the second one, the conversion is calculated using the correlation
 156 (eq.(3)) obtained by Inoue et al. [34] as a function of the ammonia to carbon dioxide ratio, the water to
 157 carbon dioxide ratio and the temperature. The urea reactor is modelled as adiabatic and isobaric.

158
$$X = 0.2616a - 0.01945a^2 + 0.0382ab - 0.1160b - 0.02732a\left(\frac{t}{100}\right) \quad (3)$$

159
$$- 0.1030b\left(\frac{t}{100}\right) + 1.640\left(\frac{t}{100}\right) - 0.1394\left(\frac{t}{100}\right)^2 - 1.869$$

159 Where a is the ammonia to carbon dioxide ratio defined as in eq. (4) and limited to the range of 3-5 [31]:

160
$$a = \frac{fc_{NH_3} + 2fc_{Carbamate} + 2fc_{Urea}}{fc_{Carbamate} + fc_{Urea} + fc_{CO_2}} \quad (4)$$

161 The parameter b is the molar ratio between water and carbon dioxide defined as in eq. (5) and within the
 162 range from 0 to 1:

163
$$b = \frac{fc_{H_2O}}{fc_{Carbamate} + fc_{Urea} + fc_{CO_2}} \quad (5)$$

164 And, finally, t is the temperature (°C) and must be in the interval between 170-220°C.

165 In this case of study, the following assumption is considered for modelling purposes: only one stream
 166 leaves the urea reactor. This assumption is supported by experimental results which show that the gas
 167 stream is 9 times smaller than the liquid stream [32]. The entire stream from the reactor is sent to the
 168 stripper where the ammonium carbamate is decomposed and the components are separated. Therefore,
 169 no gas treatment has been considered in the process.

170 3.1.2 Stripper

171 In the stripper, unreacted ammonium carbamate is decomposed (see eq.(1)) to form ammonia and carbon
 172 dioxide providing heat. Besides, mainly, ammonia and carbon dioxide are transferred to the gas phase to
 173 be recycled to the urea synthesis reactor. To model this unit, a surrogate model has been developed. A
 174 rigorous simulation has been carried out in CHEMCAD 7.0. A surface of response model has been
 175 developed using these data. The following variables have been considered: the stripper pressure (P), the
 176 inlet temperature from the reactor (T), the ratio between the heat supplied and the inlet molar flow of urea
 177 (Q/U), the ratio between the inlet molar flow of urea and the inlet molar flow of ammonia (U/NH₃), the ratio
 178 between the inlet molar flow of urea and the inlet molar flow of water (U/H₂O), the ratio between the inlet
 179 molar flow of urea and the inlet molar flow of carbon dioxide (U/CO₂) and the ratio between the inlet molar
 180 flow of urea and the inlet molar flow of carbon dioxide fed as stripping agent (U/CO_{2in}). The output
 181 variables are the liquid yields (%) for each component (Urea, Ammonia, Carbon Dioxide and Water) and
 182 the temperature of the gas and liquid streams. The equations obtained through this methodology (fitted to
 183 the equation form presented in eq.(6)) used to describe the stripper performance are shown in the
 184 supplementary material for the sake of brevity.

$$185 \quad f(x) = \beta_0 + \sum_{i=1}^n \beta_i x_i + \sum_{i=1}^n \sum_{j \leq i}^n \beta_{ij} x_i x_j + \sum_{i=1}^n \omega_i x_i^2 \quad \forall i, j \left\{ P, T, \frac{Q}{U}, \frac{U}{NH_3}, \frac{U}{H_2O}, \frac{U}{CO_2}, \frac{U}{CO_{2IN}} \right\} \quad (6)$$

186 The statistical analysis (p-value) determines the coefficients selected in each model. To minimize the
 187 corrosion problems in the urea synthesis loop, a small amount of oxygen (in the form of air mainly) is
 188 typically introduced with the inlet carbon dioxide in the stripper [27]. However, to model the performance of
 189 the system, this oxygen/air flow is neglected.

190 **3.1.3 Carbamate Condenser**

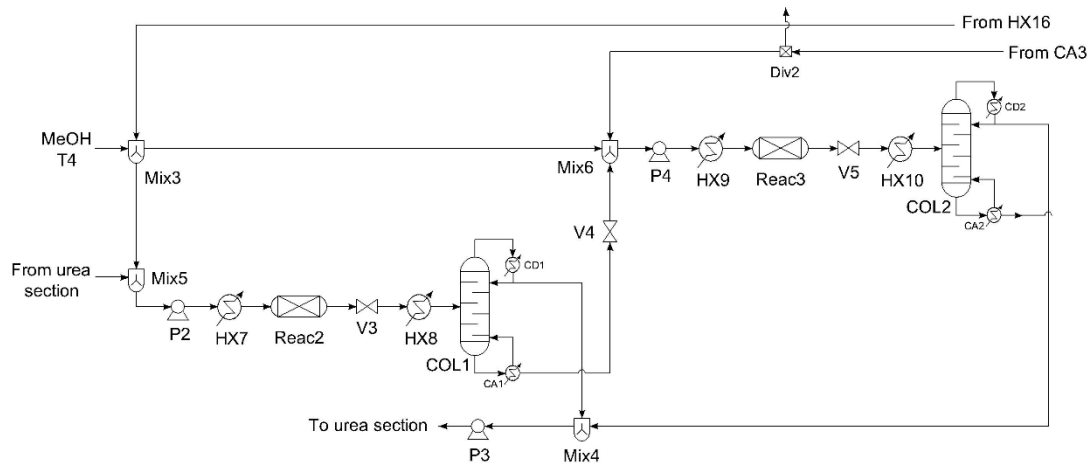
191 In the carbamate condenser, ammonia and carbon dioxide are converted to ammonium carbamate
192 following the reaction given by eq.(1). The conversion of the reaction is controlled by the heat withdrawn in
193 the condenser generating steam [35]. The remaining carbon dioxide and ammonia react in the urea
194 reactor delivering the heat necessary for the second urea formation reaction (transformation of ammonium
195 carbamate to urea, eq.(2)).

196 **3.1.4 Final Urea Purification**

197 The liquid stream leaving the stripper is expanded to a medium pressure (3-20 bar) and its temperature is
198 adjusted (273-393K) to remove a fraction of volatile gases as ammonia or carbon dioxide. The valves in
199 this work are modelled using the Joule-Thomson coefficient. The liquid fraction from the gas-liquid
200 separator is expanded again down to ambient pressure. A final removal of the gases generated is carried
201 out. The VLE equilibrium is used to model these stages. A minimum urea mass fraction of 0.9 is fixed on
202 the stream leaving the urea section. Later, a prilling or a granulation unit can be set up to form a solid urea
203 to be sold as such, but it is out of the scope of this work.

204 **3.2 DMC section**

205 The flowsheet for the synthesis of DMC is presented in Figures 3 and 4. In the first one, Figure 3, the
206 reaction section is shown. The second one, Figure 4, shows the flow diagram for the sequence of
207 distillation columns to purify the DMC.



208

209

Fig 3: Process flow diagram for the DMC synthesis section (first zone).

210

3.2.1 First DMC reactor

211

The urea produced in the first section of the process is mixed with methanol, mainly, from mixer 3. A ratio between methanol and urea equal to 2 is fixed in the inlet stream to the reactor. The flow is pumped up to 20 bar and the temperature is adjusted to 423K [28]. The following reaction takes place in this first reactor:

214



215

Urea reacts with methanol to form methyl carbamate (MC) and ammonia. The reactor is isothermal and complete conversion of urea is reached [28]. After the reactor, the stream is expanded down to 10 bar.

217

The temperature is adjusted to feed the stream as a saturated liquid into the distillation column, Column 1.

218

The objective in this distillation column is to separate the ammonia due to its negative effect in the next reaction [29]. This column is modelled using the Fenske-Underwood-Gilliland (FUG) method [36]. Antoine

219

equations are used to compute the vapour pressure for the involved components. Ammonia is selected as

221

light key component and methanol as heavy key component. The bottom stream from the distillation

222

column is expanded before being mixed in mixer 6 with a stream from mixer 5 (essentially methanol) and a

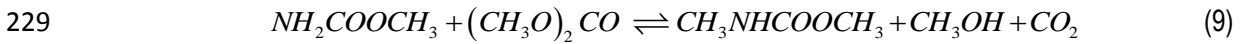
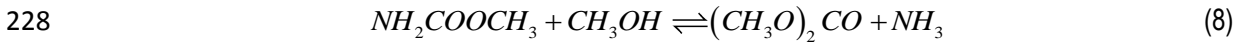
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recycled stream from the reboiler of column 3.

224

3.2.2 Second DMC reactor

225 The second reaction to form the DMC takes places in a fixed bed reactor using ZnO over alumina as
 226 catalyst [37]. A parallel reaction also occurs in the reactor producing N-methyl methyl carbamate (NMMC)
 227 from DMC and MC. The reactions are as follows:



230 An empirical correlation was developed based on the experimental data provided by Wang et al. [37] to
 231 describe the performance of this reactor. The variables are the pressure and the temperature inside the
 232 reactor and the results are the yields to DMC and to NMMC. The range of pressure is between 10-30 bar
 233 and for temperature 433-483K. Correlations with the following form have been used to fit the data:

$$234 \quad Y_i = a_0^i + a_1^i P + a_2^i T + a_3^i P^2 + a_4^i T^2 \quad \forall i \{DMC, NMMC\} \quad (10)$$

235 Where Y_i is the yield to the specie i (DMC or NMMC) in mol/inlet mol of MC, P is the reactor pressure in
 236 MPa and T is the temperature in K. The values of the coefficients for this equation are collected in Table 1.

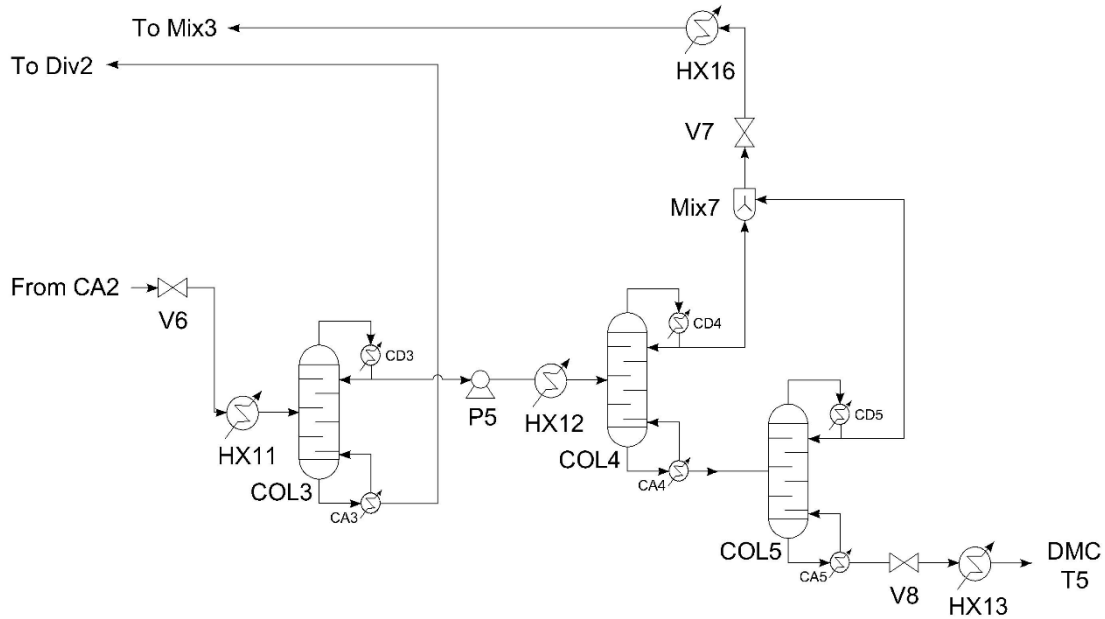
237 Table 1: Correlations to model the DMC synthesis from MC.

	a_0	a_1	a_2	a_3	a_4
DMC	-1635,91493	6,14542174	18,0202336	-7,16031083	-0,04741889
NMMC	165,693701	-6,00985703	-1,95166752	0,94781939	0,00601273

238

239 The reactor is considered isothermal and isobaric. The mass ratio between MC and methanol inlet the
 240 reactor is fixed to 0.136 according to the experimental conditions [37].

241 3.2.3 DMC purification



242

243

Fig 4: Process flow diagram for the DMC synthesis section (second zone).

244

After the reactor, the stream is expanded down to 12 bar. In Column 2, the ammonia and carbon dioxide,

245

mainly, are separated and recycled to the urea synthesis area. The FUG method is applied with ammonia

246

as light key component and methanol as heavy key component. The bottom contains ammonia, water,

247

methanol, MC, DMC, and NMMC. The next valve reduces the bottom pressure down to 1 bar. In Column 3

248

(modelled using FUG), DMC is the light key component and water the heavy key component. The heavy

249

components, namely MC, NMMC and water principally, are recycled to mixer 6 to be fed again into the

250

second reactor for the synthesis of DMC. A fraction is purged to avoid the building-up of the NMMC

251

produced in the reactor or the water from the raw materials. An increase in the pressure of the light

252

components from the column 3 is carried out up to 16 bar [29]. A couple of columns are used to separate

253

methanol from DMC. The first column (Column4) is described by the FUG equations, however, the second

254

column (Column5) is modelled using a surrogate model due to the lack of accuracy between rigorous

255

simulation and the FUG equations. The presence of the azeotrope determines the thermodynamics of the

256

system. The azeotrope concentration is equal to 97%w of methanol at the operating pressure [29]. A

257

surrogate model (see eq.(11)) was developed using rigorous simulation to compute the reflux ratio (R_{real})

258

as a function of the bottom DMC yield (R_{DMC}).

259
$$R_{real} = 2.49929 \cdot R_{DMC} - 1.64366 \quad (11)$$

260 The yield to DMC at the bottoms is a variable while the distillate methanol yield is fixed at 99.99%. The
 261 final DMC is obtained from the bottom of the column 5. The DMC is stored at ambient pressure and
 262 temperature. The distillates from the columns 4 and 5 are recycled to be mixed with the inlet methanol.

263 **4. Solution Procedure**

264 The problem of producing DMC from CO₂ via the urea route is formulated as a nonlinear programming
 265 (NLP) problem according to the model equations and assumptions presented in the section above. The
 266 decision variables correspond to the operating conditions of each unit, namely, pressure, temperature and
 267 flow ratios. A simplified profit equation is chosen as objective function as follows:

268
$$obj = F_{DMC} C_{DMC} + F_{Urea} C_{Urea} - F_{NH_3} C_{NH_3} - F_{CO_2} C_{CO_2} - F_{MeOH} C_{MeOH} \quad (12)$$

$$- F_{steam} C_{steam} - F_{cooling} C_{cooling} - W_{total} C_{elect}$$

269 The variables and parameters involved in the objective function are collected in Table 2.

270 Table 2: Variables and parameters for the objective function.

Symbol	Variable	Value	Source
F_{DMC}	DMC flow production		
C_{DMC}	DMC cost	0.820€/kg	[29]
F_{Urea}	Urea flow production		
C_{Urea}	Urea cost	0.322 €/kg	[38]
F_{NH_3}	Inlet flow of ammonia		
C_{NH_3}	Ammonia price	0.5€/kg	[39]
F_{CO_2}	Inlet flow of carbon dioxide		
C_{CO_2}	CO ₂ price	0.0509€/kg	[38]
F_{MeOH}	Methanol flow demand		
C_{MeOH}	Methanol price	0.330€/kg	[29]
F_{steam}	Steam flow demand		
C_{steam}	Steam price	2.20€/GJ	[40]
$F_{cooling}$	Cooling water flow needs		
$C_{cooling}$	Cooling water price	4.58€/kt	[40]
W_{total}	Total Power		

C_{elect}	Electricity price	7.87cent€/kWh	[41]
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272 The problem proposed above consists of about 3000 variables and 2500 equations. The equation based
 273 model is implemented and solved in GAMS using an NLP multistart optimization with CONOPT 3.0 as the
 274 preferred solver.

275 Using the results obtained from the optimization, an estimation of the capital and operating costs has been
 276 carried out. To estimate the capital cost, the factorial method proposed by Sinnott [42] is employed. The
 277 major equipment capital costs are estimated using the correlations proposed by Almena & Martín [43]. The
 278 cost of the urea reactor is estimated based on the industrial size of urea reactors [44]. For the
 279 methylcarbamate (MC) synthesis reactor from urea and methanol, the capital cost is estimated with the
 280 data provided by Sun et al. [45]. Finally, the reactor where the DMC is synthesized is a fixed bed reactor
 281 where the catalyst, ZnO over alumina, has a cost of 355 \$/ft³ [46] with a liquid hourly space velocity
 282 (LHSV) equal to 1.2h⁻¹ [37].

283 The operating costs include two main items: variable and fixed costs. The variable costs have been
 284 estimated with the prices used in the objective function (see Table 2) and the amount of raw materials and
 285 utilities from the optimization results. Within the fixed costs, labor and capital are included among others.

286 5. Results

287 5.1 Key operating variables

288 5.1.1 DMC production

289 In this section, a summary of the main operating variables from the optimization results is presented. The
 290 DMC production is more profitable according to the objective function than the urea synthesis alone,
 291 therefore, the total urea produced in the first section is sent to the DMC production section. However, for
 292 comparative purposes, the synthesis of urea is also evaluated. First, the results for the DMC production
 293 are presented. Then, the results when only urea is produced are also shown. In the DMC synthesis, the
 294 urea reactor works with a conversion of urea equal to 58.3% with the following parameters that determine

295 this conversion (see equation eq.(3)): a (NH_3/CO_2 ratio) equal to 3.111, b ($\text{H}_2\text{O}/\text{CO}_2$ ratio) equal to 0.439
 296 and the outlet temperature equal to 493K. The stripper conditions are summarized in Table 3.

297 Table 3: Main operating conditions in the urea stripper (DMC production).

	Stripper			
	Urea Reactor Out	CO ₂ in	Stripp gas out	Stripp liquid out
T (K)	493.0	450.0	494.7	500.1
P(bar)	200.0	200.0	200.0	200.0
F (kg/s)	9.544	2.000	7.508	4.036
mass fraction				
CO ₂	0.000	1.000	0.426	0.125
NH ₃	0.184	0.000	0.403	0.011
Urea	0.340	0.000	0.079	0.657
H ₂ O	0.316	0.000	0.092	0.207
Carbamate	0.160	0.000	0.000	0.000

298

299 The flowrate fed to the stripper is fixed to 2 kg/s of CO₂ both in the synthesis of DMC and in the synthesis
 300 of urea. A trade-off exists between the operating conditions in the urea reactor and the stripper and among
 301 the yields of the different species. The yields in the stripper (to the liquid stream) achieved for each
 302 component are as follows: 1.411% (NH₃), 13.589% (CO₂), 81.718% (Urea) and 54.726% (H₂O). The
 303 operating variables in the stripper model (see equations S19-S25 in the Supplementary Information) are
 304 shown in Table 5. The medium pressure stage to purify the urea is carried out at 11.9 bar and 393.7K and
 305 the final purification (low pressure) takes place at 1 bar and 371.9K. The non-reacted gases are recycled
 306 to the urea reactor via the condenser. The ammonia is also recycled from the DMC section. Due to this
 307 fact, only 1% of the inlet ammonia to the urea reactor is fresh in the DMC synthesis.

308 Table 4: Main operation conditions in the reactors of the DMC synthesis section.

	Reac2		Reac3	
	IN	OUT	IN	OUT
T(K)	423.0	423.0	447.3	447.3
P(bar)	20.0	20.0	19.8	19.8
F(kg/s)	5.653	5.653	60.0	60.0
mass fraction				
CO ₂	0.000	0.000	0.000	0.000
NH ₃	0.000	0.133	0.000	0.012
Urea	0.469	0.000	0.000	0.000

H ₂ O	0.000	0.000	0.001	0.001
MeOH	0.501	0.250	0.834	0.811
MC	0.000	0.587	0.113	0.058
DMC	0.030	0.030	0.051	0.117
NMMC	0.000	0.000	0.000	0.000

309

310 The first reactor in the DMC production section (Reac2) transforms urea and methanol to MC. The second
311 one synthesizes DMC from MC. The main conditions for these reactors are shown in Table 4. In the
312 second reactor, as it is presented in the modelling issues section, a large excess of methanol is needed
313 that, afterwards, must be separated and recycled. The operating conditions in the second reactor are
314 adjusted during the process optimization to minimize the amount of NMMC produced according to the
315 equation eq.(10). Due to the small amount of impurities generated in the reaction, the flow of the purge
316 that is necessary to separated is almost zero avoiding a loss in the non-reacted components.

317 5.1.2 Renewable Urea production

318 Another case of study is when only urea is produced instead of DMC. In this case, the model is forced to
319 not synthesize DMC from urea. Since the optimal facility leads to the production of DMC, the objective
320 function for the production of urea is worse. In this case, the parameters that determine the urea reactor
321 performance take the following values: a is equal to 3.253, b is equal to 0.569 and the final temperature
322 equal to 493K. In the stripper, the main variables are collected in Table 6. The pressure changes in
323 comparison with the previous case (160 bar vs 200 bar). The operational model variables (see eq.(6))
324 change in the stripper with respect to the production of DMC as follows, see Table 5.

325 Table 5: Variables in the stripper model for the DMC/Urea process.

Variable	DMC process	Urea process	Units
Temperature	493.0	493.0	K
Pressure	200.0	160.0	bar
Heat-Urea ratio (Q/U)	20.0	24.4	kJ/kmol U
Urea-NH ₃ ratio (U/NH ₃)	0.30	0.28	kmol U/kmol NH ₃
Urea-Water ratio (U/H ₂ O)	0.64	0.55	kmol U/kmol H ₂ O
Urea-CO ₂ from reactor ratio (U/CO ₂)	1.4	1.4	kmol U/kmol CO ₂
Urea-inlet CO ₂ (U/CO _{2in})	1.19	1.16	kmol U/kmol CO ₂

326

327 The final urea purity changes between the two processes. In the DMC process a high purity urea is
 328 obtained because water is an impurity in the DMC process. However, when only urea synthesis is
 329 evaluated the purity is fixed to 0.9 (mass fraction) because no further processing is required and,
 330 therefore, the minimum purity value is desired to hold the specifications and reduced the objective function
 331 value. This fact determines the different operating conditions in the urea section for the two alternatives.

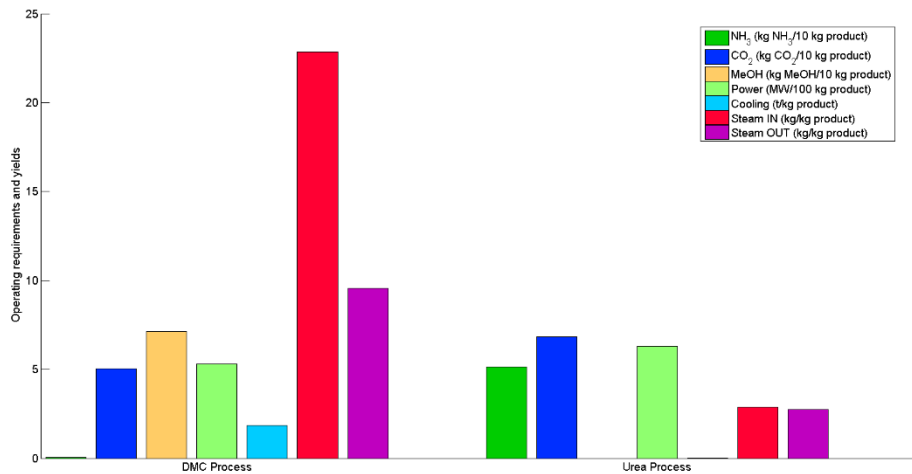
332 Table 6: Operating Variables in the Stripper (Urea production).

	Stripper			
	Urea Reactor Out	CO ₂ in	Stripp gas out	Stripp liq out
T (K)	493.0	450.0	496.4	503.2
P(bar)	160.2	160.2	160.2	160.2
F (kg/s)	9.758	2.000	7.915	3.845
mass fraction				
CO ₂	0.000	1.000	0.415	0.099
NH ₃	0.198	0.000	0.406	0.001
Urea	0.325	0.000	0.068	0.685
H ₂ O	0.176	0.000	0.112	0.216
Carbamate	0.302	0.000	0.000	0.000

333

334 A graphical summary of both processes with the main yields is presented in Figure 5. The ammonia
 335 consumption is higher in the urea process than the DMC process. A large amount of ammonia is recycled
 336 to the urea section in the DMC production and only a small make up of ammonia is needed. However, the
 337 consumption of carbon dioxide is larger in the production of urea (about 0.7 kg CO₂/kg urea) compared to
 338 the process where the DMC is synthesized (0.5 kg CO₂/kg DMC). The last raw material, methanol, is only
 339 employed when DMC is produced. The power consumption is similar in both processes. The consumption
 340 of power takes place in the compressors set up in the urea synthesis section. Therefore, the difference
 341 between the power consumption is only caused by the change in the operating conditions in the urea
 342 section in the two studied alternatives. The cooling water usage is almost zero in the urea production while
 343 for the production of DMC is it higher with a value of about 1.85 t of cooling water per kg of DMC due
 344 mainly to the condenser in the distillation columns. In the synthesis of urea the amount of steam generated
 345 and consumed is approximately the same (with a positive net consumption). However, the amount of
 346 steam needed in the DMC production is around 2-3 times the amount of steam generated in the entire

347 process. The consumption of steam in the reboilers of the columns to separate the different components
348 formed in the synthesis is the main cause of this increase.



349

350 Figure 5: Main yields for the DMC and urea processes.

351 5.2 Economic Evaluation

352 The capital costs of the facility have been estimated as it was described above, see solution procedure.

353 The total investment for the DMC production is about 91 MM€, and for the urea production only about 16

354 MM€ for a production capacity of 342 t/d and 253 t/d of DMC and urea respectively. A breakdown of the

355 capital cost is shown in Figure 6. For the production of DMC (Figure 6a), the heat exchangers (HX)

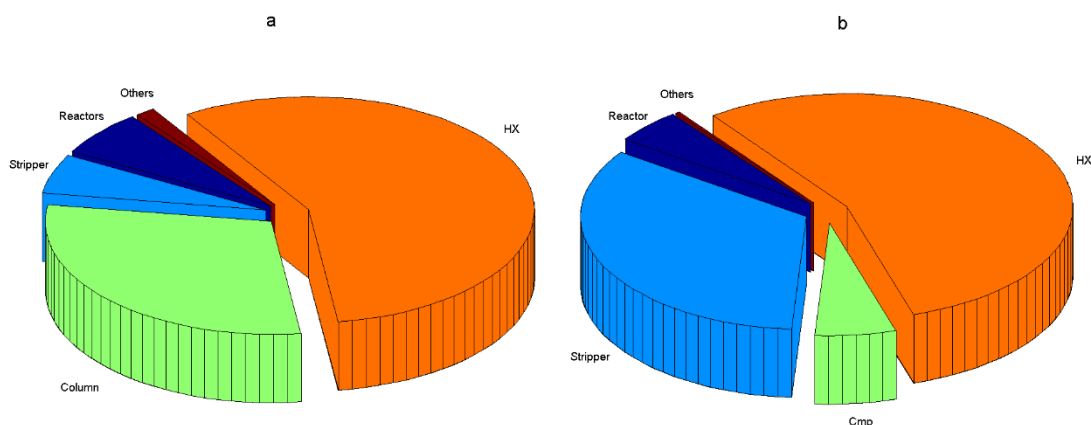
356 represent the largest share of the investment. In this section, the reboilers and condensers from the

357 distillation columns are included. These columns represent the second largest contribution to the

358 investment cost. For the production of urea alone (Figure 6b), the HX's also represent the largest

359 contribution. The stripper is another equipment with a high investment due to the complexity of the unit

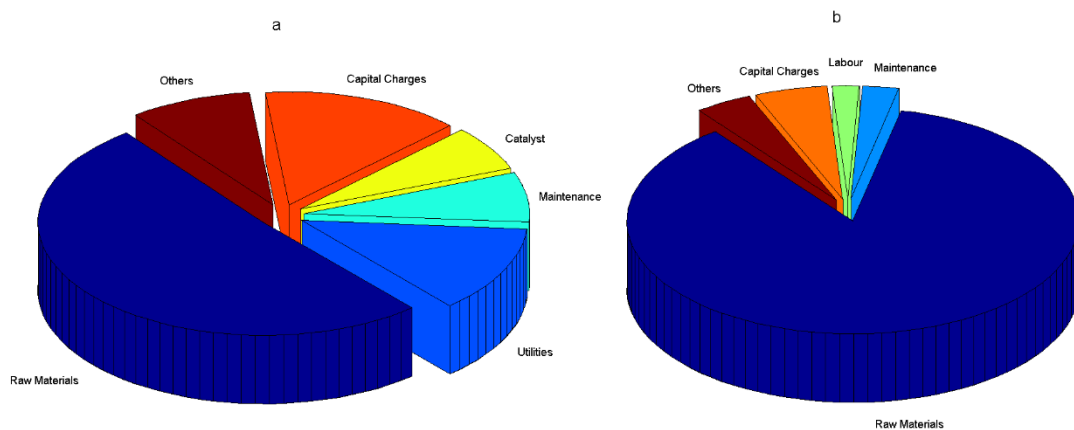
360 involving a gas-liquid contact and heat exchange.



361

362 Figure 6: Breakdown for the equipment capital cost (a: DMC process; b: Urea process).

363 The operating costs of the processes have also been estimated. The DMC production cost is about 520
 364 €/t, a very promising result according to the current prices found in the literature in the range of 820-1100
 365 \$/t [28,29]. In Figure 7a, the distribution of the production cost into the different items for the DMC
 366 synthesis is shown. The raw materials represent the largest contribution to the production cost, above all,
 367 the methanol cost due to the small amount of ammonia needed in the DMC production. The utilities
 368 include the cost of the steam, cooling water and power. The catalyst is introduced in the operating costs
 369 due to the annual replacement of it in the second DMC reactor [46]. In the urea synthesis, the production
 370 cost is about 340 €/t, slightly higher than the current production processes but in the same levels than
 371 other green urea production processes [38,47]. According to these results, an integrated plant to produce
 372 DMC and urea can provide competitive costs for both chemicals reducing the urea price with the benefits
 373 obtained from the sale of DMC. In the urea cost breakdown (see Figure 7b), the raw materials item
 374 represents almost 85% of the total operating cost. The main cause is the ammonia used as feedstock
 375 since nitrogen from ammonia is fixed in the urea and no ammonia recycle is possible.



376

377 Figure 7: Breakdown of the operating cost (a: DMC process; b: Urea process).

378 **5.3 Sensitivity analysis**

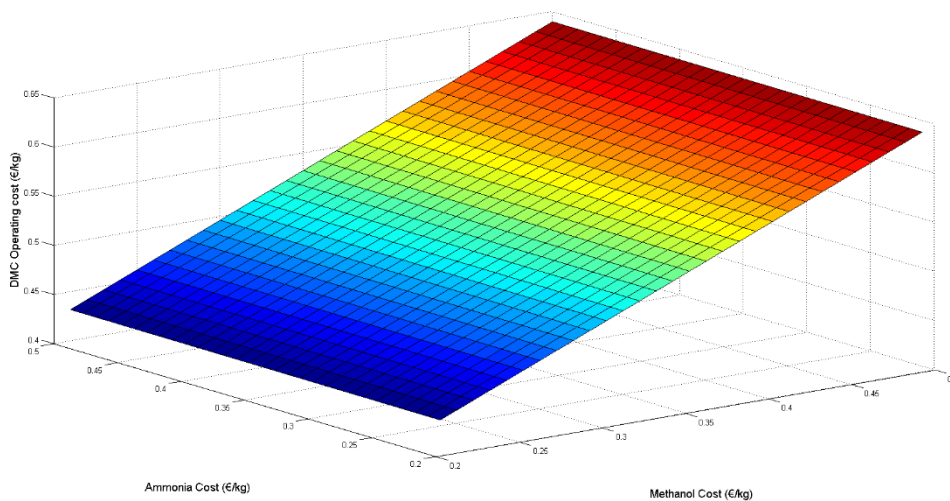
379 The prices of the raw materials play a key role in the economic performance of the urea/DMC production
 380 as it is shown in Figure 7. The price of methanol or ammonia depends a lot of the production path used to
 381 synthesize these chemicals. If an entire green process is desired, the raw materials must also be
 382 produced following a renewable path and, in general, an increase in the production cost is expected.
 383 Therefore, a sensitivity analysis is carried out to study the influence of the different prices of the raw
 384 materials according to their different production paths.

385 The methanol can be produced from a wide range of green alternatives: from switchgrass via gasification
 386 and with the possibility of combining it with the hydrogenation of carbon dioxide [23], using captured CO₂
 387 and hydrogen from electrolysis [13] or from biogas via reforming [24]. An economic evaluation for each
 388 process was carried out in the different works resulting the following price ranges: 0.34-0.36 €/kg for the
 389 switchgrass to methanol process [23], 0.21-0.45 €/kg for the hydrogenation of CO₂ with electrolyzed
 390 hydrogen [13] and 0.46 €/kg for the biogas to methanol process [24].

391 The sustainable ammonia production is gaining attention nowadays to develop a green path to produce
 392 ammonia and due to the possibility of using ammonia as a hydrogen carrier or as a fuel. Different
 393 processes have been proposed: using electrolysis to generate hydrogen, air separation (distillation,

394 adsorption or membrane) to produce nitrogen and with both synthesize ammonia [19,20] or from biomass
395 gasification or from biomass digestion [22]. The ammonia production costs for the different alternatives are
396 as follows: 1.37-5.6 €/kg for the ammonia from electrolysis and separation of air using membranes (this
397 price presents a wide range due to the different scales studied), 1.2-4.5 €/kg for electrolysis and air
398 separation using adsorbent beds and 1.36-1.6 €/kg for electrolysis and using distillation for the separation
399 of air [20], 0.38-0.69 €/kg for the ammonia production from biomass gasification and 0.87-1.24€/kg for the
400 digestion process [22].

401 Following the prices for the different species involved presented above, a sensitivity analysis is carried out
402 to study the influence of the feedstock prices in the DMC and urea production cost. Figure 8 shows
403 graphically the influence of the ammonia and methanol cost in the DMC operation cost.



404

405 Figure 8: Sensitivity analysis for the DMC production cost based on the raw materials prices.

406 The production cost of the DMC, for the ranges of prices proposed based on literature data, see Figure 8,
407 is in the interval between 0.4 and 0.65 €/kg. The influence of the methanol price in the operating cost is
408 larger than that due to the ammonia price. As it is presented previously, in the DMC production a large
409 amount of ammonia is recycled from the DMC synthesis section to the urea section and, therefore, only a
410 small amount of ammonia is required as raw material. Due to this small flow, when the ammonia price is
411 multiplied by 8 only an increase of less than 3% in the DMC production cost takes place. However, when
412 the methanol price doubles, the DMC operating cost increases by 40%. In Table 7, it is presented the

413 DMC operating cost for the lowest price of the range for each technology presented above for producing
 414 ammonia and methanol from renewable sources. The final DMC production costs are in the interval
 415 between 431.3 €/t and 614.4 €/t. The literature presents DMC price about 800 €/t, therefore, the DMC
 416 production from renewable sources can be a competitive alternative.

417 Table 7: DMC production cost sensitivity analysis for different ammonia/methanol production processes.

DMC Production Cost (€/t)		Methanol Production			
		Gasification	CO ₂ hydrogenation	Biogas reforming	
Ammonia Production	Electrolysis +	Membrane	528.7	435.8	614.4
		PSA	527.9	435.0	613.6
		Distillation	528.6	435.7	614.3
	Gasification	Indirect	524.2	431.3	609.9
		Direct O ₂ /Steam	524.9	432.0	610.6
		Direct Air/Steam	524.9	432.0	610.6
Digestion		526.4	433.5	612.1	

418

419 For the production of urea, the results are presented in Table 8. In this case, only ammonia and carbon
 420 dioxide are required for the synthesis. Here, ammonia is not recycled as in the DMC production, therefore,
 421 the ammonia price has a more important influence in the urea production cost. The range of cost for urea
 422 is 277.2-787.6 €/t. The urea cost is highly related to the ammonia production technology and, within each
 423 technology, the price presents a strong link with the facility production capacity [20].

424 Table 8: Urea production cost sensitivity analysis for different ammonia production processes.

Ammonia Production	Urea Production Cost (€/t)	
Electrolysis +	Membrane	787.6
	PSA	699.9
	Distillation	777.2
Gasification	Indirect	277.5

		Direct O ₂ /Steam	354.8
		Direct Air/Steam	359.9
	Digestion		529.9

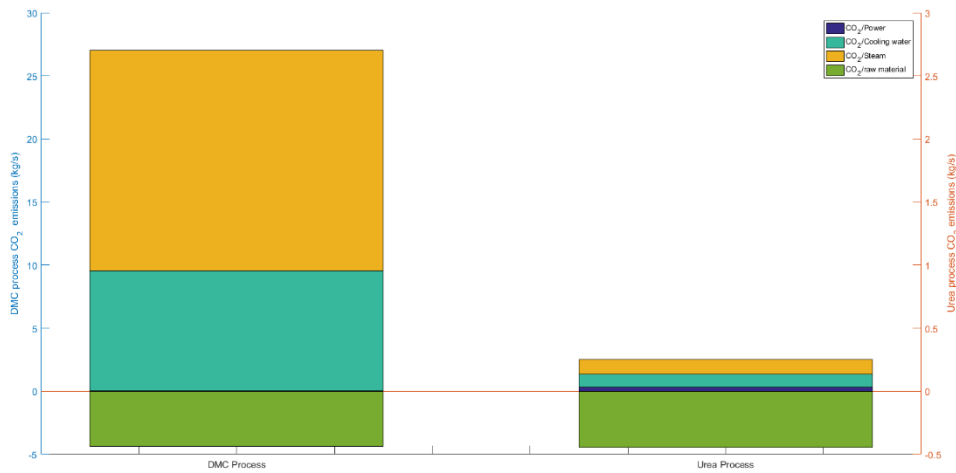
425

426 **5.4 Environmental Analysis**

427 To evaluate the environmental performance of the processes, the index proposed by Martin [48], RePSIM,
428 was employed. In this simplified metric, the processes are evaluated based on the associated CO₂
429 emissions. For this case of study, the raw materials are: methanol, ammonia and carbon dioxide. The CO₂
430 associated with the production of ammonia and methanol presents a strong relationship to the production
431 process used in its synthesis. For this environmental analysis, a level of emissions of 1.03 kg CO₂/kg NH₃
432 is considered associated with a production process based on water electrolysis and air distillation and -
433 0.84 kg CO₂/kg MeOH for the methanol production by hydrogenation of CO₂ with electrolyze hydrogen
434 [49]. The CO₂ emissions associated with the carbon capture are neglected. The CO₂ emissions associated
435 to power are taken into account using the factor of 0.632 kg CO₂/kWh [48]. The CO₂ emissions related to
436 cooling water are considered using a factor of 7775 kWh/Mgal to calculate the energy requirement and
437 with this value and the energy to CO₂ factor the emissions related to cooling water are calculated [24]. The
438 steam necessary in the process has also a CO₂ value. These CO₂ emissions are computed using the
439 energy necessary to produce it and then with the energy to CO₂ factor as previously described.

440 The results for the DMC and urea production are shown in Figure 9. The raw materials item has a negative
441 contribution to the emissions of CO₂ due to the use of CO₂ as raw material for the processes including the
442 production of ammonia and methanol. The main contribution to the CO₂ emissions is the steam needed in
443 the facility. This steam is consumed in the sequence of distillation columns to separate the different
444 components involved in the DMC synthesis reactor. Sustainable steam can be produced from renewable
445 sources to reduce the carbon dioxide emission related to the production of the utilities [50]. In the process,
446 steam is also generated in some units (for example, the urea condenser), however the net flow is positive
447 (See Figure 5) and, therefore, a contribution to CO₂ emissions takes place. The DMC process presents an

448 emission level of 5.74 kg CO₂/kg DMC and the urea one results in -0.04 kg CO₂/kg urea. The urea
 449 production is approximately carbon neutral. In this index, the CO₂ emissions related to urea hydrolysis
 450 during the application is not considered due to the fact that this index only focuses on the urea/DMC
 451 production process [51].



452

Figure 9: Contribution to the CO₂ emissions by process.

453

454 **6. Conclusions**

455 In this work, a sustainable path to produce DMC via urea has been evaluated. Furthermore, for
 456 comparison the urea synthesis alone has also been studied. An equation based modelling approach has
 457 been used to analyse the two main section of the process: the urea synthesis and the DMC synthesis.
 458 Data driven models based on experimental data or rigorous simulations and first principles are used to
 459 model the processes. The decision variables for the optimization are the operating conditions in the
 460 different units involved, for instance, pressure or temperature in the urea synthesis reactor, the urea
 461 stripper conditions, the DMC reactor outlet temperature, the inlet flows of ammonia and methanol, etc.
 462 According to the economic objective function, the DMC production is favourable with respect to the urea
 463 production. With the optimization results, an economic analysis was carried out for both alternatives. The
 464 investment for the DMC production is about 91 MM€ with a production cost of about 520 €/t. When only
 465 urea is produced, the capital cost is around 16 MM€ with a production cost of 340€/t. The sensitivity
 466 analysis shows that the methanol price plays an important role in the DMC price. The ammonia price is

467 key in the urea cost and has only a small influence in the DMC price due to high recycle rate. Finally, a
468 simple environmental analysis is presented showing the CO₂ emissions associated with the urea/DMC
469 process. Urea production is near emissions neutral.

470 7. Acknowledgement

471 The authors would like to acknowledge Salamanca Research for optimization software licenses. The
472 authors acknowledge the FPU, Spain grant (FPU16/06212) from MEC, Spain to Mr. A. Sánchez and
473 MINECO, Spain grant DPI2015-67341-C2-1-R.

474 8. Nomenclature

475 a NH₃/CO₂ ratio, eq.(3)-(4)

476 a_{0-4} Fitting parameters, eq.(9)

477 b H₂O/CO₂ ratio, eq.(3)-(5)

478 C_{CO_2} Carbon dioxide price (€/kg)

479 $C_{cooling}$ Cooling water cost (€/kt)

480 C_{DMC} DMC cost (€/kg)

481 C_{elect} Electricity cost (cent €/kWh)

482 C_{MeOH} Methanol price (€/kg)

483 C_{NH_3} Ammonia price (€/kg)

484 C_{steam} Steam cost (€/GJ)

485 C_{Urea} Urea cost (€/kg)

486 f_c Molar flow (kmol/s)

487 F_{CO_2} Carbon dioxide inlet flow (kg/s)

488 $F_{cooling}$ Cooling water consumption (kt/s)

489 F_{DMC} DMC production (kg/s)

490 F_{MeOH} Methanol inlet flow (kg/s)

491 F_{NH_3} Ammonia inlet flow (kg/s)

492 F_{steam} Net steam needed (GJ/s)
493 F_{Urea} Urea production (kg/s)
494 P Pressure (MPa), eq.(9)
495 R_{DMC} Bottom DMC yield in column 5, eq.(10)
496 R_{refl} Reflux ratio in column 5, eq. (10)
497 t Temperature (°C), eq.(3)
498 T Temperature (K), eq.(9)
499 W_{total} Total power (kWh)
500 X Conversion eq.(3)
501 Y_i Reaction yield, eq.(9)
502 β Linear coefficient, eq.(6)
503 ω Quadratic coefficient, eq.(6)

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