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CARBON FOOTPRINT OF BIOGENIC CARBON CAPTURE, STORAGE AND UTILIZATION VIA ELECTROCHEMICAL REDUCTION TO METHANOL

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1. RESUMEN

El objetivo de este trabajo es evaluar la huella de carbono de una central termoeléctrica alimentada con biomasa forestal que exporta a la red eléctrica un máximo de 270 MW y captura todo el CO_2 generado. Parte del CO_2 es almacenado en un acuífero salino. La fracción restante de CO_2 capturado es reducido en un reactor electroquímico con electricidad procedente de paneles fotovoltaicos a metanol, que posteriormente será utilizado como combustible en un vehículo. Se evaluó la incorporación al proceso de dos casos de estudio (A y B respectivamente) basados en dos tecnologías de electrorreducción con diferentes configuraciones y materiales electródicos (Albo y col., 2015b; Shironita y col., 2013).

Para determinar la huella de carbono del proceso descrito se empleó la metodología del análisis del ciclo de vida. En primer lugar se revisó el estado del arte para la cuantificación de las emisiones de CO_2 biogénicas y los procesos de captura y utilización de CO_2. A continuación se definieron los límites del sistema estudiados y se desarrolló un modelo matemático basado en los balances de materia y energía a los equipos que integran el proceso, con el propósito de su descripción. Este modelo permitió obtener el inventario de CO_2 equivalente del proceso, asignando todas las cargas ambientales del proceso a la electricidad producida.

Los resultados obtenidos demuestran que en ambos casos A y B, sin tener en cuenta ningún facto de mejora, la opción con menos emisiones de CO_2-eq (0.137 kg CO_2-eq·kWh^{-1}), es almacenar todo el CO_2 capturado y no derivar ninguna parte a la reducción electroquímica.

El caso estudiado A (Albo y col., 2015b) está limitado fundamentalmente por la excesiva demanda energética del proceso de destilación convencional para la separación metanol/agua. Se ha estimado que la concentración de metanol obtenida en el proceso de electrorreducción se debería incrementar unas 10,000 veces para que esta tecnología pueda ser aplicada con menores emisiones que en el caso de referencia.

En cuanto al caso B (Shironita y col., 2013), es posible electrorreducir una mayor cantidad de CO_2 sin comprometer la eficiencia energética de la planta, ya que por la configuración del cátodo, no requiere incorporar una etapa de purificación al proceso puesto que la corriente de CO_2 incorpora la cantidad de agua necesaria para la reacción. No obstante, las emisiones indirectas de CO_2-eq son superiores a las del caso A incluso para todas las concentraciones estudiadas, ya que los materiales que componen el electrodo en el caso B tienen una huella de carbono mucho más elevada. Sería necesario mejorar la vida útil del electrodo unas 10 veces en el caso B para que al compararlo con el caso A, en el que la concentración aumenta 4 órdenes de magnitud, las emisiones de CO_2-eq sean similares.

Si bien la huella de carbono de los procesos de producción de electricidad a partir de biomasa acoplados a un proceso de captura y almacenamiento de CO_2 (sin derivación al proceso de electrorreducción) es inferior a, por ejemplo el mix eléctrico de la Unión Europea (0.392 kg CO_2-eq·kWh^{-1}), su implementación conjunta con un proceso de valorización electroquímica de CO_2 a metanol no es viable en la actualidad para las dos referencias analizadas, bajo las hipótesis asumidas en el presente trabajo. Los principales motivos son las elevadas necesidades de energía derivada de los procesos de destilación para la separación metanol/agua (como consecuencia de la baja concentración obtenida) o la limitada vida útil de los materiales electródicos que emplean metales como platino y rutenio.

La investigación futura en relación a los procesos de electrorreducción de CO_2 se debería centrar en: i) el aumento de la concentración de metanol (para disminuir el consumo energético en la separación); y ii) el desarrollo de materiales catódicos que impliquen una baja huella de carbono a través de una mayor vida útil.

2. BACKGROUND

Current climate policies set a 2 ^{o}C increase in the global average surface temperature above pre-industrial levels as the temperature ceiling below which the most severe impacts of climate change are likely to be prevented. This implies that the atmospheric concentration of CO_2-equivalent (CO_2-eq) should not surpass 450 ppm (IPCC, 2014). According to the IEA (2013), the energy sector is responsible for two thirds of greenhouse gas (GHG) emissions; thus, the power generation sector should play a major role in climate change mitigation.

The European Union has agreed to reduce its GHG emissions to 80-95% below 1990 levels by 2050, relying on the progressive penetration of renewable energy sources (RES), carbon capture and storage (CCS) and nuclear power, along with measures to improve energy efficiency in all sectors (ECF, 2010). However, recent studies (Gasser et al., 2015; Selosse et al., 2014) suggest that this decarbonisation objective is not stringent enough and negative CO_2-eq emissions are needed to meet the 2 ^{o}C target.
In this regard, bioenergy processes coupled with CCS (BECCS) have the potential to produce negative or at least very few CO_2 emissions in comparison to traditional processes (Guest et al., 2012; Kemper, 2015).

On the other hand, the integration of RES into the electricity market presents some drawbacks. Electricity must be consumed right after it is produced, which is why as the share of fluctuating RES increases, it will become harder to match the electrical load to the supply (Grave et al., 2012). Despite the fact that the security of the electricity supply might not be warranted at moments of peak demand, some countries, such as Germany, are already facing the challenge to deal with the excess available power.

To address this issue, Sternberg & Bardow (2015) performed an environmental assessment of a number of different energy storage systems, concluding that heat pumps and battery electric vehicles contribute the least to global warming. Although their analysis comprised CO_2 conversion to various fuels through catalytic hydrogenation by means of the preceding electrolysis of water, they did not consider in their study the electrochemical reduction (ER) of CO_2 to liquid fuels. Nevertheless, the ER of CO_2 at normal temperature and pressure, which avoids the production of hydrogen as an intermediate product, may prove to be more efficient and sustainable than the more developed fuel catalytic synthesis (Pérez-Fortes et al., 2015); even though Albo et al. (2015a) agree that the ER of CO_2 is not a mature technology yet
Therefore, CO_2 electrochemical valorization is regarded as a valid strategy to simultaneously curb CO_2 emissions and to store the surplus power from intermittent RES by means of the conversion of CO_2 to liquid fuels such as formic acid or methanol, which can be later combusted (Albo et al., 2015a; Alvarez-Guerra et al., 2012).

Among the range of organic products to which CO_2 can be electrochemically reduced, methanol stands out as a valuable energy vector suitable for internal combustion engine driven vehicles (Olah et al., 2009); while direct methanol fuel cells are not suited for large scale scale stationary applications (Nedstack, 2011; Fuel Cell Today, 2013), the utilization of this chemical blended with gasoline in flexible fuel vehicles

(FFVs) is already developed and both technically and economically feasible (Methanol Institute, 2015).

One of the most relevant issues that deserve discussion is the market size. Global production of methanol was around 36.5 Mton·yr^{-1} in 2011 (Methanol Institute, 2011). If the total worldwide production of methanol was supplied by the ER of CO_2 with water, around 50 Mton of CO_2 would be utilized rather than released every year, which constitutes roughly 0.1% of global GHG emissions in 2010 (IPCC, 2014). Nonetheless, if the methanol market widened because of the generalized use of methanol in FFVs, the ER of CO_2 to methanol might prove to be an attractive method to recycle CO_2.

2.1 AIM AND SCOPE OF THE WORK

The objective of this work is to quantify by means of life cycle assessment (LCA) the environmental burdens expressed in terms of global warming potential of two combined processes that aim at mitigating climate change:

i) ER of biogenic CO_2 to methanol, which will subsequently substitute gasoline.
ii) Storage of biogenic CO_2 in a saline aquifer.

The first step taken to accomplish this goal was to review the state of the art methodology applied to quantify the CO_2-eq emissions of bioenergy processes and to perform an LCA of carbon capture and utilization (CCU) processes. In addition to that, two ER studies from the literature under different operation conditions and electrode materials were selected to be further compared and included into the environmental sustainability analysis based on the carbon footprint.

Once the system boundaries were established, a mathematical model that described the most significant material and energy balances of the process under study was developed. Following the principles and framework of ISO standards (2006), this model was later deployed to obtain the CO_2-eq profile, whose interpretation provided insight into the environmental burden of the assessed system.

2.2 QUANTIFYING THE CARBON FOOTPRINT OF BIOENERGY PROCESSES

Most LCA studies of bioenergy processes to date apply the paradigm carbon-neutral-equals-climate-neutral. Nevertheless, before being captured by biomass regrowth during the photosynthesis, CO_2 molecules spend some time in the atmosphere, absorbing radiation and contributing to global warming (Guest et al., 2013).

Cherubini el al. (2011) proposed a methodology to quantify the net CO_2 emitted in biomass combustion processes. They developed a Global Warming Potential factor (GWP) that accounted for the natural consumption of CO_2 by biomass (GWP_b).

The GWP of a certain GHG is calculated as a function of the time horizon selected, the radiative forcing of the gas and its Impulse Response Function (IRF), which describes how the atmospheric concentration of the gas decays over time after a single pulse of gas is emitted.

The decay of the atmospheric concentration of CO_2 in the atmosphere occurs because of the effect of the ocean and the terrestrial biosphere, which act as CO_2 sinks. The IRF of the biogenic CO_2 emissions (IRF_{bCO2}) developed by Cherubini et al. (2011) also takes into account the absorbed CO_2 consumed during biomass regrowth, considering that the CO_2 pulse is emitted at the time that the same amount of biomass as the required to emit that pulse is replanted. To do so, the Net Ecosystem Production (NEP), which describes the growth rate of the biomass sink as a function of its rotation period, is incorporated into the expression to calculate IRF_{bCO2}.

Thus, the GWP_b depends on two variables: the biomass rotation period and the selected time horizon. Biomass with short rotation periods take up CO_2 faster, resulting in a lower GWP_b for a given time horizon. On the other hand, the longer the time horizon selected, the more CO_2 can be absorbed by the biomass, resulting in a lower GWP_b. These trends can be easily identified in Figure 1.

Figure 1 shows the IRF of fossil CO_2 (black curve) and biogenic CO_2 with different rotation periods. GWP and GWP_b are directly proportional to the area under their corresponding curves; the area under the fossil CO_2 decay is larger than the area under the biogenic CO_2 decay.

The points of the curve below the abscissa axis indicate that, at that time, the amount of CO_2 that would otherwise remain in the atmosphere is lower than the amount of CO_2 that is being absorbed by the biomass. As can be seen in Figure 1, when the rotation period finishes, the CO_2 atmospheric concentration increases back to the original levels before the CO_2 pulse, because the replanted biomass does not take up any more CO_2.

However, if CO_2 was stored indefinitely by means of a CCS process, only the CO_2 uptake of biomass should be taken into account and therefore, negative CO_2 emissions might be achieved.

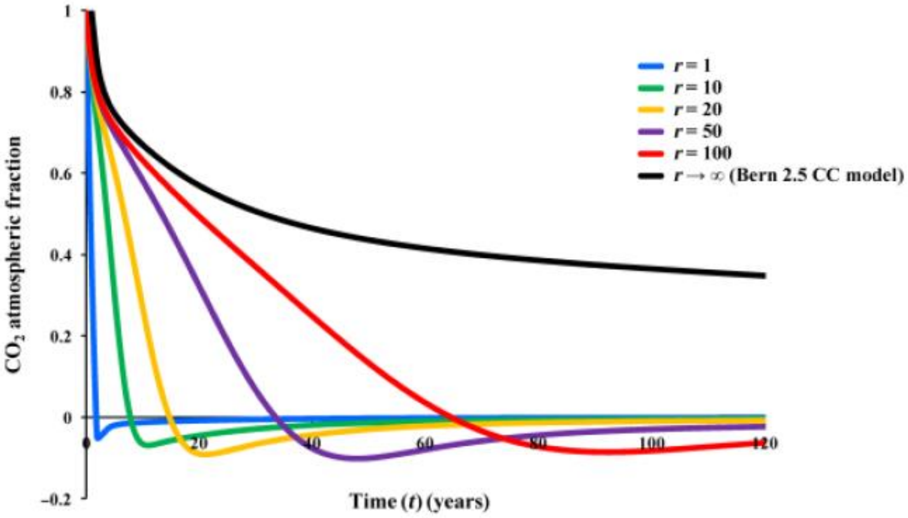

Figure 1. CO_2 atmospheric decay for different rotation periods and a time horizon of 120 years (Cherubini et al., 2011)

2.3 METHODOLOGICAL APPROACH TO LCA OF CCU

The asseveration of the environmental friendliness of a process strongly relies on LCA as a tool to guarantee that every single stage involved is accounted for, and that the rebound effect of certain processes is not missed (Finnveden, 2009).

Valorization or utilization of CO_2 is defined as the transformation of waste CO_2 emissions into valuable chemicals or products (Cuéllar-Franca and Azapagic, 2015). According to Von der Assen et al. (2013), the application of the LCA methodology to CCU processes is not properly standardized yet. They proposed a strategy regarding burden allocation and temporal considerations in order not to find inconsistencies in CCU LCA studies.

The LCA practitioner might come across a multi-functionality problem: how to allocate the environmental burdens between the chemical obtained after the CO_2 valorization process and the product intended to be obtained by means of the process that produces CO_2 as a co-product. To deal with this problem, two strategies might be applied:

1) Avoided burden/Direct substitution approach. Firstly, it must be decided what product is the main reason why the process is operating. Then, the system boundaries are expanded to include an alternative production process for the other product. Environmental burdens due to the production of the other product are subtracted from the emissions of the studied system.

2) Allocation approach. Burdens are allocated between the different products, depending on their properties (mass, energy content, economic value).

Von der Assen et al. (2013), strongly recommend not using the avoided burden approach, but to use as allocation criteria the economic value of the products instead, because of the following reasons:

- The selection of one primary product, subject to the opinion of the LCA practitioner, is avoided.
- Negative CO_2-eq emissions might be obtained with the avoided burden approach, leading to the erroneous conclusion that the process is a CO_2 sink.
- The environmental benefit is assigned solely to one product with the avoided burden approach.

On the other hand, if the new chemical is meant to be combusted or incinerated after a certain period of time, the GWP for the CO_2 released cannot be accounted for as though the CO_2 reached the atmosphere right away. To tackle this, Von der Assen et al. (2013), proposed to calculate a time-corrected GWP.

Table 1 summarizes different scopes and approaches to the quantification of the CO_2-eq employed in a number of relevant LCA publications regarding CO_2 valorization processes. These can be divided into four main categories: production of chemicals, enhanced oil recovery, mineral carbonation and biodiesel production from microalgae. The objective of Table 1 is to compare the allocation procedures and boundaries established in the different LCA studies. In addition to that, it was also determined whether the scope of these LCAs was attributional or consequential. Whereas attributional LCA focuses on describing environmentally relevant physical flows to and from a life cycle, consequential LCA aims at assessing how the environmentally relevant physical flows to and from the life cycle will change in response to possible changes (Finnveden et al., 2009; Chatterjee et al., 2015).

Two procedures to allocate the environmental burdens were identified in Table 1. They differ in whether or not CO_2 is considered an intermediate product. Feedstock CO_2 is regarded as an intermediate product if the CO_2 production process is within the system boundaries. In that case, no burdens must be allocated between the other products and the feedstock CO_2, since they can only be allocated to the products or the incoming streams of the process under study. It must be highlighted that this is the proper methodological approach: not including the process where CO_2 is generated in the gate to gate stage may lead to mistaken conclusions. The LCA studies of biodiesel production from microalgae did not consider CO_2 as an intermediate product but as an incoming feedstock. Von der Assen et al. (2013) considered these issues too but only for illustration purposes.

Moreover, when dealing with utilization options the final gate to grave stage becomes really meaningful as it describes the real implication of the utilization. For example, utilization of CO_2 for biodiesel production makes sense when its integration into the transportation system (through a functional unit such as 1 kilometer) is completed. The whole picture of the process can be under scrutiny.

In the assessed studies burdens are usually allocated depending on criteria such as the mass, energy content or economic value of the products. Another less deterministic approach was to assess several scenarios, either allocating all burdens to a different product or basing the allocation procedure on different criteria in each of them, and then carry out a sensitivity analysis. Few studies assessed the complete life cycle of the valorization processes, that is to say, from the cradle to the grave, and only one of them took into account the effects of storage (Von der Assen et al., 2013), even though it was based on a fictitious process for explanatory purposes.

Regarding the scope of the LCA, only one of the published studies assessed considered a consequential approach.

Table 1. Summary of published papers regarding the environmental sustainability of CO_2 utilization using the LCA approach

Product	**CO_2 source**	**Valorization process**	**LCA scope**	**Allocation criteria**	**Reference**
Methane	Either a pure stream from a biogas plant or MEA post-combustion capture from a coal-fired power plant	Reduction via Sabatier reaction with H_2 provided by water electrolysis using photovoltaics or wind or grid power	- Attributional - Cradle to gate	All burdens allocated to methane. Feedstock CO_2 considered an intermediate product.	Reiter & Lindorfer, 2015
Formate based products	MEA post-combustion capture from a subcritical hard coal power plant	Electrochemical reduction process integrated into the power plant	-Attributional -Cradle to gate	All burdens allocated to electricity. Feedstock CO_2 considered an intermediate product	Domínguez-Ramos et al., 2013
Methanol	Atmospheric CO_2 (air capture)	Reduction with H_2 provided by water electrolysis and photovoltaics or wind power/steam reforming of natural gas	-Attributional -Cradle to gate	All burdens allocated to methanol. Feedstock CO_2 considered an intermediate product	Von der Assen et al., 2013
Methanol	MEA post-combustion capture from a subcritical pulverized coal power plant	Reduction with H_2 provided by water electrolysis using wind power. Plants located close together: transport neglected	-Attributional -Cradle to gate	Capture and utilization processes assessed separately; thus feedstock CO_2 not considered an intermediate product. Burdens from capture process allocated between feedstock CO_2 and electricity based on their exergy and economic value. Burdens from utilization process allocated between feedstock CO_2 and methanol based on their economic value	Von der Assen et al., 2013

Polymers	Atmospheric CO_2 (air capture)	Fictitious process (data unavailable)	-Attributional -Cradle to grave Time corrected global warming metric	All burdens allocated to polymers. Feedstock CO_2 considered an intermediate product	Von der Assen et al., 2013
Polyether carbonate polyols	Real lignite power plant with a pilot plant for MEA post-combustion capture in Germany	CO_2 compressed and transported to a real polyol production pilot plant in Germany. Production using glycerol as a starter and a double metal cyanide catalyst	-Attributional -Cradle to gate	2 allocation options assessed: 1) All burdens allocated to polyols 2) All burdens allocated to electricity. Feedstock CO_2 considered an intermediate product	Von der Assen et al., 2014
Dimethyl carbonate	MEA capture from flue gases of steam reforming, ammonia production and power plants	Reaction of urea and methanol synthesized from CO_2	-Attributional -Cradle to gate	Burdens generated in the production processes of H_2, NH_3 and MEA allocated between the coproducts according to 2 criteria: 1) mass and 2) economic value. Feedstock CO_2 considered an intermediate product	Aresta et al., 1999
Crude oil	Pre-combustion capture via a water-shift reactor and a Selexol unit from an integrated coal gasification combined cycle power plant fed with bituminous coal	CO_2 compressed and transported to oil fields in the US for Enhanced Oil Recovery. Excess CO_2 stored in aquifers	-Attributional -Cradle to grave Gate to grave analysis comprises oil transport, refining and combustion	4 allocation options assessed: 1) Energy content of oil and electricity 2) Economic value of oil and electricity 3) All burdens allocated to oil 4) All burdens allocated to electricity Feedstock CO_2 considered an intermediate product	Jaramillo et al., 2009
Crude oil	MEA post-	CO_2 compressed and transported	-Hybrid LCA:	Impacts associated with capture of CO_2	Hertwich

	combustion capture from a natural gas combined cycle power plant in Norway	to an oil field in Norway for Enhanced Oil Recovery. Electricity for CO_2 injection supplied either from the power plant or with gas turbines	attributional / consequential -Cradle to gate	allocated to electricity; impacts related to transport and storage of CO_2 allocated to oil. Feedstock CO_2 considered an intermediate product	et al., 2008
Crude oil	MEA post-combustion capture from a natural gas combined cycle power plant in Mexico	CO_2 compressed and transported to an oil field in Mexico for Enhanced Oil Recovery.	-Attributional -Cradle to gate		Lacy et al., 2015
Magnesium carbonate	MEA post-combustion capture from a natural gas combined cycle power plant in Singapore	Mineral carbonation of serpentine from Australia with CO_2 (with and without heat recovery)	-Attributional -Cradle to gate	All burdens allocated to electricity. Feedstock CO_2 considered an intermediate product	Khoo et al., 2011a
Magnesium carbonate	Either MEA post-combustion capture or the flue gas stream (without capture) from a natural gas combined cycle power plant in Singapore	Mineral carbonation of $Mg(OH)_2$ with CO_2 in a pressurized fluidized bed reactor without heat recovery. $Mg(OH)_2$ produced by reacting serpentine from Australia with $(NH_4)_2SO_4$	-Attributional -Cradle to gate	All burdens allocated to electricity. Feedstock CO_2 considered an intermediate product	Khoo et al., 2011b
Magnesium	MEA post-combustion capture	CO_2 compressed and transported to the mineralization plant in	-Attributional -Cradle to gate	3 allocation options assessed: 1) Mass of $Mg(OH)_2$ and byproducts	Nduagu et al., 2012

carbonate	from a bituminous coal power plant in Canada	Canada. Mineral carbonation of $Mg(OH)_2$ with CO_2 in a pressurized fluidized bed reactor with and without heat recovery. $Mg(OH)_2$ produced by reacting serpentine with $(NH_4)_2SO_4$		(iron and calcium hydroxides) 2) System boundary expansion based on mass of $Mg(OH)_2$ and byproducts 3) All burdens allocated to $Mg(OH)_2$ Feedstock CO_2 considered an intermediate product	
Biodiesel	Unspecified industrial sources	CO_2 injected along open raceway ponds where microalgae are cultivated in different conditions (normal culture and low nitrogen culture). Oil produced by dry or wet lipid extraction. Transesterification with methanol	-Attributional -Cradle to grave Gate to grave analysis comprises biodiesel combustion	Burdens allocated between biodiesel and glycerol according to their energy content. All burdens from the CO_2 production process allocated to unspecified industrial sources. Additional burdens allocated to CO_2 in the compression and injection processes. Feedstock CO_2 not considered an intermediate product	Lardon et al., 2009
Biodiesel	Power or ammonia plant	CO_2 injected along open raceway ponds in Phoenix where microalgae are cultivated. Oil produced by lipid extraction. Transesterification with methanol	-Combinatorial LCA (160 process pathways) -Attributional -Cradle to gate	Burdens allocated between biodiesel and glycerol according to their economic value. All burdens from the CO_2 production process allocated to electricity or ammonia (depending on the CO_2 source). Additional burdens allocated to CO_2 in the compression and injection processes. Feedstock CO_2 not considered an intermediate product	Brentner et al., 2011
Biodiesel	1) Pure CO_2 from	CO_2/flue gas injected along open	-Attributional	All burdens allocated to biodiesel.	Campbell

and bioelectricity	adjacent ammonia plant 2) Flue gas from adjacent fossil-fuel power station 3) Commercially produced CO_2 delivered by truck	raceway ponds in Australia where microalgae are cultivated. Oil produced by lipid extraction. Transesterification with methanol. Anaerobic digestion of residual biomass to produce CH_4 to be combusted and generate electricity	-Cradle to grave Gate to grave analysis comprises biodiesel combustion in trucks and anaerobic digestion of residual biomass	All burdens from the CO_2 production process allocated to electricity, ammonia or CO_2 (depending on the CO_2 source). Additional burdens allocated to CO_2 in the compression and injection processes. Feedstock CO_2 not considered an intermediate product	et al., 2011
Biodiesel and bioelectricity	1) CO_2 produced via steam reforming 2) Carbon capture at a coal-fired power plant 3) Direct delivery of flue gas	CO_2/flue gas injected along open raceway ponds in southwestern USA where microalgae are cultivated. Oil produced by lipid extraction. Transesterification with methanol. Direct combustion or anaerobic digestion of residual biomass to produce CH_4-derived electricity	-Attributional -Cradle to grave Gate to grave analysis comprises biodiesel combustion, CH_4 combustion and CO_2 recycle and residuals management	When CO_2 produced via steam reforming is considered, half the emissions are allocated to CO_2 and half the emissions are allocated to H_2. In the other cases, burdens allocated between fossil-fueled electricity, biodiesel and bioelectricity according to their energy content. Feedstock CO_2 not considered an intermediate product	Clarens et al., 2011
Biodiesel	Flue gas from a fossil fuel power plant	Flue gas injected along open raceway ponds in Israel where	-Attributional -Cradle to	Burdens generated in the lipid extraction process allocated between algal oil,	Passell et al., 2013

		microalgae are cultivated. Oil produced by wet lipid extraction. Transesterification with methanol	grave Gate to grave analysis comprises biodiesel combustion	hydrocarbons and algae residue, according to their energy content. Burdens generated in the transesterification process allocated between biodiesel and glycerol according to their energy content. All burdens from the CO_2 production process allocated to electricity. Additional burdens allocated to CO_2 in the compression and injection processes. Feedstock CO_2 not considered an intermediate product	
Biodiesel	Flue gas from power plants	Flue gas injected in a flat-plate photobioreactor where microalgae are cultivated. Oil produced by lipid extraction. Transesterification with methanol	-Attributional -Cradle to grave Gate to grave analysis comprises biodiesel combustion and production of CH_4 and bioethanol from algae residue	Burdens allocated between biodiesel, bioethanol and methane according to their energy content. All burdens from the CO_2 production process allocated to electricity from power plant. Additional burdens allocated to CO_2 in the compression and injection processes. Feedstock CO_2 not considered an intermediate product	Soratana et al., 2013
Biodiesel, renewable	Either industrial flue gas or MEA post-	CO_2/flue gas injected along open raceway ponds in Phoenix where	-Attributional -Cradle to	Burdens allocated between biodiesel, renewable diesel, glycerin, propane,	Zaimes and

diesel and electricity	combustion capture from natural gas power plant	microalgae are cultivated. Oil produced by wet or dry lipid extraction. Either renewable diesel (obtained hydrotreating algal oil) or biodiesel (obtained by transesterification of algal oil) produced. Residual deoiled biomass used for cogeneration via combined heat and power or anaerobic digestion to generate electricity	grave Gate to grave analysis comprises transport of biodiesel, renewable diesel, glycerine and fertilizers	fertilizer, heat and electricity via system boundary expansion based on energy content. All burdens from the CO_2 production process allocated between electricity from power plant and algal derived energy. Feedstock CO_2 not considered an intermediate product	Khanna, 2013
Biodiesel and bioelectricity	Flue gas from a gas-fired power plant	Flue gas injected along open raceway ponds or air-lift tubular reactors in the U.K. Oil produced by lipid extraction. Transesterification with methanol. Anaerobic digestion of residual biomass to produce CH_4 to be combusted and generate electricity	-Attributional -Cradle to grave Gate to grave analysis comprises transport and combustion of biodiesel	Burdens allocated between biodiesel, glycerol, algal residue and potassium phosphate via system boundary expansion based on economic value. All burdens from the CO_2 production process allocated to electricity from power plant. Additional burdens allocated to CO_2 in the compression and injection processes. Feedstock CO_2 not considered an intermediate product	Stephenson et al., 2010

2.4 ELECTROCHEMICAL REDUCTION CASE STUDIES

Albo et al. (2015a) reviewed efficient methods reported in the literature for the continuous ER of CO_2 to methanol. They stressed the relevance of research on the development of new cathode materials and cell configurations. Thus, two different approaches to achieve the ER of CO_2 to methanol were analyzed with the purpose of comparing their environmental potential to be integrated into the studied process, assuming they are suitable for large scale-up:

Case A.
Albo et al. (2015b) investigated the electroreduction of CO_2 to methanol in a filter press electrochemical cell. Using a Cu_2O-based cathode a methanol concentration of 5.85 ppm and a 45.7% faradaic efficiency are obtained. The production of hydrogen competes with the CO_2 reduction at the cathode. Oxygen is also produced at the anode.

Case B.
Shironita et al. (2013) studied the electroreduction of CO_2 to methanol at a Pt-Ru/C electrode in a reversible fuel cell based on a membrane electrode assembly. Under the reported experimental conditions, the hydrogen evolution reaction barely competes with the CO_2 reduction at the cathode; therefore, it is assumed that the stoichiometric amount of water to react with the CO_2 is introduced into the reactor. Under a CO_2 atmosphere a 75% faradaic efficiency is achieved: CO_2 is also reduced to ethanol, which does not entail a separation problem since FFVs in the European Union are allowed to run on a mixture of gasoline, methanol and ethanol (EP & EC, 2009). Oxygen is obtained at the anode as a byproduct of the hydrogen evolution reaction.

Table 2 shows the electrochemical reactions expected to occur in both cases.

Table 2. Electrochemical reactions for CO_2 conversion to methanol

Cathode	$CO_2 + 6H^+ + 6e^- \rightleftarrows CH_3OH + H_2O$
Anode	$3H_2O \rightleftarrows 1.5O_2 + 6H^+ + 6e^-$
Overall	$CO_2 + 2H_2O \rightleftarrows CH_3OH + 1.5O_2$

Moreover, the following parallel competitive reduction reactions take place at the cathode in each case:

1) Case A. Hydrogen evolution reaction.
   $2H^+ + 2e^- \rightleftarrows H_2$

2) Case B. Ethanol production.
   $2CO_2 + 12H^+ + 12e^- \rightleftarrows C_2H_5OH + 3H_2O$

The desired reduction reaction requires 6 moles of electrons per mole of methanol produced whereas the hydrogen evolution reaction only takes up 2 moles of electrons per mole of hydrogen; hence, hydrogen production may be favored over CO_2 reduction.

Table 3 compiles the life cycle inventory of cases A and B. The electrolyte consumption of case A is not taken into account, since it is not specified by Albo et al. (2015b).

Table 3. ER inventories for cases A and B (functional unit: 1 kg of methanol)

	Unit	Case A	Case B
Infrastructure			
Cathode area	m^2	20.40	$6.67 \cdot 10^{-2}$
Anode area	m^2	20.40	$6.67 \cdot 10^{-2}$
Membrane area	m^2	20.40	$6.67 \cdot 10^{-2}$
Chemicals			
Reagents			
Carbon dioxide	kg	1.38	18.33
Water (net)[1]	kg	3.13	1.41
By-products and excess reagents			
Hydrogen	kg	0.22	-
Oxygen	kg	3.28	2.00
Ethanol	kg	-	0.24
Carbon dioxide	kg	-	16.50
Electrode materials			
Cuprous oxide	kg	0.20	-
Platinum	kg	-	$4.35 \cdot 10^{-4}$
Ruthenium	kg	-	$2.25 \cdot 10^{-4}$
Carbon	kg	-	$6.73 \cdot 10^{-4}$
Energy			
Electricity	kWh	23.10	10.08

---

[1] It is assumed that the excess water is recirculated back to cell, along with the methanol produced.

3 PROCESS DESCRIPTION

The CO_2 source assessed in this work is a thermal power plant with a maximum power output of 250 MW that deploys biomass with a lower calorific value of 7.3 MJ/kg (IEA, 2009) as feedstock. CO_2 is captured from the flue gas stream by post-combustion technology using monoethanolamine (MEA), and pure CO_2 is obtained after a thermal desorption process, which applies steam produced at the thermal power plant. A fraction of the CO_2 stream is sent to the ER section (this parameter will be referred to hereafter as the derivation ratio or DR), and the remaining CO_2 is compressed and injected into a saline aquifer. The electricity required to compress the CO_2 is generated at the power plant, as well as the electricity needed to pump water into the reactor and compress the byproducts of the electrochemical reaction. It is assumed that the energy required for transport, recompression and injection of CO_2 is taken from the spanish grid mix.

The energy supplied to the reactor to reduce CO_2 comes from photovoltaic (PV) panels installed in the neighborhood of the power plant. On the other hand, the steam produced at the boiler is distributed between the turbine and the CO_2 desorption and the methanol distillation processes.

The main material and energy flows of cases A and B integrated into the process are shown in Figures 3 and 4.

3.1 SYSTEM BOUNDARIES

Figure 2 comprises the main processes and material and energy flows taken into account in this study.

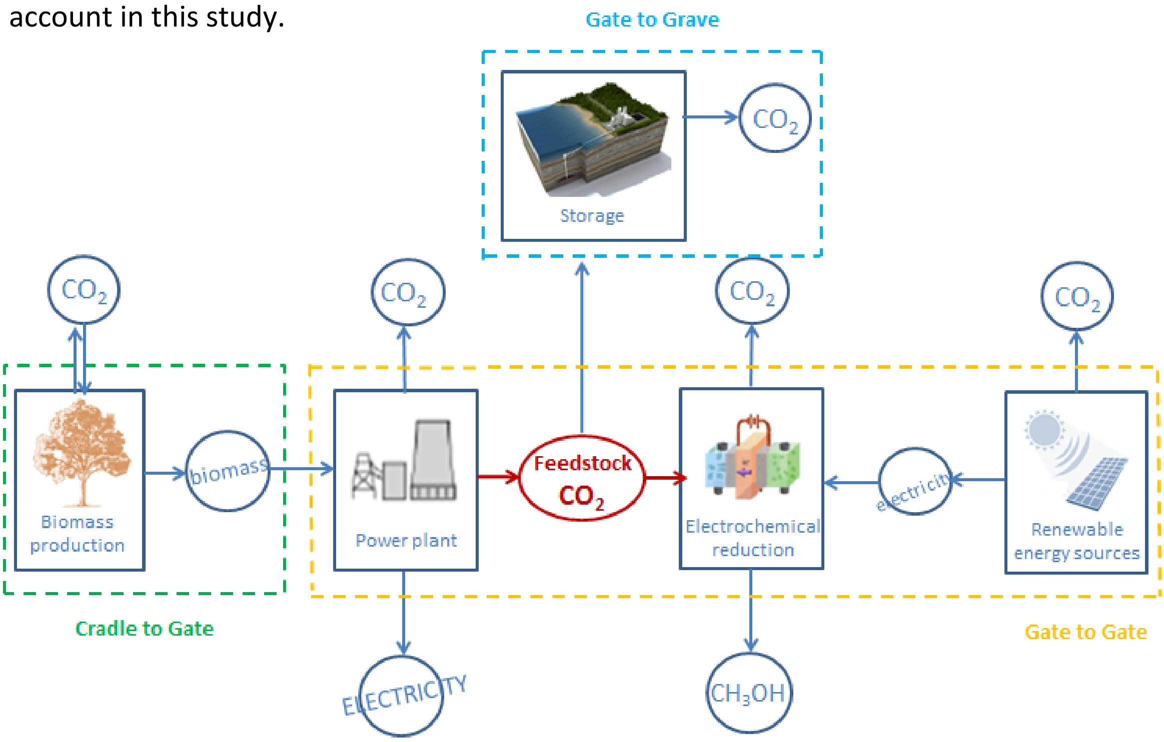

Figure 2. Overview of the boundaries of the system under study

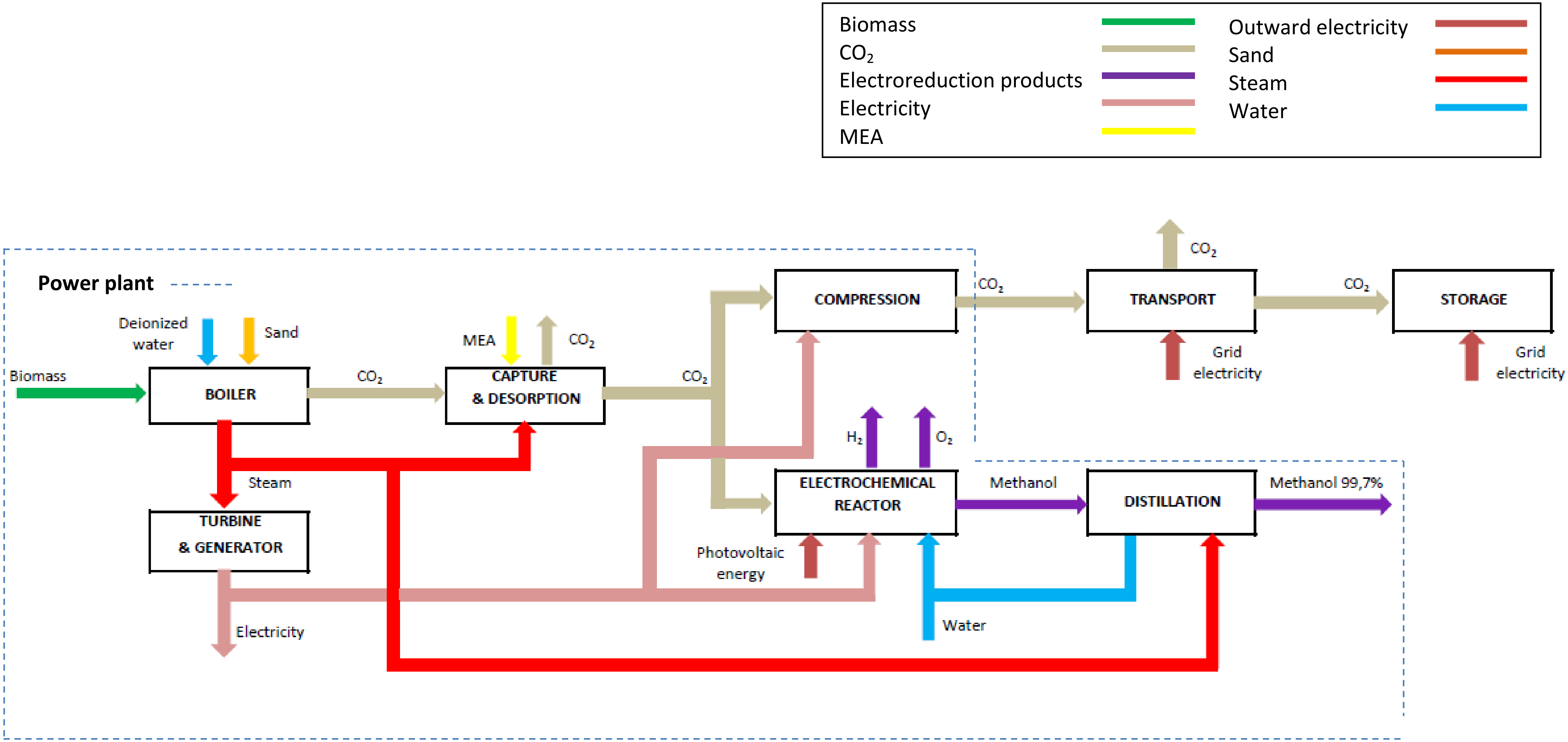

Figure 3. Block diagram of the process (case A)

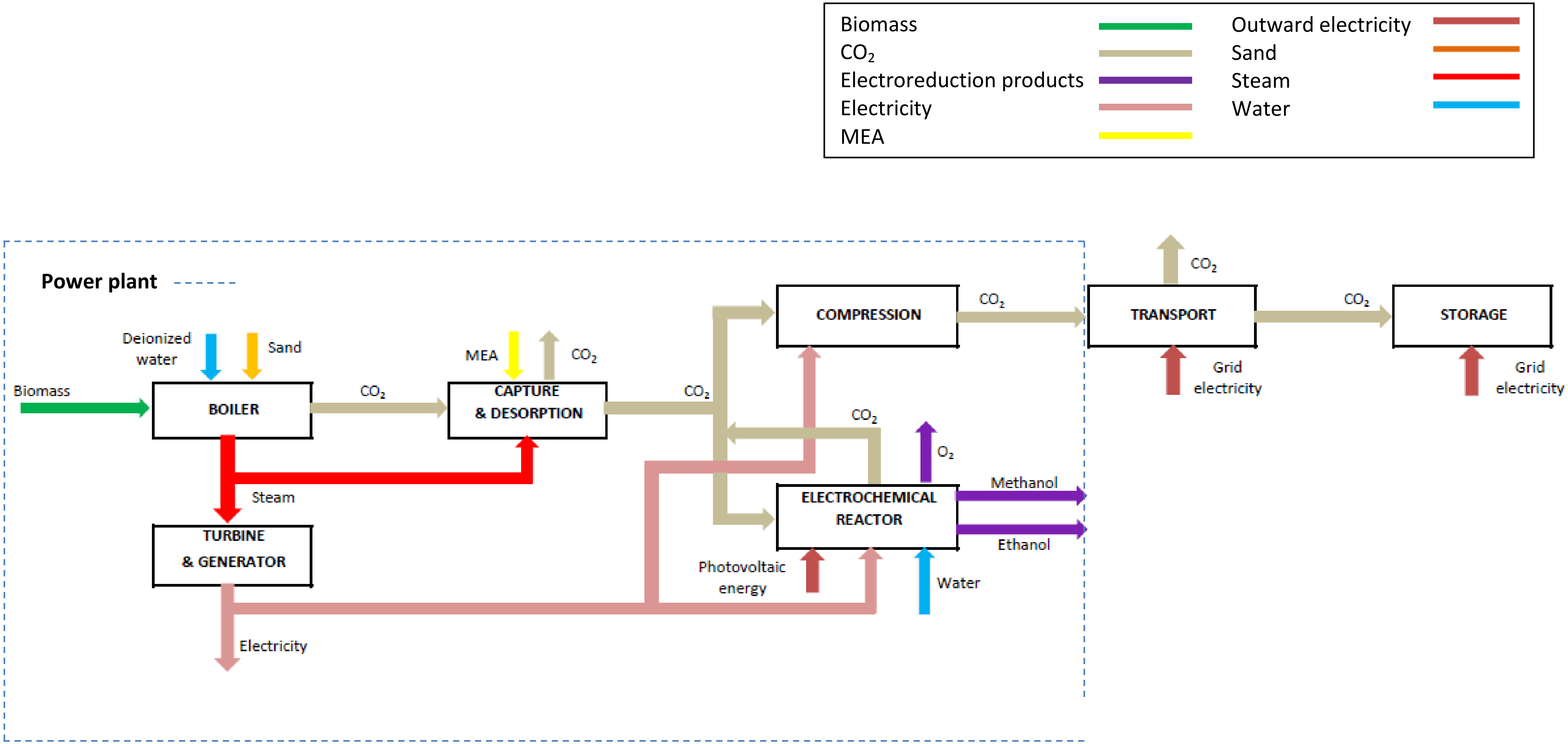

Figure 4. Block diagram of the process (case B)

3.2 MATHEMATICAL MODEL

A simplified mathematical model was proposed to describe the behavior of the process under study. The model was based on the material and energy balances of the units that compose the system, depicted in Figures 3 and 4. It was implemented in Microsoft Excel.

The developed model identifies input variables, output variables and parameters. The parameters can be found in the appendix 9.1.

The DR is a common input variable to both cases. Moreover, the other input variable for case A is the methanol concentration at the reaction outlet, whereas case B has two input variables: the CO_2 conversion and the electrode lifetime. The value of the input variables was altered throughout the study to perform a sensitivity analysis.

On the other hand, two kinds of output variables can be differentiated:

- Those that quantify the mass and energy flow of the process streams.
- Those that quantify the carbon profile of the life cycle stages.

4 METHODOLOGY

An attributional LCA was performed to determine the carbon footprint of the process described above. The methodology proposed by Cherubini et al. (2011), which considers the natural consumption of CO_2 by biomass, was applied to quantify the net CO_2 emitted in the biomass combustion process. A biomass rotation period of 10 years, consistent with fast-growing species such as eucalyptus (FAO, 2001), and a 100-year time horizon were assumed. Under these conditions, GWP_b is 0.04. The stored CO_2 is assumed to remain in the technosphere without additional accounting.

The studied process is a multi-output system, from which two major valuable products (electricity and methanol) are obtained. In addition to those, hydrogen and oxygen are also obtained as by-products of the ER. Thus, a decision as to how to assign the resulting CO_2-eq emissions of the process to each product must be taken.

Although, as explained in section 1.2, von der Assen et al., (2013) recommended using an allocation procedure based on the economic value of the products, the ISO standards (2006b) state that whenever possible, system expansion should be used to avoid allocation problems.

Given that in this particular case study it is clear that the primary purpose of the process is the production of electricity, and that the methanol (and ethanol, in case B) produced is intended to substitute gasoline in combustion engines, as a first approach the system boundaries were expanded to include the production of gasoline and the by-products of the ER; that is to say, it was established that the products of the ER displace the gasoline, hydrogen and oxygen produced by traditional methods. As a consequence, the CO_2-eq emissions from the conventional production processes of these chemicals are avoided. Future work should study the influence of the allocation method on the results.

Table 4 specifies to what stage X_i of the life cycle correspond the direct (D) and indirect (I) CO_2-eq emissions accounted for in the CO_2-eq inventory of the process. For the sake of simplicity, the combustion of methanol (and ethanol, in case B) in FFVs was not included in the system boundaries.

Following this methodology, the use of different functional units is avoided. The functional unit selected to perform the LCA of the system is 1 kWh of electricity exported from the power plant.

The data used was compiled from the Ecoinvent Centre database (2008) and the references found in the literature.

Table 4. Stages considered in the CO_2-eq inventory

Cradle to Gate		**Gate to Gate**		**Gate to Grave**	
D	**I**	**D**	**I**	**D**	**I**
	X_1				
	X_2				
	X_3				
		X_4			
			X_5		
			X_6		
			X_7		
			X_8		
			X_9		
			X_{10}		
			X_{11}		
				X_{12}	
					X_{13}
					X_{14}
					X_{15}

X_1	Biomass chip production
X_2	Biomass transport to the power plant
X_3	Sand transport to the power plant
X_4	CO_2 capture
X_5	MEA production
X_6	Deionised water production
X_7	Photovoltaic energy
X_8	Electrochemical reactor infrastructure
X_9	Hydrogen production (Avoided CO_2)
X_{10}	Oxygen production (Avoided CO_2)
X_{11}	Plant and CCS infrastructure
X_{12}	CO_2 transport (leakages)
X_{13}	Electricty for transport and storage
X_{14}	Gasoline production (Avoided CO_2)
X_{15}	Fuel transport to distribution points

5 RESULTS AND DISCUSSION

The carbon footprint of the process is determined by the value of the captured CO_2 fraction that is derived to the electrochemical reactor; thus, the results of cases A and B were calculated as a function of the DR.

5.1 CASE A

As it has been mentioned before, Albo et al. (2015b) obtained a very dilute concentration of methanol at the outlet of the electrochemical reactor (≈5.85 ppm); this is the reason behind the large amounts of steam required in conventional separation processes, suggesting that this technology is unsuitable for the process under study at the current level of development. Consequently, it was estimated how much the concentration achieved by the experimental reactor configuration from Albo et al. (2015b) should be increased so that the process was feasible from a carbon footprint point of view. Table 5 compiles the three different values of methanol concentration assessed, along with its corresponding improvement factor.

The performance of two distillation columns in series with different feed methanol concentrations was simulated with Aspen Plus® software. The steam requirements in the reboiler to obtain a methanol composition in the distillate stream of 99.7%-wt., which according to the reference from The Methanol Institute (2015) is the typical methanol purity required FFVs, are shown in Table 4:

Table 5. Steam required in the distillation process

Improvement factor	$[CH_3OH]$ ($g \cdot L^{-1}$)	Steam ($kg \cdot kg\ CH_3OH^{-1}$)
100	**0.585**	125.54
1,000	**5.85**	12.27
10,000	**58.5**	2.02

The steam requirement for the lowest methanol concentration in Table 5 is too high; thus, the carbon footprint of case A was solely assessed for methanol concentrations at the reactor of 5.85 and 58.5 $g \cdot L^{-1}$, which correspond to 3 and 4 orders of magnitude higher than those values obtained originally by Albo et al. (2015b), respectively.

Castillo et al. 2015 reported values in the order of several $g \cdot L^{-1}$ of formate thanks to the deposition of Sn nanoparticles of around 150 nm over gas diffusion electrodes, which constitutes an improvement of several orders of magnitude compared to the initial studies using Sn plates (Alvarez-Guerra, 2013). Consequently, whereas the improvement of 3 orders of magnitude is feasible, reaching tens of $g \cdot L^{-1}$ will demand much more effort under the current hypothesis.

Total CO_2-eq emissions of case A (calculated as the sum of direct and indirect CO_2-eq emissions) are shown in Figure 5.

Direct CO_2-eq emissions of both cases are much lower than indirect CO_2-eq emissions; this is because according to Cherubini et al. (2011) the GWP_b under the established conditions is just 0.04, while the GWP of indirect CO_2 (non-biogenic emissions) is 1. Thus, the total CO_2-eq emissions of case A follow the same trend as the indirect CO_2-eq emissions.

As expected, the lower the methanol concentration, the worse the carbon footprint of the process, since more energy is required to separate it from the water.

Direct CO_2-eq emissions increase with the DR. The only direct CO_2 emissions taken into account (see Table 4) are due to the inefficiency of the CO_2 capture process (X_4) and the CO_2 leakages produced in the CO_2 transport process to the storage site, which means that as the DR increases, X_4 does too; in other words, it is necessary to burn additional biomass (because more energy is required) to valorize CO_2 than to store it.

Indirect CO_2-eq emissions decrease with the DR for the best case scenario, given that as the DR increases, so do the avoided CO_2 emissions (X_9, X_{10} and X_{15}). Nevertheless, the scenario with the lowest methanol concentration, where emissions increase as the DR increases, does not share this behavior. This is because for such a low methanol concentration the amount of energy required by the separation process is so large that the avoided CO_2 emissions do not make up for the CO_2-eq emitted. As shown in Figure 5, only the scenario with the lowest methanol concentration exceeds the CO_2-eq emissions of electricity production in the European Union: 0.392 kg CO_2-eq·kWh^{-1} (EEA, 2015; Eurostat, 2015).

The power plant efficiency η', defined as the ratio between the electrical energy exported and the thermal energy released in the combustion process, is represented in Figure 6 as a function of the DR and the methanol concentration at the reactor outlet. The efficiency of the power plant without carbon captured, η, is assumed to be 41.7% (IEA, 2009).

Figure 6 shows that only very small DRs are feasible. DR values higher than 0.02 imply that the power plant efficiency diminishes below half the efficiency of the studied power plant without carbon capture (20.85%).

The most sensible scenario in terms of power plant efficiency is that in which all the CO_2 captured is sent to the storage site. In that case the power plant efficiency, η_0', is 24.07%.

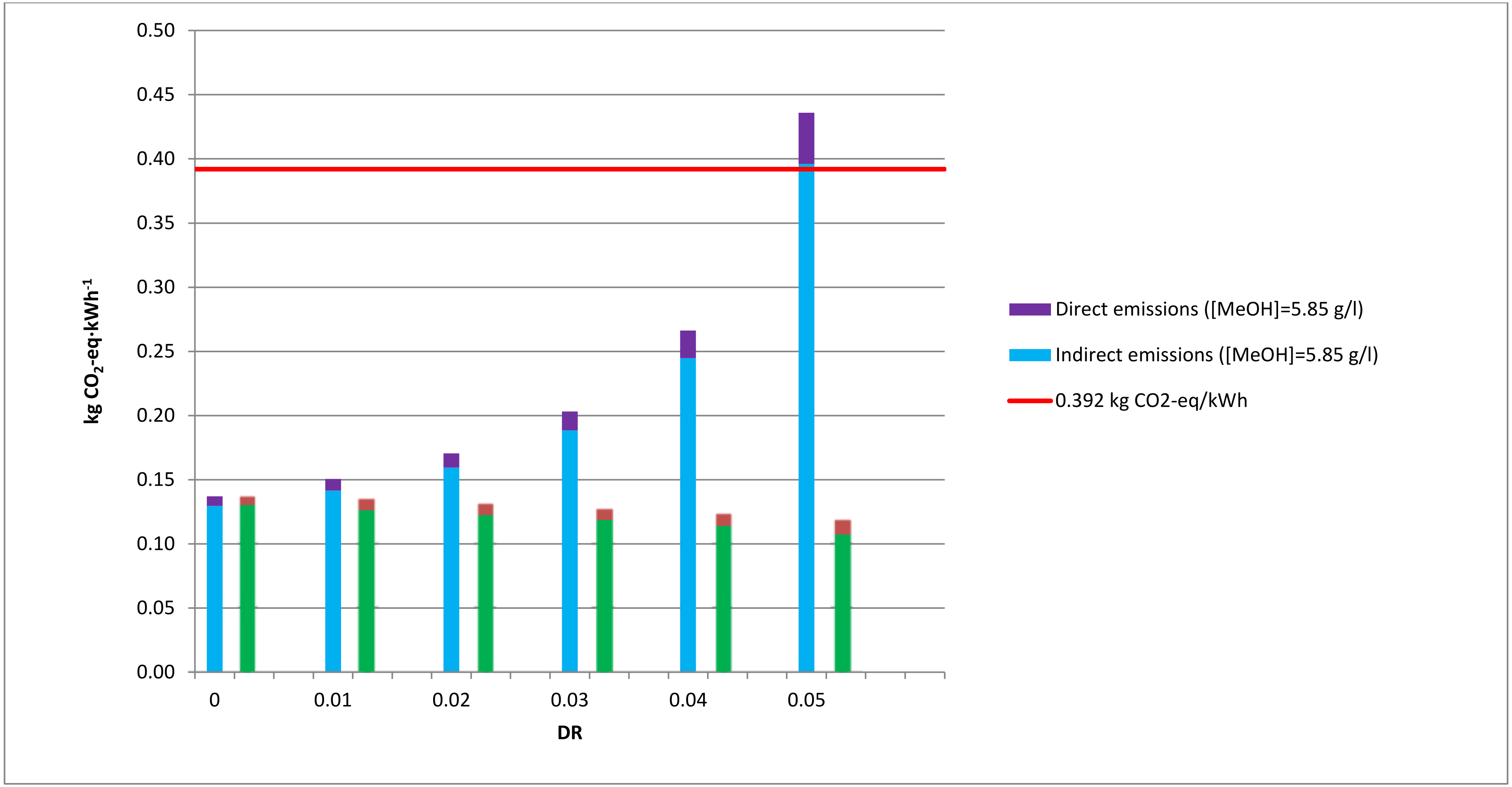

Figure 5. Total CO_2-eq emissions of case A as a function of the D

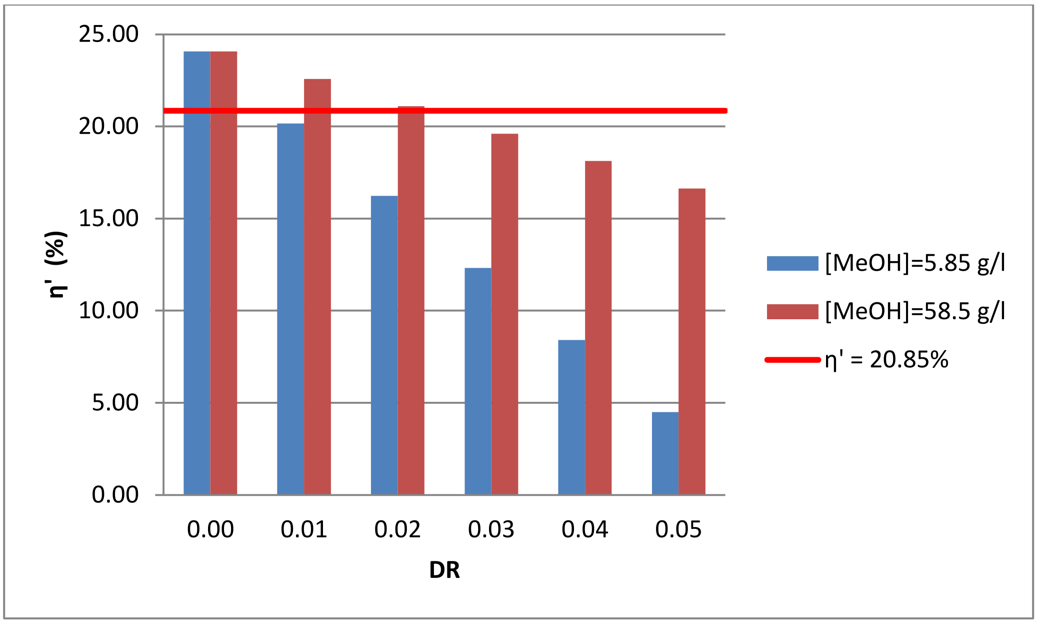

Figure 6. Power plant efficiency in case A as a function of the DR

5.2 CASE B

Regarding case B, Shironita et al. (2013) conducted their experiments under a CO_2 atmosphere, with a CO_2 conversion of 7.5%. Figure 4 shows that in this study the unreacted CO_2 is recirculated back to the reactor.
A sensitivity analysis was carried out to evaluate the influence of the CO_2 conversion per pass on the results. To do so, it was assumed that the inventory compiled from Shironita et al. remained unchanged when modifying the conversion, except for the area of the electrochemical reactor, which was progressively increased in order to raise the CO_2 conversion.

The CO_2-eq emissions of case B are shown in Figure 7. In this case, total CO_2-eq emissions follow the same trend as indirect CO_2-eq emissions, since direct CO_2-eq emissions are negligible.

Direct CO_2-eq emissions (Figure 7, right side) increase with the DR, which means that as the DR increases, the increase in the energy extracted from the power plant required to pump water into the reactor, to recompress CO_2 and to send it back to the reactor and to compress the oxygen produced (which implies that X_4 is higher), is higher than the decrease in the CO_2 leakages that occur during CO_2 transport (X_{12}).

Indirect CO_2-eq emissions (Figure 7, on the left) also increase with the DR; that is to say, as the DR increases, the increase in the CO_2 emissions associated with the PV energy (X_7), the reactor infrastructure (X_8) and the fuel transport to the distribution points is higher than the decrease of the avoided emissions (X_{10} and X_{15}).

It was verified that the major contribution to indirect CO_2-eq emissions was due to the large carbon footprint of the electrode materials. Hence, the influence of the electrode lifetime (E_{LT}) on the CO_2-eq emissions of the process was analyzed. To serve that purpose, it was assumed that the E_{LT} was 7000 hours, which corresponds to 10 times the value reported in the literature (Cheng et al., 2005).The results are depicted in Figure 8. The comparison of Figures 7 and 8 proves that a remarkable improvement in the carbon footprint of the process could be achieved if the E_{LT} was extended. Nonetheless, this parameter has no effect over direct CO_2-eq emissions or the energy penalty on the power plant.

Finally, the efficiency of the power plant is shown in Figure 9 as a function of the DR and the CO_2 conversion. As the DR and the CO_2 conversion increase, the efficiency of the power plant decreases, reaching values lower than the efficiency achieved if all the CO_2 is sequestered (η_0'), albeit the variations in the efficiency values are moderate. The reason why this happens is the same as why direct CO_2-eq emissions increase with the DR.

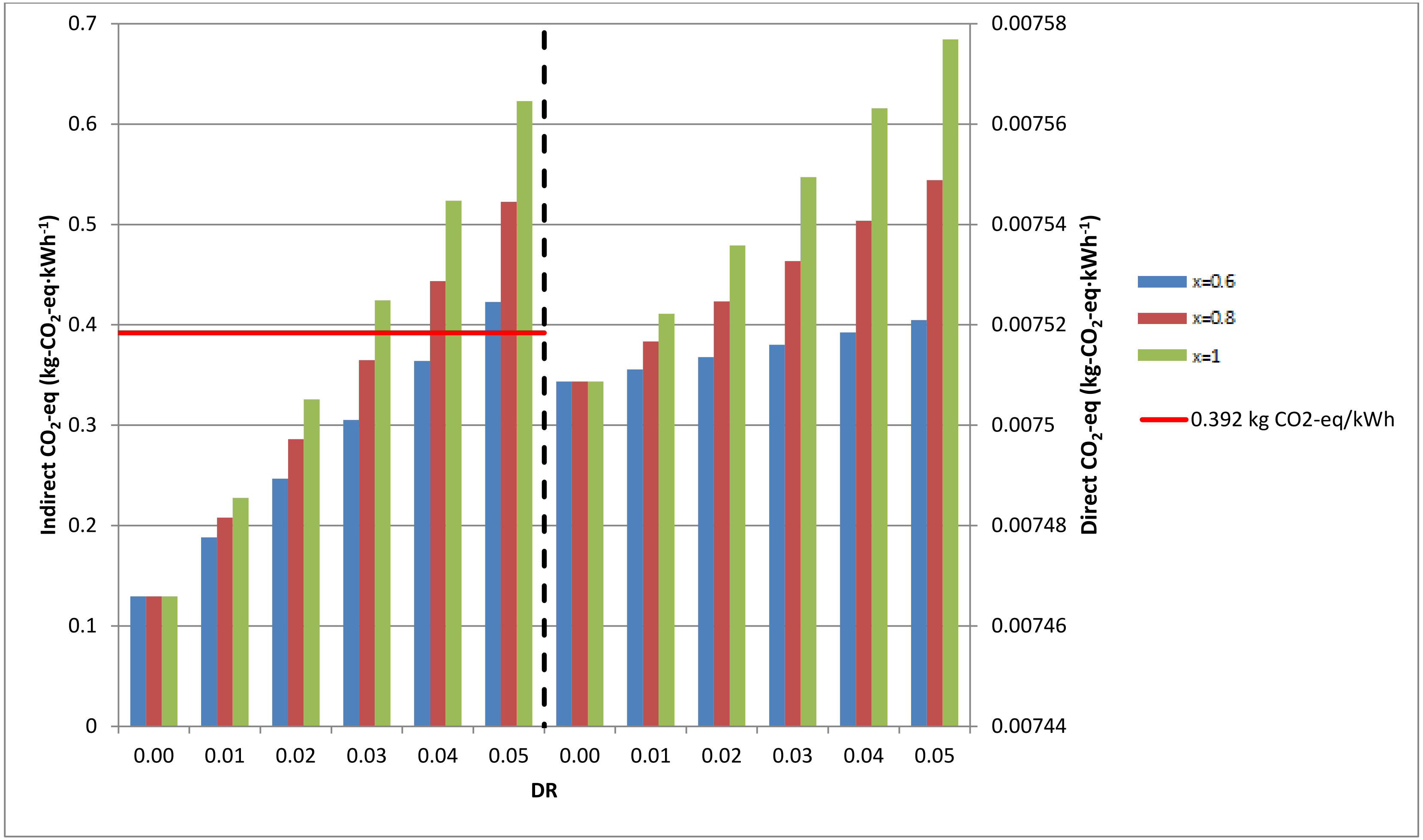

Figure 7. Direct and indirect CO$_2$-eq emissions of case B (E$_{LT}$: 700 h) as a function of the DR

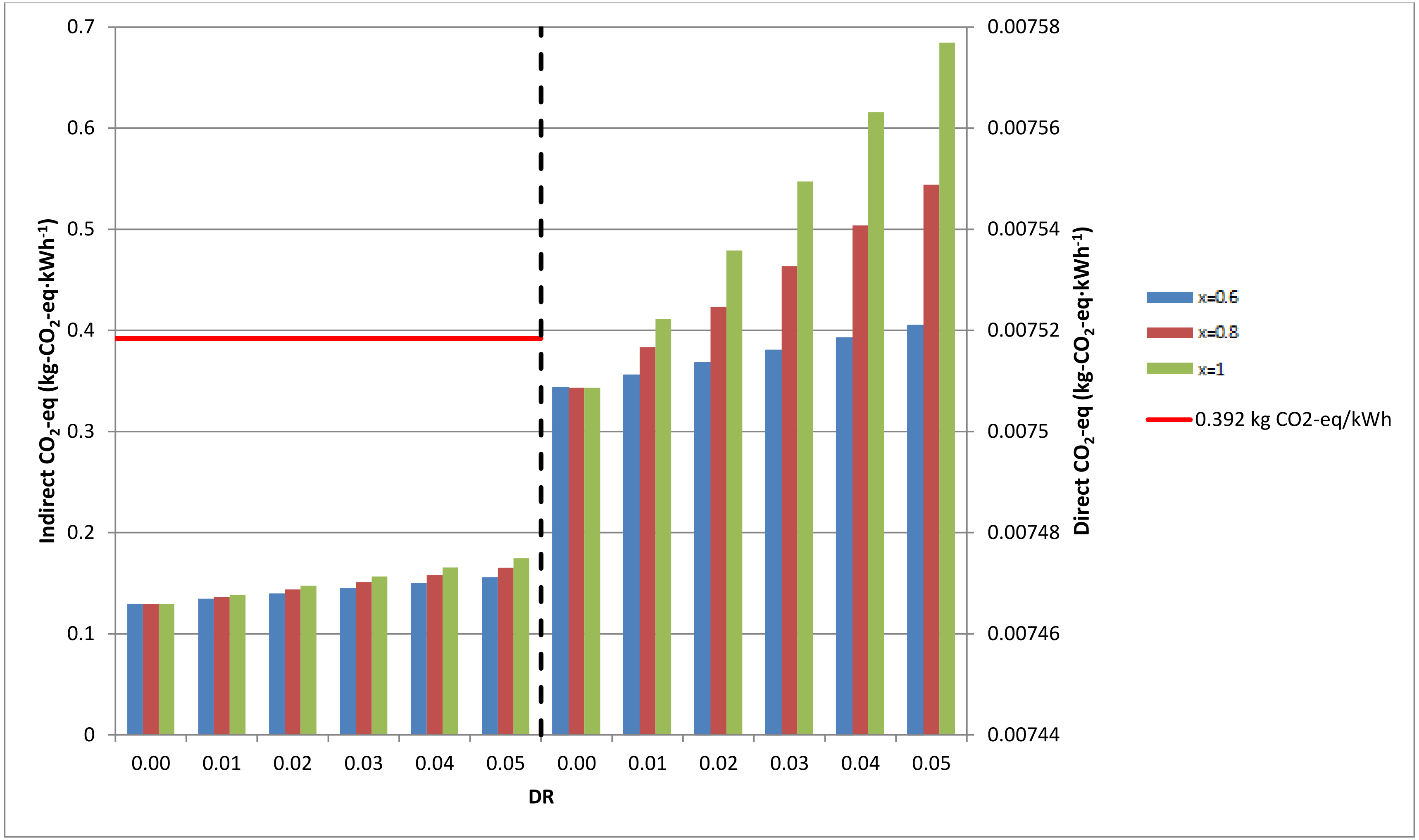

Figure 8. Direct and indirect CO_2-eq emissions of case B (E_{LT}: 7000 h) as a function of the DR

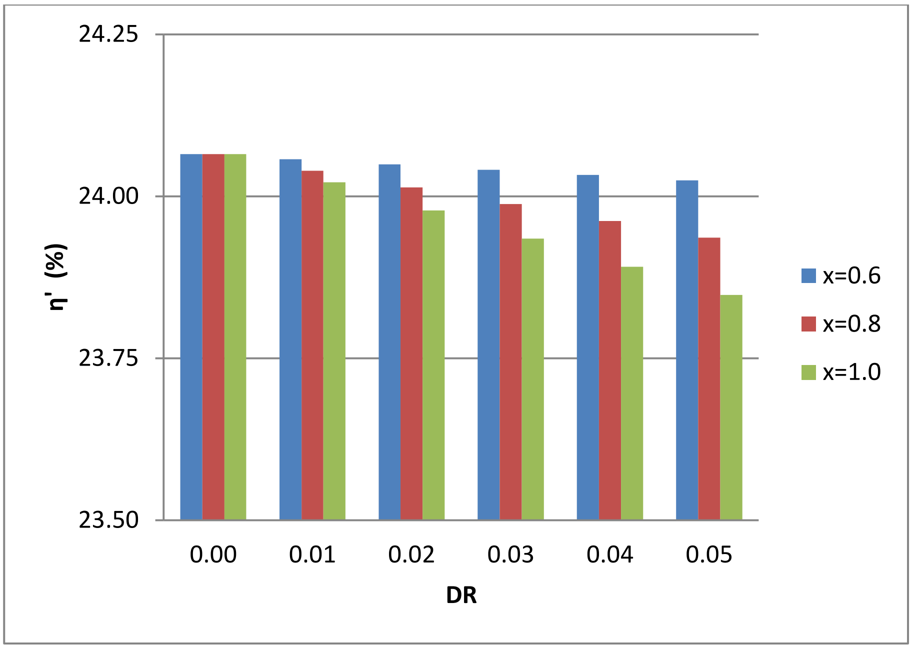

Figure 9. Power plant efficiency in case B as a function of the DR

5.3 COMPARISON OF CASES A AND B

It is noteworthy that in both cases there is a correlation between the direct CO_2-eq emissions and the power plant efficiency: the most energy intensive scenarios emit the most CO_2 per kWh, as can be seen in Figure 10.

Figures 10 and 11 show the direct and total CO_2-eq emissions of both cases (for the scenarios depicted in Figures 5 to 9), as a function of the power plant efficiency.

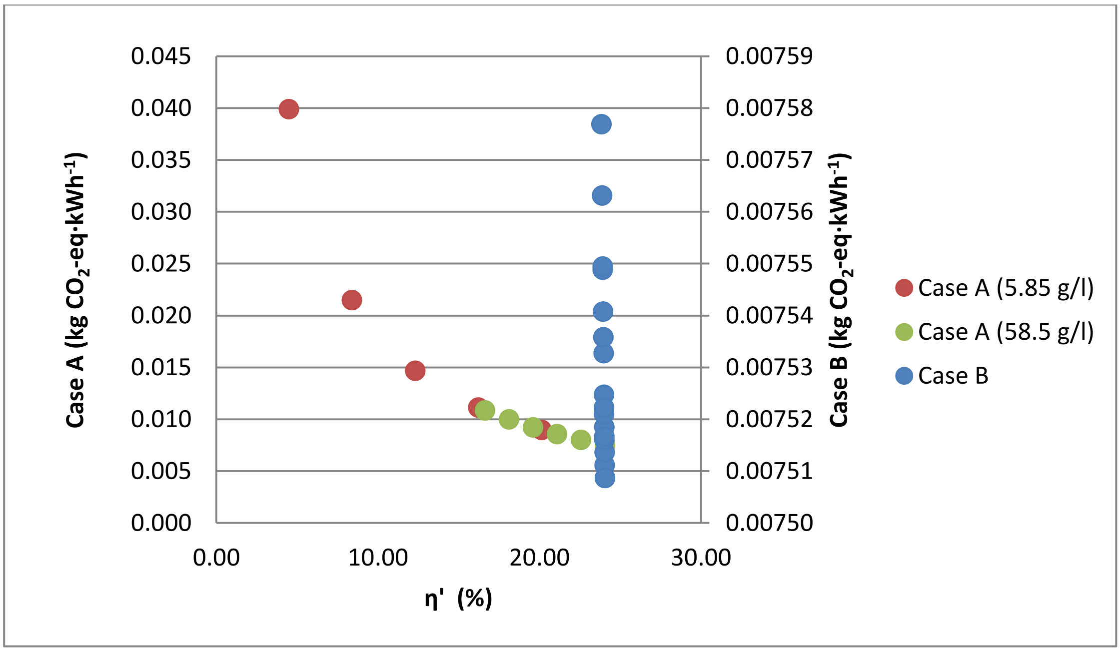

Figure 10. Direct CO_2-eq emissions of cases A and B as a function of η’

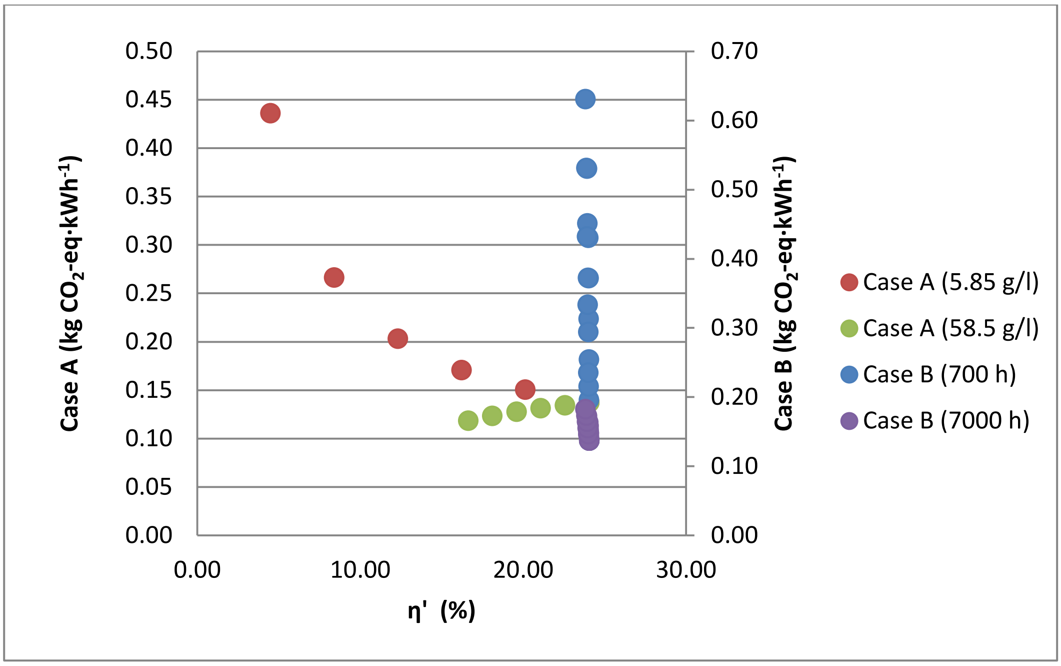

Figure 11. Total CO_2-eq emissions of cases A and B as a function of η'

In case A additional energy is required to separate methanol from water, which implies that more biomass needs to be burnt, releasing more CO_2 in the capture and transportation processes. However, the materials that compose the electrodes of the electrochemical reactor of case B (platinum and ruthenium) have a much higher carbon footprint than the Cu_2O present in the cathode of case A (14,780 kg CO_2-eq·kg^{-1} versus 1.93 kg CO_2-eq·kg^{-1} according to Ecoinvent Centre (2008)). That is why while case B has significantly lower direct CO_2-eq emissions than case A, for the originally assumed 700 hour E_{LT}, indirect (and total) CO_2-eq emissions of case B are higher than those of case A, albeit the scenario that contemplates an E_{LT} of 7,000 hours for case B presents considerably lower CO_2-eq emissions.

With such a wide range of emission and efficiency values, it is hard to simultaneously study both cases. Therefore, it was established that only the scenarios with power plant efficiencies higher than half the value of the power plant without carbon capture and CO_2-eq emissions lower than those of the grid mix of the European Union would be assessed. Another restriction to the system was the ratio between the power of the PV solar plant and the power from the thermal facility exported to the grid (PV/Th): only values below 0.2 were considered.

The DR values above which these proposed restrictions are not applied were calculated for cases A and B and compiled in Table 6. Case B was assessed for the conversion value with the largest carbon footprint and PV energy consumption (complete CO_2 conversion).

Table 6. Maximum DR values to abide by the proposed restrictions (%)

	CO_2-eq <0.392 kg CO_2-eq·kWh^{-1} [a]	η' > 20.85 % [b]	PV/Th < 0.2 [c]
Case A ([MeOH]=5.85 g·L^{-1})	4.83	0.82	0.63
Case A ([MeOH]=58.5 g·L^{-1})	–	2.16	0.68
Case B, (E_{LT}=700 h, x=1)	2.59	–	2.15
Case B, (E_{LT}=7000 h, x=1)	–	–	2.15

[a] Below the European grid mix

[b] Over half the original power plant efficiency

[c] Ratio photovoltaic to thermal

For the four case studies of Table 6, the limiting restriction determining the value of the selected DR, is the ratio PV/Th.

In order to properly compare all the cases, DRs below 0.63% (the most restrictive DR of Table 6) were selected. The CO_2-eq emissions and power plant efficiencies of the four scenarios assessed for this range of DRs are depicted in Figure 12. Under the aforementioned conditions, the total CO_2-eq emissions vary linearly with the power plant efficiency and the DR.

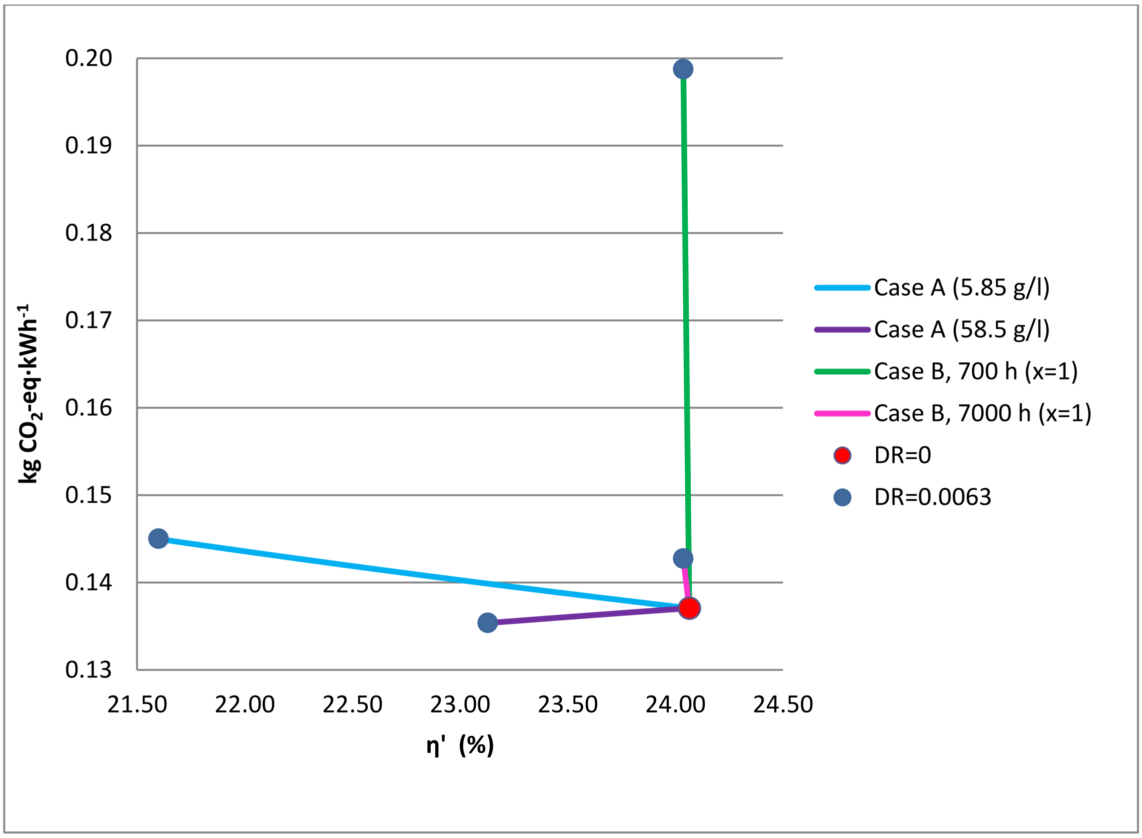

Figure 12. Total CO_2-eq emissions of cases A and B
as a function of the power plant efficiency and the DR

In Table 7, the power provided by the PV panels and the power supplied to the grid mix are compared for the maximum DR considered in all the studied cases. It shows that for a given DR, case B requires a PV plant of a size significantly smaller than case A, because of the higher faradaic efficiencies.

Taking into account that the power of the current largest PV plant in the world is around 579 MW (SunPower, 2015), this range of DRs is already technically feasible from the point of view of the integration of renewable energy into the process. However, from a practical point of view, it is not reasonable to deploy such an extensive area of PV panels only for auxiliary purposes.

Table 7. Power provided by the PV modules vs power exported from the thermal plant for DR=0.63%

	PV/Th (%)	**Power to the grid (MW)**	**PV power to the ER (MW)**
Case A ([MeOH]=5.85 g·L^{-1})	0.20	129.5	25.8
Case A ([MeOH]=58.5 g·L^{-1})	0.19	138.7	25.8
Case B, (E_{LT}=700/7000 h, x=1)	0.0112	144.4	1.7

Considering that for the maximum DR studied (0.63%) the difference between the CO_2-eq emissions of case A (for a methanol concentration of 58.5 g·L^{-1}) and case B (for an E_{LT} of 7000 h) is only of 7.4 g·kWh^{-1}, it can be concluded that no relevant differences can be used to justify the selection of any option. However, as the improvement factor applied for the E_{LT} of case B to lower its CO_2-eq emissions is around 10, and the factor applied to the methanol concentration at the outlet of the reactor is 10,000 for case A, it is possible to suggest case B with a lifetime of 7,000 hours as the option with the best chance to be scaled-up.

5.4 CO_2-EQ INVENTORIES

Finally, for a DR of 0.0063, the CO_2-eq inventories of cases A (for a methanol concentration of 5.85 and 58.5 g·L^{-1} at the reactor outlet) and B (assuming that all the CO_2 is reduced to methanol and considering 700 and 7,000 hours as the E_{LT}) were compared in Tables 8 and 9, setting 1 kWh as the functional unit. The results in these Tables were multiplied by a factor of 10,000 for a better visualization.

One of the major contributors to CO_2 emissions is clearly the capture process. However, direct CO_2 emissions come from a biogenic source, and as a result they must be multiplied by a GWP_b of 0.04 (Cherubini et al., 2011). Therefore, they represent a small fraction of the total CO_2-eq emissions.

The relative contribution to the CO2-eq inventory of every life cycle stage in case A is the same, regardless of the methanol concentration at the reactor outlet. Oppositely, the absolute contribution of each life cycle stage of case B does not vary with the E_{LT}, except for the CO_2-eq emissions due to the reactor infrastructure (X_9), which are 10 times lower for the largest E_{LT}.

Figure 13 represents the two life cycle stages that contribute the most to the scenario with the largest carbon footprint, (case B considering a 700 h E_{LT}); that is to say, the biomass chip production (X_1) and the reactor infrastructure (X_8). In all the studied cases the life cycle stage that contributes the most to the CO_2-eq inventory is X_1. The significant decrease in the impact of the reactor infrastructure due to the increment in the E_{LT} can easily be appreciated in Figure 13.

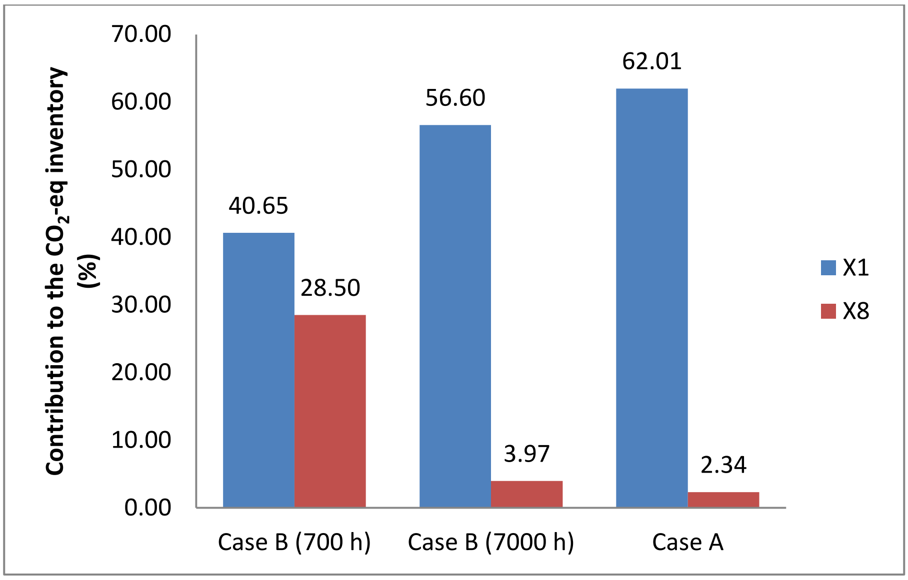

Figure 13. Contribution to the CO_2-eq inventory of life cycle stages X_1 and X_8

It is worth highlighting that in case A the avoided burdens of hydrogen and oxygen (X_9 and X_{10}) play a more important role that in case B: despite the fact that less methanol is produced in case A as a consequence of the lower faradaic efficiency, hydrogen is produced as a counter effect. Moreover, in the course of the hydrogen evolution reaction, more oxygen is produced through water electrolysis.

Table 8. CO_2-eq inventory (x10,000) of case A for a DR of 0.0063. Functional unit: 1 kWh

	CASE A ([CH_3OH =5.85 g·L^{-1})						**CASE A ([CH_3OH =58.5 g·L^{-1})**					
	Cradle to Gate		**Gate to Gate**		**Gate to Grave**		**Cradle to Gate**		**Gate to Gate**		**Gate to Grave**	
	D	**I**	**D**	**I**	**D**	**I**	**D**	**I**	**D**	**I**	**D**	**I**
X_1		899.05						839.59				
X_2		24.43						22.81				
X_3		2.38						2.23				
X_4			83.58						78.05			
X_5				92.44						86.32		
X_6				1.16						0.84		
X_7				99.53						92.95		
X_8				33.94						31.70		
X_9				-149.10						-139.24		
X_{10}				-28.90						-26.99		
X_{11}				311.19						290.58		
X_{12}					0.08						0.07	
X_{13}						105.80						98.80
X_{14}						-26.59						-24.83
X_{15}						0.90						0.84
TOTAL	0.00	925.87	83.58	360.26	0.08	80.11	0.00	864.63	78.05	336.16	0.07	74.81

Table 9. CO_2-eq inventory (x10,000) of case B for a DR of 0.0063. Functional unit: 1 kWh

	CASE B (E_{LT} = 700 h, x =1)						**CASE B (E_{LT} = 7000 h, x =1)**					
	Cradle to Gate		**Gate to Gate**		**Gate to Grave**		**Cradle to Gate**		**Gate to Gate**		**Gate to Grave**	
	D	**I**	**D**	**I**	**D**	**I**	**D**	**I**	**D**	**I**	**D**	**I**
X_1		807.86						807.86				
X_2		21.95						21.95				
X_3		2.14						2.14				
X_4			75.10						75.10			
X_5				83.06						83.06		
X_6				0.62						0.62		
X_7				29.27						29.27		
X_8				566.49						56.65		
X_9				0.00						0.00		
X_{10}				-11.87						-11.87		
X_{11}				341.25						290.83		
X_{12}					0.07						0.07	
X_{13}						95.07						95.07
X_{14}						-24.24						-24.24
X_{15}						0.77						0.77
TOTAL	0.00	831.96	75.10	1008.81	0.07	71.59		831.96	75.10	448.55	0.07	71.59

6 CONCLUSIONES

Se evaluó la sostenibilidad ambiental en términos de la huella carbono de una central termoeléctrica alimentada con biomasa y acoplada a un proceso de captura y almacenamiento de carbono y a la valorización electroquímica del CO_2 a metanol, empleando la metodología del análisis del ciclo de vida. Para ello, se utilizaron como referencia dos tecnologías de reducción descritas en la literatura y estudiadas a escala de laboratorio.

Con la alternativa propuesta por Albo y cols. (2015b) se obtienen concentraciones de metanol muy bajas a la salida del reactor, haciendo el proceso de separación agua-metanol muy intensivo en energía y aumentando la penalización energética de la planta más allá del escenario en el que todo el CO_2 es almacenado (eficiencia de la planta del 24.07%). Se estimó que la concentración de metanol conseguida por Albo y cols. (2015b) debería incrementarse unas 10,000 veces para que su implementación a gran escala en una central termoeléctrica fuese medioambientalmente viable desde el punto de vista de la huella de carbono. Incluso asumiendo dicho incremento en la concentración de metanol, solo ratios de derivación muy pequeños podrían ser implementados sin incrementar significativamente la demanda energética del proceso. Sin embargo, aumentar el ratio de derivación tiene un efecto positivo sobre las emisiones totales de CO_2-eq debido al CO_2 evitado en la producción de hidrógeno, oxígeno y gasolina en los procesos convencionales. Por tanto, en un escenario muy optimista, las emisiones de CO_2-eq por kWh pueden verse reducidas aplicando ratios de derivación elevados, pero la producción de electricidad en la planta disminuiría drásticamente. Para mantener la eficiencia energética de la planta se requeriría un proceso de purificación menos intensivo en energía que la destilación, incluso para elevadas concentraciones de metanol del orden de decenas de $g \cdot L^{-1}$.

El metanol obtenido en la electrorreducción de CO_2 descrito por Shironita y cols. (2013) se encuentra disuelto únicamente en etanol, un combustible válido para los vehículos de combustible flexible. Consecuentemente, ya que en este caso no se requiere un proceso de separación, se pueden considerar ratios de derivación más altos sin comprometer la eficiencia energética de la planta, aunque están restringidos por la huella de carbono del proceso. En este caso, la penalización energética y las emisiones de CO_2-eq más bajas (0.137 kg CO_2-eq$\cdot$kWh^{-1}) se obtienen si todo el CO_2 capturado es enviado al almacenamiento geológico. Esto ocurre incluso cuando se incrementa un orden de magnitud la esperanza de vida del electrodo, dado que la infraestructura del reactor electroquímico es responsable de una parte significativa de las emisiones de CO_2-eq.

No obstante, la valorización del CO_2 también implica una mayor implantación de energías renovables en detrimento de los combustibles fósiles, ya que el exceso de electricidad puede ser almacenado en forma de combustible. Por tanto, las líneas de trabajo futuras deberían investigar los beneficios derivados de la ampliación de la capacidad de las energías renovables en la red eléctrica y su conexión con el sistema de transporte a través de la reducción electroquímica de CO_2, posiblemente mediante la herramienta de análisis del ciclo de vida consecuencial.

De la comparación de los dos casos de estudio se concluye que la integración de la tecnología de reducción electroquímica descrita por Albo y cols. (2015b) en el proceso estudiado muestra menores emisiones de CO_2-eq que la descrita por Shironita y cols. (2013), pero también presenta una mayor penalización energética. Las menores emisiones de CO_2-eq de Albo y cols. (2013) no se deben principalmente al desplazamiento en el mercado de los productos de la electrorreducción y las consiguientes emisiones de CO_2-eq evitadas, si no a la notablemente más baja huella de carbono de los materiales electródicos. Esto sugiere que, a pesar de las excelentes eficiencias faradaicas conseguidas por Shironita y cols. (2013), la investigación debería centrarse en la optimización de la reducción electroquímica de CO_2 basada en materiales electródicos con huellas de carbono más bajas o en la ampliación de la esperanza de vida de los electrodos con los materiales con los que se alcanzan eficiencias faradaicas tan altas.

Además, se infiere que los procesos de electrorreducción sostenibles y rentables deben basarse en materiales económicos y abundantes, dado que las esperanzas de vida de los electrodos no son muy elevadas.

Otra conclusión que se puede extraer de este estudio es que la viabilidad del proceso propuesto depende en gran medida del tamaño de la planta que suministra energía procedente de fuentes de energía renovables al reactor electroquímico; solo se pueden implementar ratios de derivación lo suficientemente bajos para que el uso del suelo de las fuentes de energía renovables no exceda los límites razonables.

Por último, dada la gran cantidad de oxígeno generado en el reactor electroquímico como co-producto, (2 – 3.28 kg por kg de metanol), se recomienda explorar la posibilidad de sustituir el proceso de captura post-combustión por un proceso oxi-combustion alimentado con el oxígeno producido en el reactor electroquímico.

7 NOMENCLATURE

Greek symbols

η'	Power plant efficiency with CCUS
η_0'	Power plant efficiency when all the CO_2 is sequestered

[MeOH]	Methanol concentration at the reactor outlet
CCS	Carbon capture and storage
CCU	Carbon capture and utilization
CCUS	Carbon capture, utilization and storage
CO_2-eq	CO_2-equivalent
D	Direct CO_2-eq emissions
DR	Derivation ratio
E_{LT}	Electrode lifetime
ER	Electrochemical reduction
FFV	Flexible fuel vehicles
GHG	Greenhouse gas
GWP	Global Warming Potential
GWP_b	Global Warming Potential of biogenic CO_2
I	Indirect CO_2-eq emissions
IRF	Impulse response function
IRF_{bCO2}	Impulse response function of a biogenic CO_2 pulse
LCA	Life cycle assessment
MEA	Monoethanolamine
NEP	Net ecosystem production
PV	Photovoltaic
RES	Renewable energy sources
x	CO_2 conversion in the electrochemical reactor

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9 APPENDIX

9.1 MODEL PARAMETERS

Table A.1. Process parameters

	Parameter	Value	Unit	Range	Reference
Greek symbols					
ΔP	Pressure drop to be overcome by pumps	50000	Pa	–	–
η	Efficiency of power plant fed by biomass without CCS	0.417	–	0.360[2] - 0.417[3]	IEA, 2009
η_m	Motor efficiency	0.9	–	–	Biegler et al., 1997
η_p	Pump efficiency	0.5	–	–	Biegler et al., 1997
AB_{MEA}	Mass of MEA lost in the absorption of 1 ton of CO_2[4]	1.5	$kg \cdot ton^{-1}$	1.5 - 1.6 (Singh et al., 2011a)	Korre et al., 2010; Singh et al., 2011b
BC_e	Direct CO_2 emissions of biomass combustion	0.915	$kg \cdot kg^{-1}$	0.694 (IPCC, 2006) - 0.964 (IPCC, 2006)	IEA, 2009
C	CO_2 removal efficiency in the absorption process	0.9	–	0.898 (Domínguez-Ramos et al., 2015) - 0.95 (Korre et al., 2010)	IEA, 2009; Pehnt & Henkel, 2009; Schreiber & Zapp, 2009.
D_f	Distance from the	10	km	0 - 80[5]	–

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[2] Bubbling fluidized bed boiler with subcritical steam and steam superheating in a 75 MW power plant; steam superheating.

[3] Circulating fluidized bed boiler with subcritical steam in a 250 MW power plant; steam superheating and single steam reheating.

[4] A solvent make-up of 1.5 kg/ton CO_2 is needed due to its loss via vapors and formation of degradation products

[5] According to Cuellar (2012), the maximum distance that biomass can be obtained and economically transported is 80 km.

	power plant to the forest				
D_m	Distance from the power plant to methanol distribution points	100	km	–	–
D_s	Distance from sand distribution point to power plant	50	km	–	–
D_{ss}	Distance from the power plant to the CO_2 storage site	400	km	–	Wildbolz, 2007
En_c	Energy to compress CO_2 to 11 MPa for pipeline transport	0.111	$kWh\cdot kg^{-1}$	–	Koornneef et al., 2008
En_{H2}	Energy to liquefy hydrogen	15.2	$kWh\cdot kg^{-1}$	14 (Schwart, 2011) - 15.2	Mannan, 2012
En_i	Energy to inject CO_2 into storage site	$6.86\cdot10^{-3}$ [7]	$kWh\cdot kg^{-1}$	$5.84\cdot10^{-4}$ [6] (Singh et al., 2011b) - 0.0286[7] (Wildbolz, 2007)	Wildbolz, 2007; Koornneef et al., 2008
En_{O2}	Energy to separate oxygen from air	0.2	$kWh\cdot kg^{-1}$	0.16 (Tranier et al., 2009) - 0.20	Schreiber et al., 2013; Tranier et al., 2009
F	Faraday constant	96485.3	$C\cdot mol^{-1}$	–	Zoski, 2007
En_r	Energy to recompress CO_2 during pipeline transport[8]	0.011	$kwh\cdot km^{-1}\cdot ton^{-1}$	0.0042 (Singh et al., 2011a) - 0.011	Wildbolz, 2007
GWP_b	Global Warming Potential of CO_2 from biomass with a rotation period of 10 years for a 100-year time horizon	0.04	–	–	Cherubini et al., 2011
H_{des}	Enthalpy of desorption of CO_2 from MEA solution	3.40	$MJ\cdot kg^{-1}$	2.76 (Von Der Assen & Bardow, 2014) -	TCM, 2014

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[6] Geological storage of CO_2 in a saline aquifer.

[7] Geological storage of CO_2 in a gas field.

[8] It is assumed that a recompression stage is required after 200 km.

H_{st}	Enthalpy of high pressure steam	3.469	MJ·kg^{-1}	3.40 –	IEA, 2009
I	Fraction of total CO_2-eq emissions due to infrastructure[9]	0.09	–	0.07 - 0.09	Singh et al., 2011a
L	CO_2 leakage rate during pipeline transport	$2.6 \cdot 10^{-4}$	kg·km^{-1}·ton^{-1}	$6.7 \cdot 10^{-6}$ (Koornneef et al., 2008) $7.7 \cdot 10^{-4}$ (Koornneef et al., 2008)	Wildbolz, 2007
LCV	Lower calorific value of biomass	7.3	MJ·kg^{-1}	7.3 - 18 (CTA, 2015)	IEA, 2009
m_b	Fraction of feed methanol in the bottom streams of the distillation process	0.02	–	0.004 – 0.04[10]	–
R	Ratio gross electric energy/steam to the turbine	0.330	kWh·kg^{-1}	0.273[3] - 0.330[4]	IEA, 2009

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[9] Infrastructure associated with power plant, fuel production and transport and storage.

[10] Range of m_b obtained in the Aspen Plus® simulations for the different methanol concentrations studied.

Unless otherwise stated, all the data compiled in Tables A.2 and A.3 can be found in Albo et al. (2015b) and Shironita et al. (2013), respectively.

Table A.2. Parameters of case A

	Parameter	**Value**	**Unit**
$[m]_i$	Methanol concentration at the reactor outlet obtained by Albo et al. (2015b)	$5.85 \cdot 10^{-6}$	$kg \cdot L^{-1}$
E_a	Reduction potential at the anode (Ag/AgCl, sat. KCl as reference electrode)[11]	1.035	V
E_c	Reduction potential at the cathode (Ag/AgCl, sat. KCl as reference electrode)	-1.3	V
E_{LT}	Electrode lifetime	7	hours
FE	Faradaic efficiency	45.7	%
j	Current density	6.93	$mA \cdot cm^{-2}$
M_{Cu2O}	Mass of Cu_2O per unit area of cathode	1	$mg \cdot cm^{-2}$
q	Electric charge applied during the experiments	374.2	C
r_m	Methanol production rate	$6.08 \cdot 10^{-5}$	$mol \cdot m^{-2} \cdot s^{-1}$

Table A.3. Parameters of case B

	Parameter	**Value**	**Unit**
A	Ratio membrane area/cathode area (assumed)	1	
E_a	Reduction potential at the anode (SCE as reference electrode) (Albo et al., 2015a)	0.99	V
E_c	Reduction potential at the cathode (SCE as reference electrode)[13]	-0.45	V
E_{LT}	Electrode lifetime (Cheng et al., 2005)	700	hours
FE	Faradaic efficiency	75	%
j	Current density	15	$mA \cdot cm^{-2}$
M_M	Mass of metal per unit area of electrode	1	$mg \cdot cm^{-2}$
M_C	Mass fraction of carbon on the electrode	0.505	–
M_{Pt}	Mass fraction of platinum on the electrode	0.326	–
M_{Ru}	Mass fraction of ruthenium on the electrode	0.169	–
r_m	Methanol production rate[12]	$1.86 \cdot 10^{-4}$	$mol \cdot m^{-2} \cdot s^{-1}$

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[11] The water oxidation potential, -0.99 V vs the saturated calomel electrode SCE (Albo et al., 2015a), was converted to the Ag/AgCl reference electrode with the calculator from Resources for electrochemistry (2015).

[12] Value calculated by Albo et al. (2015a) from the data reported by Shironita et al. (2013).

Table A.4. CO_2-eq emissions of different operations in a 100-year time horizon

	Operation	Value	Unit	Range	Reference
E_b	Chip production	0.039[13]	kg·kg^{-1}	0.029 - 0.039	Dias, 2014
E_{CuO}	CuO production[14]	1.93	kg·kg^{-1}	–	Ecoinvent Centre, 2008
E_g	Gasoline processing	0.729	kg·kg^{-1}	–	Ecoinvent Centre, 2008
E_{EE}	Electricity production in the EU	0.392[15]	kg·kWh^{-1}	–	EEA, 2015; Eurostat, 2015
E_{MEA}	MEA production	3.28	kg·kg^{-1}	–	Ecoinvent Centre, 2008; Pehnt & Henkel, 2009
E_{O2}	Oxygen separation from air	0.102	kg·kg^{-1}	0.102 - 0.409 (Ecoinvent Centre, 2008)	–[16]
E_{Pt}	Platinum production	14780.33	kg·kg^{-1}	–	Ecoinvent Centre, 2008
E_{PV}	Manufacture of photovoltaic modules	0.050	kg·kWh^{-1}	0.023 - 0.050	Dominguez-Ramos et al., 2010a
E_{Ru}	Ruthenium production[17]	14780.33	kg·kg^{-1}	–	Ecoinvent Centre, 2008
E_{SE}	Electricity production in Spain	0.511[18]	kg·kWh^{-1}	0.511 - 0.542[19] (Foidart et al., 2010)	Dominguez-Ramos et al., 2010b
E_t	Transport by truck	0.107	kg·km^{-1}·ton^{-1}	–	Ecoinvent Centre, 2008
E_w	Production of deionized water	0.00102	kg·kg^{-1}	–	Ecoinvent Centre, 2008

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[13] It includes forest management operations, felling, collection and chipping.

[14] The CO_2-eq emissions of Cu_2O production was not found in the Ecoinvent database (Ecoinvent Centre, 2008) or elsewhere; therefore, it is assumed that they are the same as the corresponding to CuO production.

[15] Year 2012.

[16] Calculated from the values of E_{GM} and En_{O2}.

[17] Ru is mostly obtained as a byproduct in the production of Pt (Greenwood & Earnshow, 1997); since the CO_2-eq emissions of Ru were not found, they are assumed to be the same as E_{Pt}.

[18] Year 2007.

[19] Year 2005.

Table A.5. Properties of compounds

	Property	Value	Unit	Range	Reference
Greek symbols					
Υ_e	Ethanol energy density	26.8	$\mathrm{MJ \cdot kg^{-1}}$	–	Thomas, 2000
Υ_g	Gasoline energy density	34.2	$\mathrm{MJ \cdot l^{-1}}$	–	Albo et al., 2015a
Υ_m	Methanol energy density	15.6	$\mathrm{MJ \cdot l^{-1}}$	–	Albo et al., 2015a
ρ_e	Ethanol density	0.789	$\mathrm{kg \cdot L^{-1}}$	–	Bechtold, 1997
ρ_g	Gasoline density	0.750	$\mathrm{kg \cdot L^{-1}}$	700 - 800	Knovel, 2008
ρ_m	Methanol density	0.792	$\mathrm{kg \cdot L^{-1}}$	–	Methanol Institute, 2015
ρ_w	Water density	1	$\mathrm{kg \cdot L^{-1}}$	–	–
H_m	Latent heat of vaporization of methanol	2258.89	$\mathrm{kJ \cdot kg^{-1}}$	–	Smith et al., 2005
H_w	Latent heat of vaporization of water	1100.31	$\mathrm{kJ \cdot kg^{-1}}$	–	Smith et al., 2005
mm_{CO2}	Molar mass of CO_2	0.044	$\mathrm{kg \cdot mol^{-1}}$	–	–
mm_{H2}	Molar mass of hydrogen	0.002	$\mathrm{kg \cdot mol^{-1}}$	–	–
mm_m	Molar mass of methanol	0.032	$\mathrm{kg \cdot mol^{-1}}$	–	–
mm_{O2}	Molar mass of oxygen	0.032	$\mathrm{kg \cdot mol^{-1}}$	–	–
mm_w	Molar mass of water	0.018	$\mathrm{kg \cdot mol^{-1}}$	–	–
SH_m	Specific heat of methanol	1.859	$\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$	–	Yaws, 2014
SH_w	Specific heat of water	4.18	$\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$	–	Yaws, 2014

9.2 METHANOL-WATER SEPARATION PROCESS

The separation of methanol at different concentrations from water by means of two distillation columns in series was simulated using the Peng-Robinson thermodynamic method with the Aspen Plus® software. The specifications of the distillation columns are shown in Table A.7; they are based on the conventional single column studied by Chiang & Luyben (1983), in which heat integration is not applied.

Table A.7. Column specifications

Operating pressure	17 psia
Number of stages	64
Feed tray location	18
Type of condenser	Total
Type of reboiler	Kettle

The molar reflux ratio of the second column was set as 1.15; a sensitivity analysis was carried out to determine the molar reflux ratio of the first column that enables to obtain a methanol composition in the distillate of the second column higher than 99.7 wt.%. The steam required in both columns and the reflux ratio of the first column with which the desired methanol concentration is achieved are compiled in Table A.8. It is shown that for the lowest methanol concentrations studied, extremely high reflux ratios are needed, and as a consequence, the required steam flow rates are unfeasible. Therefore, feed methanol concentrations lower than 5.85 $g\cdot L^{-1}$ (that is to say, 1,000 times the concentrations reported by Albo et al. (2015b)) are not assessed.

Table A.8. Molar reflux ratios of column 1 and total steam requirements for different methanol concentrations in the feed stream

[m] ($g\cdot L^{-1}$)	Molar reflux ratio of column 1	Total steam ($kg\cdot kg\ CH_3OH^{-1}$)
0.585	200	125.54
5.85	17	12.27
58.5	2.5	2.02

A linear expression was calculated to determine the total steam required to distillate methanol at low concentrations (5.85 – 58.5 $g\cdot L^{-1}$):

$$st = 13.407 - 0.195 \cdot [m] \quad (eq.\ A.1)$$

The feed stream of the first column must be previously heated with steam from the power plant so that the distillation process is more effective. Low methanol concentrations in the feed stream require higher temperatures, as described by equation A.3, which is estimated by means of non-linear regression:

$$T_{DS} = 110.4 \cdot [m]^2 - 109.92 \cdot [m] + 103.99 \quad (eq.\ A.2)$$