Towards the decarbonization of hard-to-abate sectors: A case of study of the soda ash production

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KEYWORDS: decarbonization; carbon footprint; hard-to-abate sectors; carbon dioxide utilization; techno-economic assessment

ABSTRACT

Decarbonizing the so-called “hard-to-abate” sectors is considered more technically challenging than others such as energy or transportation since they entail emissions not only from heat and power generation but also from manufacturing and process industries. The opportunities for them are less obvious and the challenges are greater so their shift or transition to zero emissions are still relatively unexplored. In this case of study, we aim to analyze the environmental impact and the techno-economic viability of the integration of a carbon capture and utilization (CCU) plant that produces CO_2-based methanol (CO_2-MeOH) by means of electrochemical reduction (ER) in the hard-to-abate sector of synthetic soda ash. With a rigorous emphasis on the goal of net zero-CO_2 emissions, life cycle assessment (LCA) and techno-economic assessment (TEA) were used as tools in order to guide further research and development towards its potential final commercialization. LCA and TEA results have demonstrated that it is possible to reduce the carbon footprint (CF) of the synthetic soda ash production at a reasonable cost within proper medium/long term developments. Several scenarios have been assessed considering the future innovation of the CCU-ER technology as well as the future evolution of the electricity and CO_2 market prices, due to the application of instruments such as Power Purchase Agreements (PPAs) and the European Union Emissions Trading System. The scenarios analyzed suggest that the complete electrification of the integrated plants of soda ash through electric heat (EH) is positive from the environmental perspective. This EH represents the direct conversion of renewable electricity to industrial heat. The results displayed a reduction in the CF of soda ash up to 74% as long as the entire integrated plant was run on renewable electricity and considering the commercialization of the ER side products such as H_2 and O_2. Not considering the selling of these two products leads to more modest reduction around 41%. However, this complete electrification has major implications on the economics profile under the current combination of electricity and CO_2 market prices. Low-cost electricity, *e.g.*, using surpluses of renewable electricity and/or PPAs, and a higher CO_2 price, which can be expected in the short/mid-term are required to ensure economic feasibility. A 50% reduction of the current average wholesale electricity price that was used as a reference in the present study (43 $€\cdot MWh^{-1}$) will ensure economic feasibility under the proper ER technology development. The insights gained in this study may be of assistance in the sustainable implementation of CCU in energy-intensive manufacturing processes.

INTRODUCTION

The transition of our society toward a new CO_2-free model is one of the most critical challenges for our 21st century global community.[1] The integral transformation that is required to decarbonize our social and productive systems results in pitfalls and opportunities, especially for the industrial sector. The decarbonization of other sectors such as transportation, building, or even our energy production system is currently better understood and mature since their markets are less open to international competition. However, the opportunities for decarbonizing industry, especially the heavy or basic manufacturing (based on intensive-energy processes), are still less obvious. These sectors were traditionally largely absent from the climate change mitigation proposals. The emissions of the so-called hard-to-abate[2] basic industry encompass those coming from steel, cement, plastic, paper, aluminium and chemicals as synthetic sodium carbonate. According to the last available figures of the EU emission trading system (EU-ETS), the emissions from hard-to-abate sectors decreased rapidly during the 2008 to 2012 period but they have remained obstinately flat in recent years.[3] These sectors are major carbon emitters representing about 64% of the total EU industrial emission,[4] while responsible for over 20% of global greenhouse gas emissions in latest years.[5] Their decarbonization is generally considered more technically challenging in comparison with lighter industry sectors. With no action, emissions from hard-to-abate sectors could increase by 50% by mid-century.[2] Lighter manufacturing industry that consists of specialized down-stream manufacturers of value-added products, such as pharmaceuticals and electronics, involves relatively lower emissions and typically energy (both heat and electricity) represents a small share of their production costs in comparison with those up-stream basic manufacturers. While the main challenge of these down-stream light industries is the ability to innovate new climate-friendly products or adapting them to a green demand which brings an opportunity to grow into new markets,[6] the decarbonization of the up-stream basic industry, which are the mentioned hard-to-abated sectors, is an uphill struggle. In these basic sectors, energy and feedstock constitute a considerable share of their production costs. Therefore CO_2 emissions cannot be abated only by changing fuels but important modifications in basic process technologies may be required.[7] Considering that these industrial processes are highly integrated, any change to one section of a process triggers modifications to other parts. Indeed, decarbonizing basic industry means that same material or chemical compound will be produced in a more expensive way so the opportunities are still uncertain and options and strategies relatively unexplored. Four broad technical strategies for decarbonizing these hard-to-abate production processes have been proposed: (i) the use of biomass as fuel or feedstock; (ii) the integration of carbon capture and utilization (CCU); (iii) the electrification of heat; or even (iv) the use of electrolytic hydrogen as a carbon-neutral substitute for natural gas.[4] Among them, CCU has the potential to generate economic benefits and positive social/political perspectives.[8] Some techno-economic studies have already been undertaken for CCU technology integrated into power plants[19,20] but there is a lack of techno-economic and environmental studies to explore the feasibility of CCU in the basic industry.[21,22] An example of a CCU strategy currently being commercially exploited is Carbon Recycling International (Iceland), which has a 4,000 t of methanol production capacity per year from CO_2 captured in an adjacent geothermal power plant.[9] Further CO_2-based products are expected to enter global markets in the near-term[10,11] increasing the demand for CO_2 as a commodity. On the other hand, the proposed renewable electrification of heat as the concept electric heat (EH),[12] by the direct conversion of electricity into heat using electric boilers or heat pumps, is an attractive decarbonization pathway for the industry sector.[13] No doubt, heat coming from renewable electricity contributes to a circular economy through an effective use of resources, reducing material losses due to oxidation in combustion furnaces. Typically, 2%-4% of material is lost in fossil burners while in electric furnaces the percentage is kept below 1%.[14] The difference seems negligible, but it can be very significant when accounting the full life cycle environmental impact of thermal processes. It has been recently reported that electricity accounts only for around 7% of global heat production (mostly in buildings) but electrification of industrial processes through heat pumps or electric boilers is gaining momentum[15] and it is expected to grow 20% in the industry sector through 2023[16] and to nearly 45% by 2050.[17] Lower investment expenditures are found for electric boilers which can operate profitably while heat pumps have the advantages of converting power more efficiently (~99%).[18] The basic value when assessing the efficiency of a heat pump is the Coefficient of Performance (COP), defined as the ratio of produced useful heat and electricity needed for the power of the heat pump, which typically ranges between 2 and 3.5.[18] On an industrial scale, typical installations consist of electric boilers (*e.g.* high voltage electrode boilers) with capacities between 50 MW to 70 MW, and a steam output of up to 45 bar at 260 °C.[13] Undoubtely, the introduction of EH in the basic industry can be a promising alternative to the fossil based steam production due to their ease of scalability.[19] The implementation of these abatement options in the hard-to-abate sectors will need a huge investment to build or upgrade key machinery and/or infrastructure. Achieving such radical transformation will require coordinated efforts across the entire value chain by collaborating with other stakeholders, in order to find opportunities and fostering the development for more promising decarbonization technologies.

In this work, a case of study illustrates the possibilities of decarbonizing the hard-to-abate sodium carbonate (soda ash) production sector using both CCU and EH schemes. The conventional production route of synthetic soda ash (based on the well-known Solvay process) was used as a benchmark. We analyzed the impact in both the environment and economics resulting from the integration of a CCU plant to produce CO_2-based methanol (CO_2-MeOH) and a EH unit (an electric boiler) to supply heat from renewable electricity. The CCU scheme was based on the latest technological developments. It is considered the use of monoethanolamine (MEA) for CO_2 capture [20,21] from exhausted gases and the production of CO_2-MeOH by the electrochemical reduction (ER) of CO_2, which has been demonstrated to be a potential environmentally friendly production alternative to the fossil-dependent conventional route under medium/long term developments.[22] The tools techno-economic assessment (TEA) and life cycle assessment (LCA) are used in this study as they have been proposed as the most suitable for guiding research and development towards commercialization.[23] A mathematical model based on mass and energy balances was used to check the technical feasibility of the novel integrated approaches, which was later used to obtain the requested inventories to conduct the environmental assessment by LCA. Then, an economic feasibility analysis has been carried out to determine all the expected costs involved together with the impact of the CCU plant integration. Considering the unfeasibility under current low Technology Readiness Levels (TRL) of the ER of CO_2 to produce CO_2-MeOH and the existing combination of electricity and CO_2 market prices, a sensitivity analysis was performed. The analysis evaluates the feasibility in a short/mid-term the integrated plant in terms of net present value (NPV) and the cost of CO_2 avoided (CA_{CO2}). We chose the economic parameters that are likely to change in the short/mid-term such as energy consumption, CO_2 and MeOH prices. In terms of LCA, this study provides the impact of the CCU integration in the carbon footprint (CF) of the soda ash production using the indicator Global Warming Potential (GWP). Two representative time-horizons have been evaluated, 20 yr and 100 yr. The results of the present study aim to contribute to accelerating the efforts for rapid decarbonization of the hard-to-abate sectors and the expected actions from key, industries and finance players.

MATERIALS AND METHODS

In this paper, we do investigate the impact caused in the environmental and techno-economic figures of the basic soda ash production sector by the integration of a CCU plant and renewable EH. It should be noted that the technical analysis of this study must be read as preliminary, due to be analyzed by the mass and energy balance based mathematical model built by the authors. A detailed process simulation including the corresponding mass flows, compositions, P&T in the involved streams is out of the scope of the present study. The considered CCU plant produces the added-value chemical methanol using CO_2 captured (CO_2-MeOH) from the soda ash plant. The novelty of this study is the consideration of renewable heat, supplied through a EH unit, as well as the integration of a CO_2 capture unit from a hard-to-abate sector such as soda ash. This specific CO_2 source has been excluded from the system boundaries in previous studies of the authors.[22,24,25] The benchmark values used for fair comparison purposes are: (i) the carbon footprint (CF) and (ii) the production cost estimated for the manufacture of 1 ton of synthetic soda ash based on the traditional Solvay process. The production capacity of the reference system used as the benchmark is 200 $kton \cdot yr^{-1}$, which fits a traditional soda ash plant.

Process description and system boundaries

Conventional process

The Solvay process (Figure 1) uses brine (mainly NaCl) and limestone ($CaCO_3$) as main raw materials. Ammonia (NH_3) is also used in the process being regenerated and recycled back into the process, trying to minimize losses. NH_3 is absorbed (1) to form the ammoniated brine (NH_4OH)

that reacts with CO_2 to form intermediate compounds: ammonium carbonate ($(NH_4)_2CO_3$) (2) and then ammonium bicarbonate (NH_4HCO_3) (3). CO_2 is continuously injected while cooling the solution, precipitation of sodium bicarbonate ($NaHCO_3$) is achieved and ammonium chloride (NH_4Cl) is formed (4). Coke is used to heat $CaCO_3$ in the lime kiln, as it is necessary to obtain the highest CO_2 concentration possible. CO_2 is required in the main reaction of the process and it is produced by heating (*i.e.* calcination) of the limestone between 950 °C and 1100 °C (5). Then, it is produced the hydration of calcium oxide (CaO) (6). The whole chemical reactions of the process are given next:[26]

$$NaCl + H_2O + NH_3 \rightarrow NaCl + NH_4OH \quad (1)$$

$$2NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O \quad (2)$$

$$(NH_4)_2CO_3 + CO_2 + H_2O \rightarrow 2NH_4HCO_3 \quad (3)$$

$$2NH_4HCO_3 + 2NaCl \rightarrow 2NaHCO_3 + 2NH_4Cl \quad (4)$$

$$CaCO_3 \rightarrow CaO+CO_2 \quad (5)$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (6)$$

During limestone burning in the lime kilns, CO and CO_2 are produced from both the combustion of coke and decomposition of limestone. An excess of CO_2 is required by the Solvay process to compensate for non-ideal absorption of CO_2 in the carbonation towers. These towers discharge the unreacted gases. Despite the gas being cleaned with brine in a washer to recover NH_3 and H_2S -if present-, and to recycle these components back into the process, CO_2, CO and other inert gases pass out to the atmosphere. The associated amount of CO_2 vented directly to the atmosphere (per unit of mass of soda ash) ranges between 200 $kg \cdot ton^{-1}$ to 400 $kg \cdot ton^{-1}$ and it represents a typical percentage of CO_2 between 36% vol. and 40% vol. depending on the detailed plant configuration.[26] Heat is assumed to come from steam, which is a critical energy input into the Solvay process to drive a full range of machinery including turbo-generators, gas compressors, vacuum machines, etc. and as a thermal energy carrier for decomposition, distillation and drying.[26] The consumption of energy in the form of electricity is required for the CO_2 gas compression, which is directly linked to the gas concentration.[26] The background data used to calculate the benchmark values was extracted from literature [26] (Table 1). Note that the average values shown in table 1 are used in this study. Of course, different combinations between the upper and lower values of each range will be found in real plants depending on the detailed plant configuration/operation.

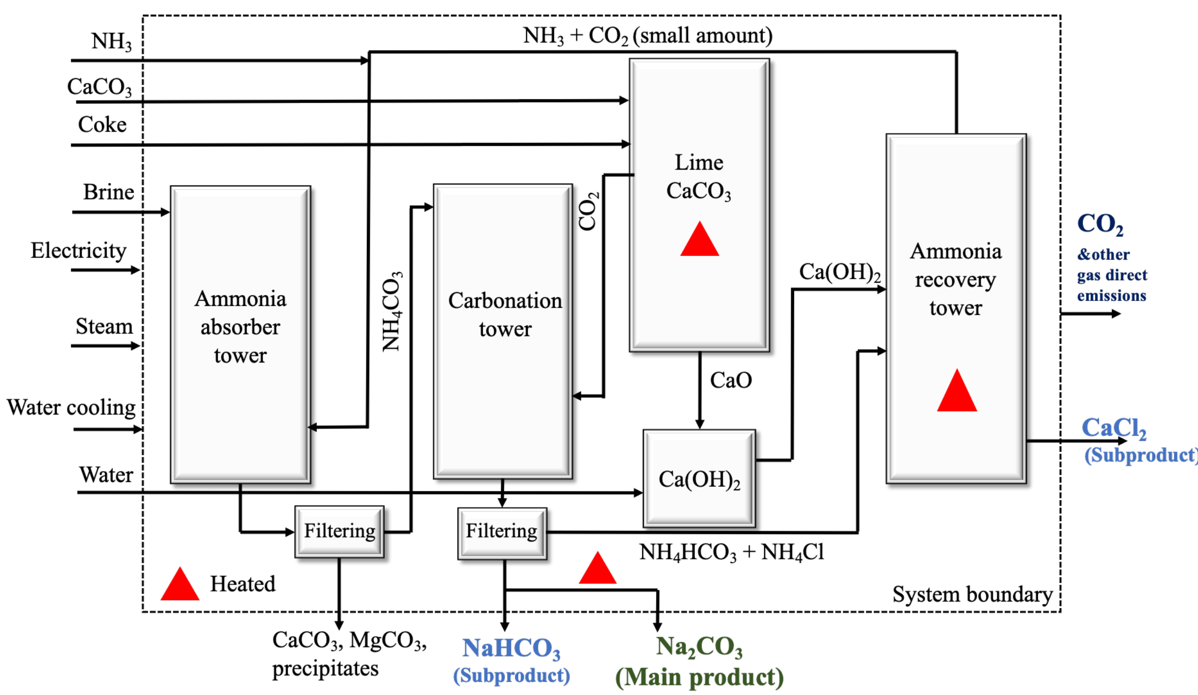

Figure 1. Layout and system boundary of reference soda ash plant.

Table 1. Soda ash Solvay process main input/output levels[26]

Main Raw Materials	Average	Lower	Upper	Unit per ton of soda ash
Ammonia (NH_3) make up [(1)]	1.45	0.8	2.1	kg
Lime ($CaCO_3$)	1455	1090	18220	kg
Brine (NaCl)	1665	1530	1800	kg
Water cooling	75	50	100	m^3
Water [(2)]	3.05	2.5	3.6	m^3
Energy				
Heat (Steam)	9.15	7.5	10.8	GJ
Electricity	90	50	130	kWh
Coke (kiln)	2.5	2.2	2.8	GJ
Gas emission				
CO_2	300	200	400	kg
CO	12	4	20	kg
NH_3	<1.5			kg
Solid emissions				
Total solid waste	115	20	210	kg

(1) The indicative upper value of input NH_3 make-up can be lower than the sum of upper limit outputs of gaseous and liquid NH_3 emissions, as the extreme emission values do not normally sum up[26]

(2) Process water. The main consumer of water is the slaker, where the lime coming from the lime kilns reacts with water to produce milk of lime.

Carbon capture and utilization (CCU) plant

The system boundaries have been expanded to integrate a CCU plant (Figure 2) in order to evaluate the impact in both the CF and the economics of the process. This CCU plant captures CO_2 from the soda ash direct gas emission stream. The direct CO_2 emissions are 300 $kg\cdot ton^{-1}$ expressed as the mass of CO_2 emitted per unit of mass of soda ash produced.[26] As mentioned before, the CCU scheme was based on the latest technological developments, basically, we considered the use of monoethanolamine (MEA) for CO_2 capture[20,21] and the production of CO_2-MeOH by the electrochemical reduction (ER) of CO_2.[22] On one hand, the capture technology based on absorption using MEA was selected as is a well-established end-of-pipe technology. A make-up quantity of 5 g of MEA is required per kg of CO_2 that enters the system. The MEA process requires a substantial amount of heat for solvent regeneration while the power supply is required for operating fans and pumps as well as for compression and dehydration of the CO_2 captured. Energy consumptions of 4.26 MJ and 0.13 kWh per kg of CO_2 captured are required.[27] CO_2 is captured with an efficiency of 90% as found in the literature under similar flue gas composition that is around 34% vol.[20] The CCU plant is considered as a sub-process or a secondary user of the main soda ash plant that provides CO_2 at zero cost to the utilization plant. On the other hand, the CO_2 utilization process selected in the study involves three main steps: the ER of CO_2 based on a stack of individual cells, the distillation of the azeotropic mixture MeOH/water up to the desired purity (99.7% wt.) and the compression of the subproducts H_2 and O_2 to the liquid forms to be ready to transport. Energy consumption is considered in the form of photovoltaics (PV solar) electricity for the reduction step and heat as electric steam (from the EH unit)[28] for the separation step according to the nature of each single process. As stated before, the novelty of the present study is the consideration of renewable heat in the CCU plant instead of using fossil heat (*i.e.* steam from natural gas). An electric boiler with a 99% heat/electricity efficiency was considered for heat supply. Electric boilers are suitable for larger installations as they can use higher voltages and power capacities at lower installation expenses. CO_2-MeOH is supposed to be synthesized in the ER stack at 40% wt. accordingly with the mid-long term target value found in our previous study.[22] This value likely ensures a carbon-neutral cycle when benchmarking CO_2-MeOH synthesis by ER and the synthesis of fossil-based MeOH (*i.e.* by conventional steam reforming). Electrochemical parameters such as faradaic efficiency (FE), current density (j) and overall cell voltage (E) are fixed in this work at 45.7%, 6.93 mA·cm^{-2} and 2.335 V, respectively.[29,30] A detailed description of the mathematical model that describes the ER of CO_2 and the separation steps was built on the basis of mass and energy balances and can be found in our previous study[22] as well as in the Supporting information.

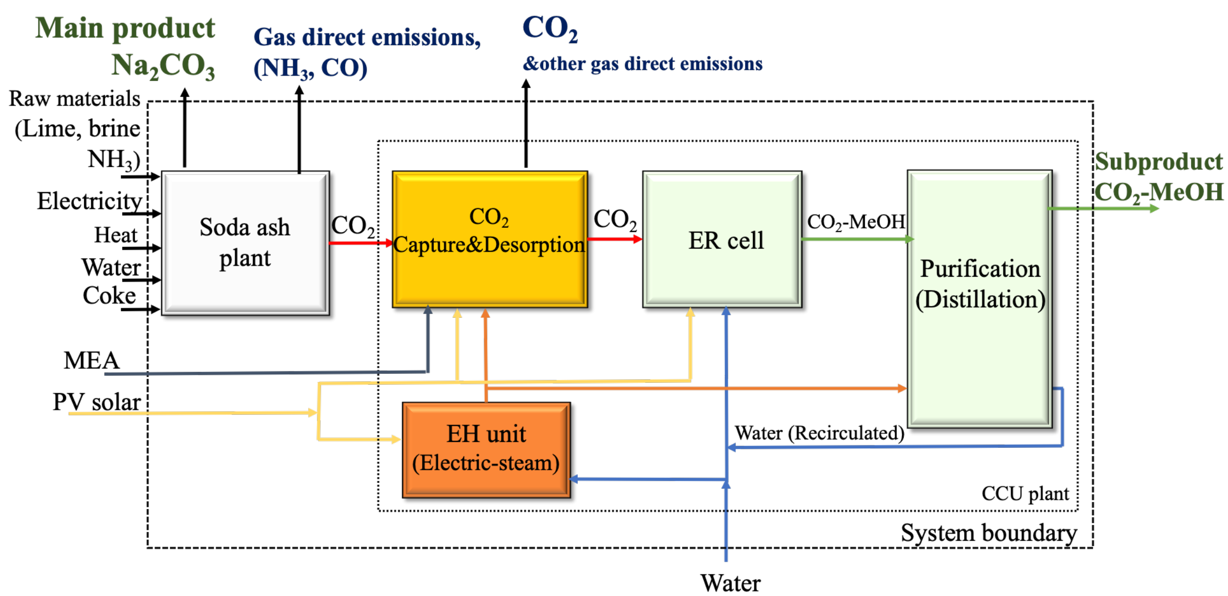

Figure 2. Layout and system boundary of the CCU plant integrated into the soda ash plant.

Carbon footprint assessment

An attributional LCA following a cradle-to-gate approach was carried out in order to evaluate the carbon footprint (CF) of the conventional synthetic soda ash plant (benchmark) of 200 kton·yr^{-1} capacity and the impact of the integration of the CCU and the EH units. The functional unit used in this work is 1 ton of soda ash. According to the mathematical model, it was determined that the

CCU plant produces 38.8 kton·yr^{-1} of CO_2-MeOH (at MeOH commercial purity of 99.7% wt.) (Figure 2) during 20 years, considered as a conservative estimation of the lifetime of the plant. In order to analyze the CFs, two scenarios labelled as CONV and CONV+CCU were created and assessed by LCA. CONV is the conventional plant analyzed by the average values shown in Table 1. CONV+CCU represents the integration of the CCU plant that produces CO_2-MeOH in the conventional plant. In this scenario, the entire CCU plant is based on renewables sources: heat is provided as steam, which is produced in the EH unit, thus using electricity. Therefore both the electricity for the steam and the electricity for the ER unit come exclusively from PV solar. The soda ash process configuration was initially kept as the conventional route in which energy needs are supplied by heat (steam from fossil fuels) and electricity (sourced from the grid mix). The inventory data (Table 2) was obtained from the mathematical model previously described.

Table 2. Inventory of the CCU plant integrated in the main soda ash plant (scenario CONV+CCU). Otherwise stated, the preferred geographical location is the EU-28

Inventory components	**Value**	**Unit**	**Reference process used in the background system**
Main Raw Materials			
Ammonia make up	1.45	kg	Haber- Bosch- Process
Lime	1455	kg	Crushed stone fines
Sodium chloride	1665	kg	Sodium chloride (rock salt)
Water cooling	75.00	m^3	Tap water from groundwater
Water	3.050	m^3	Tap water from groundwater
Water ER	614.0	kg	Process water
MEA make-up	0.432	kg	Estimated from literature [31]
Energy			
Electricity	90.00	kWh	Electricity grid mix
Energy (as steam) (Soda ash)	9.150	GJ	Process steam from natural gas 90% efficiency

Coke (kiln)	2.500	GJ	Coke mix
Electricity Capture	29.49	kWh	Electricity from photovoltaics
Electricity EH (ER+Capture)	1228	kWh	Electricity from photovoltaics
Electricity ER	5747	kWh	Electricity from photovoltaics
Products			
MeOH[(1)]	197	kg	
Soda ash	1.000	ton	
Subproducts			
O_2	644	kg	Substituting oxygen by system expansion (via cryogenic air separation)
H_2	43.74	kg	Substituting hydrogen by system expansion (via steam reforming from natural gas)

(1) Note that an amount of water of 0.589 kg is not shown in the table as it is considered in the 99.7% wt. MeOH product

A third scenario called CONV+CCU$_{(RWs)}$ was also created. This scenario represents the case in which the entire plant is based on renewables which means that PV solar is also used to supply energy needed (both electricity and heat in the form of electricity based steam) by the conventional soda ash process. In this third scenario, the consumption of PV solar electricity by the electric boiler per unit of mass of soda ash produced raises up to 3783 kWh·ton^{-1} and therefore no steam from natural gas is requested in the conventional process.

The LCA assessment was performed using GaBi Professional software.[32] The method "IPCC AR5" was selected in this study as it contains the characterization factors determined by the Intergovernmental Panel on Climate Change (IPCC) in the 5th Assessment Report (AR5)[33] to calculate the indicator global warming potential (GWP) as a basis for obtaining the corresponding CF of the processes both for a 20 yr and a 100 yr horizon.

It must be taken into account that soda ash is the main product of the overall process, but we also must consider CO_2-MeOH as another main product after the integration of the CCU plant. Therefore, after the CF calculation of the overall process, a cost based allocation procedure between these two main products has been carried out. By definition, cost allocation is the partitioning of the output impact (or input/outputs streams) of the process to the products of the system under study according to the products cost or selling price (economic value). Taking into account that these products have noticeable different market prices, cost allocation is preferred over mass allocation. Market prices of 270 $€\cdot ton^{-1}$ and 440 $€\cdot ton^{-1}$ were fixed for soda ash and fossil-based MeOH, respectively.[34] The side products such as H_2 and O_2 were defined here as avoided products from their conventional production processes; therefore, their environmental burden from production are avoided. As later discussed, not taking into account the burdens from these two side products is also considered in one of the scenarios. In order to illustrate the CF changes with the chosen time horizon, we first determine the impact over a period of 100 yr (GWP100) which is the default timeframe for a wide majority of published carbon footprint studies. Then, the CF values were calculated at a 20-yr timeframe (GWP20) as we assume it is a suitable period for the current global policy goals and strategies. Pairing GWP20 and GWP100 will reflect both long-term and near-term climate impacts and reduce uncertainty.[35] It is worthy to highlight that other environmental categories than CF were excluded from this study because the viability of the suggested option should be fulfilled at least for the impact category indicator that is intended to benefit from the CCU process. An LCA study including others environmental impact categories must be considered as future work. GaBi Professional database[32] was used to provide the datasets to calculate the CO_2 equivalent emissions (in terms of GWP100 and GWP20) for the requested utilities such as electricity, heat (as steam), coke, etc., and the CO_2 equivalent emissions for the needed raw materials (sodium chloride, lime and ammonia).

Economic and sensitivity analysis

An economic analysis has been conducted to estimate the Total Cost of Production (TCP) required to synthesize 1 ton of soda ash using the conventional process (selected as the benchmark). After that, the economic impact in the TCP of soda ash caused by the CCU plant (including the EH unit) integration was evaluated. The mass and energy balances inventories of the studied plant under the suggested scenarios were used for the economic assessment. In addition to the TCP estimation, the cost of CO_2 avoided (CA_{CO2}), expressed as € per unit of mass of CO_2, was determined based on the TCP of soda ash and the equivalent specific emissions of the soda ash plant with and without CCU plant as shown in Equation (7):

$$CA_{CO_2} = \frac{TCP_{CCU} - TCP_{ref}}{CF_{ref} - CF_{CCU}} \quad (7)$$

The capital (CAPEX) and operational expenditures (OPEX) were also estimated together with the calculation of the key performance indicators (KPIs) such as the NPV and the CA_{CO2}. The currency exchange rate used in the study is €2018, which was based on Eurostat data (European Commission, 2018). The preferred geographical location of this analysis is the EU-28. In order to perform under very conservative consideration, both the lifetime of the soda ash plant and its integrated CCU plant is assumed to be 20 yr. This approach simplifies the later interpretation of the results. The reader must note that at the current TRL values of the ER technology, it is not suitable to envisage larger plant lifetimes. The features and prices considered for the CCU plant are shown in Table 3. The CAPEX of the ER process (including distillation) has been estimated from the CAPEX value obtained in our previous study (12.5 M€ for an annual capacity of 12 kton of the CO_2 ER product).[25] Note that the CO_2 ER product here (CO_2-MeOH) is not the same that in our previous study; however, we considered that the CAPEX value of the plant would be similar in both studies as the investment for the main equipment used (ER cell, distillation column, pumps and compressors) will have a similar order of magnitude. Then, the estimated CAPEX value has been scale to the present CO_2-MeOH production rate by using the "0.6 rule"[36] considering that the present CCU plant has a higher production capacity. Therefore, a CAPEX value of 25.4 M€ for a plant capacity of 38.8 $kton \cdot yr^{-1}$ of CO_2-MeOH has been estimated and used in this work. The capital cost of the CO_2 capture unit has been estimated as 180 $€ \cdot ton^{-1} \cdot yr^{-1}$ according to literature.[37] As mentioned before, an industrial-size electric boiler was considered as the main equipment in the EH plant. A capital cost of 0.23 $M€ \cdot MW^{-1}$ found in literature[14] was considered in this study. Prices for raw materials, utilities, products and by-products, are estimated for the year 2018. They were considered constant for the analyzed period. OPEX consists of Fixed and Variable Operating Costs (FCP and VCP, respectively). VCP include the costs of: i) raw materials consumed by the processes, ii) utilities, and iii) consumables. FCP involve: i) operating labour, ii) supervision, iii) direct salary overhead, iii) maintenance, iv) property taxes and insurance, and v) interest. FCP costs and NPV were estimated as discussed in the Supporting Information.

Table 3. Plant features and unit prices of raw materials, utilities, products and byproducts

	UNIT	Value	Ref.
Production rate CO_2-MeOH	$ton \cdot yr^{-1}$	38836.4	
Production rate Soda ash	$ton \cdot yr^{-1}$	200000	
CO_2 avoided	$ton \cdot ton_{MeOH}^{-1}$	1.38	
Lifetime (Plant)	yr	20	
Operation time	$days \cdot yr^{-1}$	350	
Shift per day	h	8	

Hourly labour cost (EU-28;2018)	€·h^{-1}	27.4	[38]
Discount rate, d		0.09	
Electricity market price (average EU-28)	€·MWh^{-1}	43	[39]
CO_2 price (EU ETS)	€·ton^{-1}	27$^{(1)}$	[40]
MeOH market price	€·ton^{-1}	400	[41]
Soda ash market price	€·ton^{-1}	270	[42]
H_2 market price	€·kg^{-1}	1.3	[43]
O_2 market price	€·ton^{-1}	50	[41,44]
$CaCl_2$ market price	€·kg^{-1}	0.12	[45]
$NaHCO_3$ market price	€·kg^{-1}	0.24	[45]

$^{(1)}$ Reference CO_2 price value from the CO_2 European Emission Allowances in September, 2019

A sensitivity analysis was performed in order to evaluate the feasibility in the short/mid-term sub-scenarios of the integrated plant in terms of soda ash production cost. We investigated the sensitivity of the NPV and the CA_{CO2} to the relative increment/decrement of the affecting parameters. We chose the economic parameters that are likely to change in the short/mid-term such as energy consumption, CO_2 prices and the market price of MeOH.

Monte-Carlo simulation

The uncertainty in the results of the environmental impact (in terms of CF) and economics (in terms of NPV) has been evaluated by a Monte-Carlo simultation (MCS). The scenario CONV+$CCU_{(RWs)}$ was chosen to run the simulation. MCS is a widely used method to perform error propagation for model parameters, especially used in LCA[46,47]. The MCS method uses a relation between the uncertainties and variables that are described in a model by probability distribution functions. Our previous study[22] revealed that the energy consumption by the ER of

CO_2 and the purity of MeOH that is synthesised in the ER cell were the most critical variables in the environmental impact results, due to the current low TRL of this technology. On the other hand, economics are strongly influenced by the electricity market price, thus it is expected to vary also in the near future. In order to study the uncertainties associated to them, we have performed a MCS. Two triangle distributions were selected to describe the energy consumption and MeOH purity and a normal distibution was used to describe the electricity market prices as they are the most commonly used distributions.[47] Briefly, a tiangle distribution is characterised by 3 parameters: i) minimun value (min); ii) most likely value (ML); and iii) maximun value, while a normal distrution is characterised by i) the mean value (mean); ii) the standard deviation (StDev); and iii) the minimum (min). The MCS considered a run of 1500 times. Values for the distributions of each variable is presented in Table 4. The output results are obtained in the form of probability distributions.

Table 4. Distributions of the selected variables in the MCS

Variable	Unit	Distribution type					
		Triangle			Normal		
		Min	ML	Max	Mean	StDev	Min
Energy consumption	(kWh·kg $MeOH^{-1}$)	6.1	25.68	30.82			
[MeOH]	(% wt.)	20	40	40			
Electricity market price	(€·kWh^{-1})				40	10	1

RESULTS AND DISCUSSION

Carbon footprint assessment

The CF results of conventional manufacture (scenario CONV) of 1 ton of soda ash (green bars) and the scenarios CONV+CCU (blue bars) and CONV+$CCU_{(RWs)}$ (yellow bars) obtained by the LCA approach are shown in Figure 3. It is noteworthy that in the scenario CONV+CCU, the soda ash process configuration was initially kept as the conventional route in which energy needs are supplied by heat (steam from fossil fuels) and electricity (from the grid mix). Reductions in the CFs of soda ash around 44% and 43% were found in the 100 yr and 20 yr time horizons after the CCU integration. For a fair comparison, CONV+$CCU_{(RWs)}$ displays the case in which the whole plant was based on renewables which means that PV solar is also used to supply energy to the conventional soda ash process including heat as electric steam (shown in yellow bars). A relevant 74% of reduction of the soda ash CF was achieved for the renewable-based integrated plant.

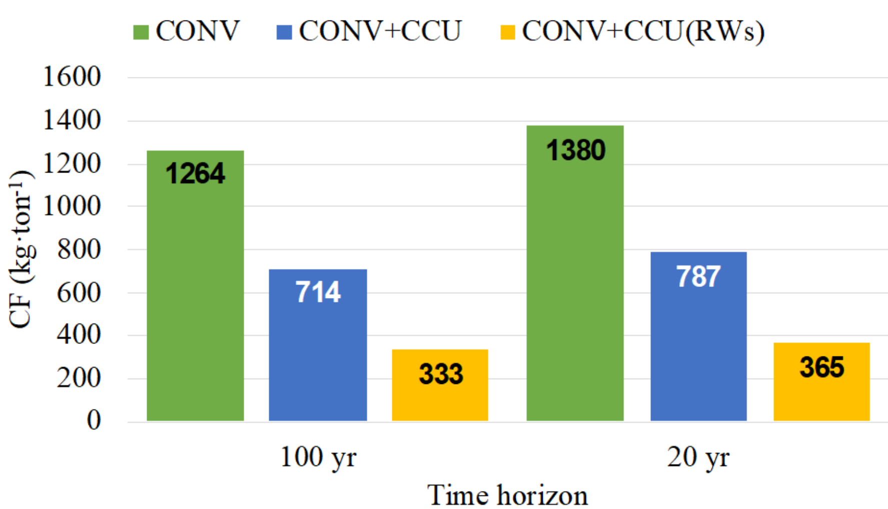

Figure 3. Impact in the CF of the CCU plant integration in the soda ash manufacture of the selected scenarios.

In the CONV scenario, CF values (expressed as a unit of mass of CO_2-eq. per unit of mass of soda ash produced) of 1264 kg·ton^{-1} and 1380 kg·ton^{-1} were estimated for a 100 yr- and 20 yr time horizons, respectively. The CF breakdown results are shown in Figure 4. Heat consumption, as steam (from natural gas), is the main contribution to the CF with a share between 52% and 54%, followed by the CO_2 process direct emissions. Specifically, heat contribution to the total CFs in the 100 yr and 20 yr time horizons are 687 kg·ton^{-1} and 774 kg·ton^{-1}, respectively. The difference between these two-time horizon values is explained because of the relation between CH_4 with industrial heating energy, mainly natural gas. It is well-known that some greenhouse gases, especially CH_4, are removed from the atmosphere relatively quicker than others involving more impact on climate change in the 20-yr timeframe than in the 100-yr timeframe.[48] According to last available figures from Eurostat, 75% of the European heating is still generated from fossil fuels[49] and natural gas presents a share of 39% of the heat demand for industry.[18] In this study, heat is considered to come from steam according to a typical/conventional plant configuration.[26] Another minor contribution to the CF is coke that is used to heat $CaCO_3$ in the lime kiln, with a share between 5.6% and 5.9%. Electricity and sodium chloride contribute to the CF with percentages around 2.9% and 10.9%, respectively.

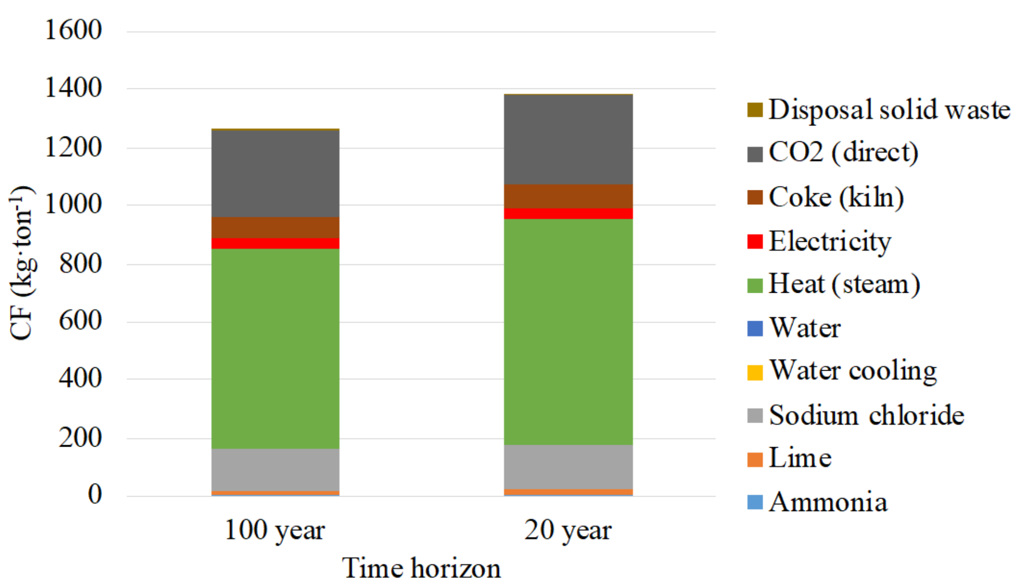

Figure 4. Carbon footprint breakdown of the conventional manufacture of 1 ton of soda ash (scenario CONV).

The CF breakdown results of the scenarios CONV+CCU and CONV+$CCU_{(RWs)}$ are shown in Figure 5. As it was expected, heat consumption by the soda ash production process continues to be the main contribution to the CF in the integrated process for the scenario CONV+CCU (Figure 5(a)). Electricity consumption by the CCU plant is the second contribution to the CF in the aforementioned scenario. This fact did not come as a surprise because the CCU plant is a fully-electrified-based process. On one hand, the ER of CO_2 process still presents a low TRL, which results in an overall low efficiency and/or high electricity consumption. On the other hand, heat was supplied by a EH unit increasing the overall electrical consumption. Note that in this study, we have assumed the conservative electrical consumption in the ER cell of 25.7 $kWh \cdot kg^{-1}$, expressed as the needed amount of electricity per unit of mass of MeOH produced from CO_2. This value could be lower in future developments considering that the minimun/theoretical energy consumption value can be as low as 6.10 $kWh \cdot kg^{-1}$ (*i.e.* the case in which FE is maximum (100%) and the cell potential (E) is the minimum thermodynamic (1.214 V)).[22] Using the minimun/theoretical energy consumption value, a reduction percentage of the electricity requirements was around 76% with the subsequent CF reduction. The results obtained for the scenario CONV+$CCU_{(RWs)}$ (Figure 5(b)) show that PV solar is the main contribution to the CF in this case. It should be recalled that heat (as steam), consumed by the soda ash plant, is now supplied by the EH unit. Another important element is the substantial emission burden that is avoided when the compression and commercialization of the ER-side products O_2 and H_2 is considered. Values around 400 $kg \cdot ton^{-1}$ and 490 $kg \cdot ton^{-1}$ are being avoided in the overall CFs for the 100 yr and 20 yr time horizons, respectively. Thus, to consider the compression and commercialization of H_2 and

O_2 ER-side products is a relevant hypothesis in order to obtain an overall reduction in the CF of soda ash up to 74% as long as the entire integrated plant was run on renewable electricity (scenario CONV+$CCU_{(RWs)}$). Future work is also oriented to the market analysis of the side products H_2 and O_2.

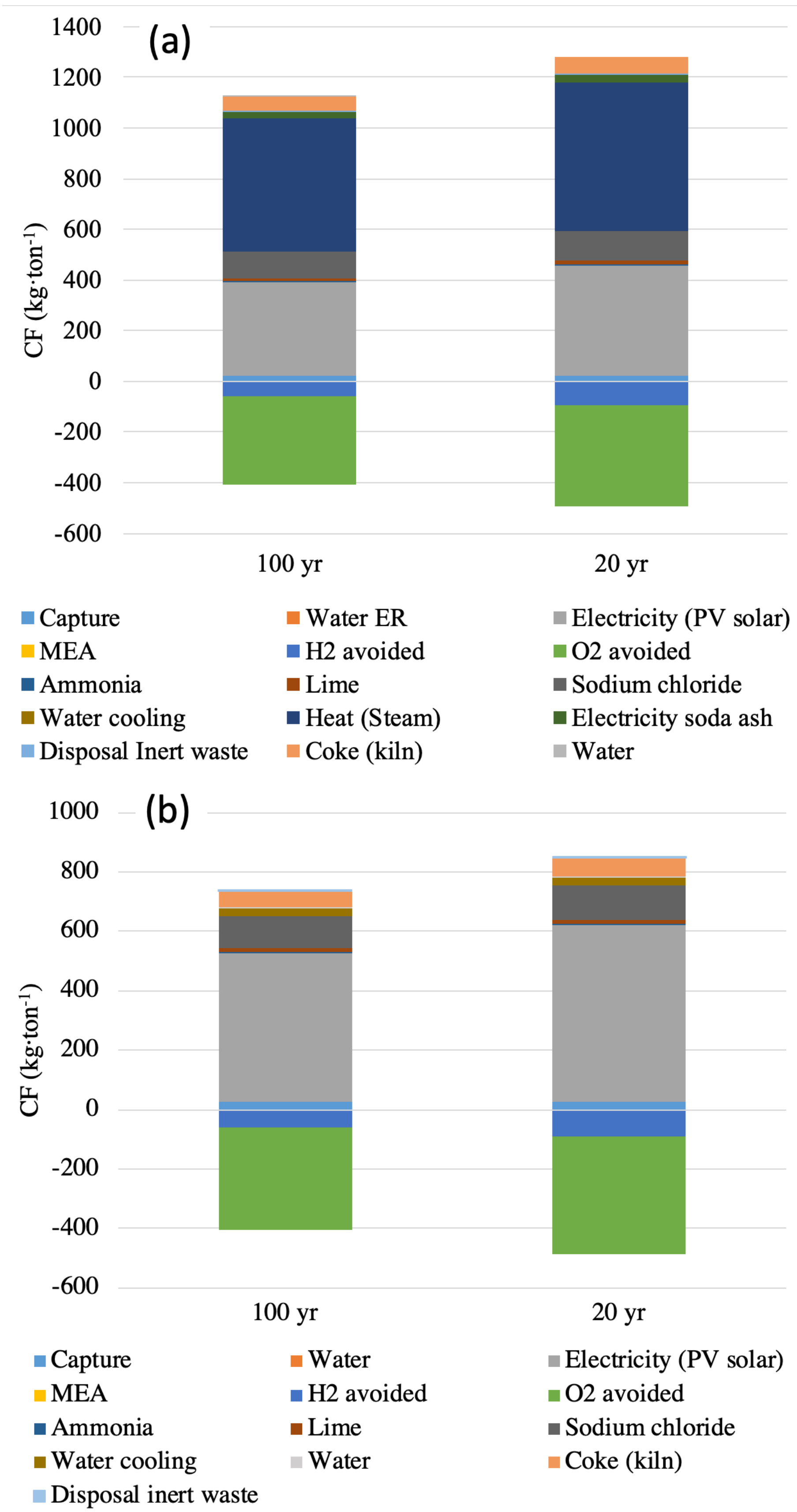
(a)
1400
1200
1000
800
600
400
200
0
-200
-400
-600
CF (kg·ton-1)
100 yr
20 yr
Capture
Water ER
Electricity (PV solar)
MEA
H2 avoided
O2 avoided
Ammonia
Lime
Sodium chloride
Water cooling
Heat (Steam)
Electricity soda ash
Disposal Inert waste
Coke (kiln)
Water
(b)
1000
800
600
400
200
0
-200
-400
-600
CF (kg·ton-1)
100 yr
20 yr
Capture
Water
Electricity (PV solar)
MEA
H2 avoided
O2 avoided
Ammonia
Lime
Sodium chloride
Water cooling
Water
Coke (kiln)
Disposal inert waste

Figure 5. Carbon footprint breakdown of 1 ton of soda ash produced by the CCU+EH integration in the conventional plant: (a) scenario CONV+CCU; (b) scenario CONV+$CCU_{(RWs)}$.

Economic and sensitivity analysis

The economic KPIs were estimated for the benchmarked conventional plant (scenario CONV) and the integrated plant with CCU-ER (scenario CONV+CCU). The economic impact of the CCU-ER integration was analyzed by means of a different combination of electricity prices and heat sources (Table 5). Initially, soda ash process configuration in the integrated plant was kept as the conventional route in which energy needs are supplied by heat (steam from natural gas) and the electricity from the grid mix. Likewise, the electricity market price used for supplying the CCU plant in the first sub-scenario was the same as the one used for the conventional plant (43 €·MWh^{-1}). As it was expected, the NPV indicator obtained in the first scenario (-88 M€) showed that the project is unfeasible from an economic perspective. According to our previous study, the technology ER of CO_2 would be competitive in the mid-term as long as an inexpensive renewable source is available (*i.e.* electricity market prices lower than 20 €·MWh^{-1}). Then, the following sub-scenarios assumed a considerable cheaper electricity source to supply the CCU-ER plant. A market price value of 20 €·MWh^{-1} was used according to our previous study[25] and the latest prospective of Levelized Cost of Electricity (LCOE) values for 2030.[50] It should be highlighted that LCOE is an indicator of the per-kWh cost of building and operating a generation plant over its financial life. LCOE indicator has been also regarded as the minimum cost at which electricity must be sold in order for a PV project to break-even.[51] For that reason, we have used those prospective values of PV solar LCOE [50] as equivalent to the future perspective of PV electricity market prices. In any case, the final decision to buy electricity from the market or build an ad-hoc PV plant in order to supply the soda ash plant (partially or completely) is out of the scope of the present study and will definitely depend on a specific real-life facility. Second sub-scenario considers that heat was fully supplied by steam from natural gas. This case would result feasible from an economic perspective; however, it must be highlighted that steam consumption by the CCU separation step would increase considerably the CF value of soda ash. Third sub-scenario integrates EH only in the CCU plant but the market electricity price is still assumed as 20 $€\cdot MWh^{-1}$. The economic results indicate that the integrated plant would be feasible only under a low-cost energy source. For a fair comparison, the last scenario, $CCU+CONV_{(RWs)}$ was also evaluated, but only in the best case of an electricity price of 20 $€\cdot MWh^{-1}$. According to the results, when all the heat requirements in the integrated plant comes from electric steam, the TCP obtained for soda ash may be as low as 135 $€\cdot ton^{-1}$. When a cheap electricity source is available to supply the CCU plant (*e.g.* 20 $€\cdot MWh^{-1}$), negative abatement costs (CA_{CO2}) are obtained, which indicate that greenhouse gas emissions can be abated by reducing the overall production costs. In general, it can be stated that the higher the electricity price the higher the abatement costs will be, which will result in the necessity of other market incentives to ensure economic competitiveness.[23] In this context, new instruments have raised to support low-carbon technology deployment, such as the Corporate Renewable Power Purchase Agreements or PPAs. The instrument PPAs introduces a new possibility for a risk-controlled agreement to purchase and sale energy between the utility and the PV solar electricity generator, resulting in significant market growth and cost reductions.[52]

Table 5. Summary of total plant costs and economic KPIs for the conventional and the CCU plant

KPI	Scenario/	CONV	CONV + CCU			CONV + $CCU_{(RWs)}$
	CCU heat source/	Steam (no CCU)	Electric steam	Steam from fossil fuels	Electric steam	Electric steam
	Units/Electricity price	43 €·MWh^{-1}	43 €·MWh^{-1}	20 €·MWh^{-1}	20 €·MWh^{-1}	20 €·MWh^{-1}
CAPEX	M€	166	218	202	218	218
VCP	€·kg^{-1}	0.20	0.49	0.35	0.33	0.30
FCP	M€·yr^{-1}	6.40	6.8	6.50	6.80	6.80
OPEX	M€·yr^{-1}	46.2	105	76.0	74.4	68.0
CCOP	M€·yr^{-1}	16.6	40.0	10.0	8.90	6.04
$TCP_{soda\ ash}$	€·ton^{-1}	156.3	305.4	150.0	149.9	135
NPV	M€	184	-89	196	195	221
BCR		1.73	0.89	1.80	1.81	2.00
CA_{CO2}	€·kg^{-1}	N/A	0.256	-0.015	-0.011	-0.021

The impact of some of the most affecting parameters on the KPIs of NPV and CA_{CO2} of the plant was assessed through a sensitivity analysis for the scenario called $CONV+CCU_{(RWs)}$. It was selected because it is the most favourable from an environmental perspective. Figure 6 displays the influence of the relative increment/decrement of the CO_2 market price (as in the EU ETS), MeOH market price and the electricity price in both the NPV and the CA_{CO2}. These three variables were selected as they are expected to change substantially in the short/mid-term. The results have indicated that the purchasing electricity price is the most affecting parameter to the plant economics. In contrast, the CO_2 price (considered as a tax on direct emissions from the plant) is the less sensitive parameter to the economics. Even though the CO_2 market price is expected to vary considerably in the short/mid-term, the variation of the economic figures of the integrated plants with CCU will be mild in comparison with the influence of the electricity or MeOH prices. Table 6 summarized the main results obtained in the environmental and techno-economic assessments. According to the results, by means of the CCU integration and the consideration of the co-production of the CO_2-MeOH (as an electrocommodity that results of the benefits of the chemical industry electrification), it would be possible to reduce up to 74% the CF of the main product (soda ash) with a reasonable TCP of 135 €·ton^{-1} under medium/long term developments. This percentage of reduction and TCP can be obtained within the hypothesis of compression and commercialization of the considered ER-side products H_2 and O_2. It must be also mentioned that this percentage of reduction would be up 41% and a TCP of 294 €·ton^{-1} without the consideration of the avoided burdens by the H_2 and O_2 commercialization. The economics of the integrated plant are not feasible under the current electricity purchase price. Considering the future evolution of the electricity market price, a value of 20 €·MWh^{-1} was selected as the electricity purchase price to ensure the economic feasibility of the CCU integration in the studied hard-to-abate sector.

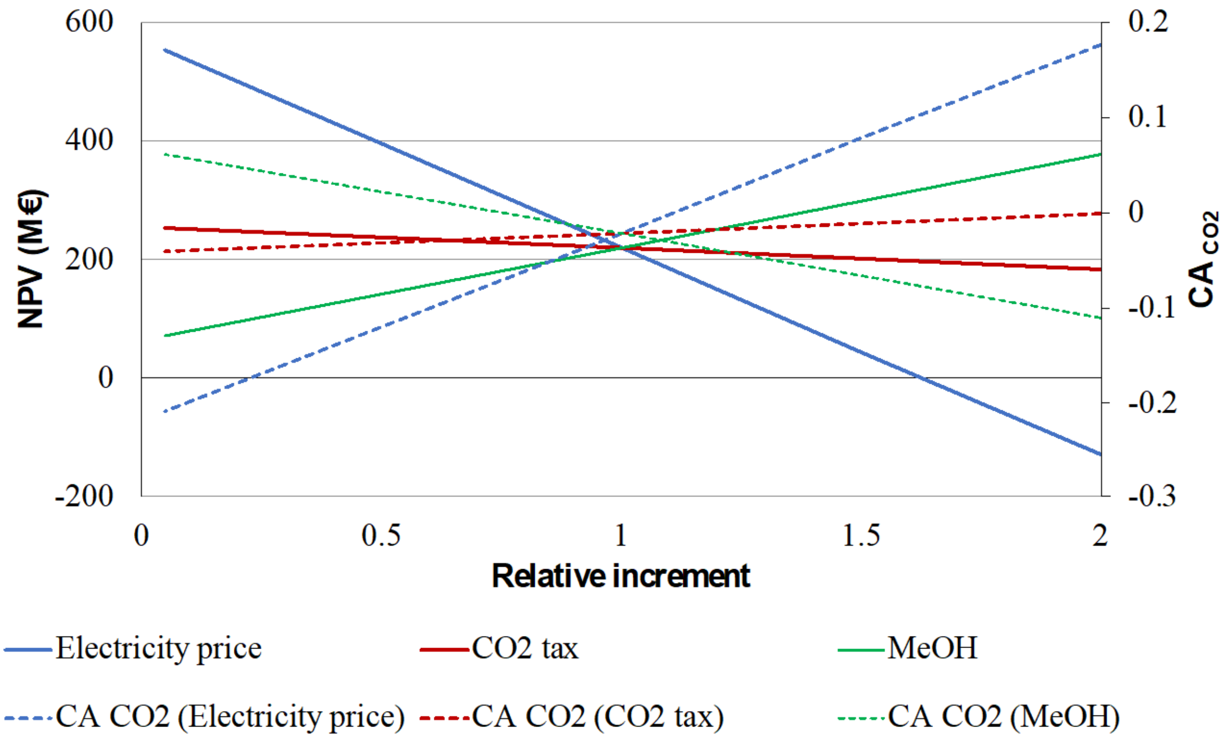

Figure 6. NPV (—) and CA_{CO2} (- -) variations with prices of MeOH, CO_2, and electricity. These are represented by relative increments/decrements towards the original values considered.

Table 6. Summary of the main techno-economic results

	GWP100 CF (kg·ton^{-1})	GWP20 CF (kg·ton^{-1})	TCP (€·ton^{-1})	Electricity purchase price used in the TCP estimation (€·MWh^{-1})
CONV	1264	1380	156.3	43
CONV+CCU	714	787	149.9	20
CONV+$CCU_{(RWs)}$	333	365	135	20
CONV+$CCU_{(RWs)}$*	738	852	294	20

* Summary results without the hypothesis of commercialization of ER-side products H_2 and O_2

Monte-Carlo simulation

MCS was carried out in order to estimate the standard deviations from the mean values of the KPIs CF, NPV and TCP according to the probability distributions of the risk parameters previously defined (ER-energy consumption, MeOH purity and the purchase electricity price). The probability distributions were estimated using the scenario CONV+CCU$_{(RWs)}$ and the corresponding results are displayed in Table 7. More sensitive impact characterisations display wider probability spreads while narrow probability distribution spreads indicate a less sensitive impact. The kurtosis values for the CFs are lower than 3, which indicate that there is a low concentration of values around their mean. Considerable environmental benefits can be attained by improving the energy efficiency and the production rate. The kurtosis values for the economic KPIs are closer to 3 which indicates a normal distribution. The standard error values indicate that the uncertainty is higher in the economic assessment results. This fact was expected as the technology is still found at low TRL remaining unfeasible under current combination of electricity market prices. It shoud be recalled that a mean value of 40 €·MWh^{-1} was selected for the electricity price distribution in the MCS. This fact supports the necessity of new instruments such as PPAs for a proper low-carbon technology deployment.

Table 7. Monte Carlo simulation results for the selected indicators

Indicator	Units	Mean	Stdev	Kurtosis	Skewness	Standard Error
CF-100 yr	kg·ton^{-1}	288.8	55.3	2.3	-0.43	1.42
CF-20 yr	kg·ton^{-1}	316.5	63.4	2.4	-0.50	1.63
NPV	M€	-152	-162	2.8	-0.26	4.22
TCP	€·ton^{-1}	340.8	89.4	3.0	0.30	2.3

CONCLUSIONS

The results obtained in this study have demonstrated that it is possible to reduce the carbon footprint (CF) of the synthetic soda ash production up to 74% with a reasonable cost aiming at 135 $€·ton^{-1}$ of soda ash as Total Cost of Production (TCP) under proper medium/long term developments assuming the hypothesis of the commercialization of the ER side products H_2 and O_2. A reduction of the soda ash CF up to 41% and a soda ash TCP of 294 $€·ton^{-1}$ would be obtained considering a PV electricity market price of 20 $€·MWh^{-1}$ without the mentioned hypothesis related to the side products. The co-production of CO_2-based MeOH by the electrochemical reduction of the CO_2 captured (CCU-ER) from the main soda ash plant has been considered in this study within the novel concept of electrocommodity production. This is an example of the benefits of the electrification of the chemical industry, which no longer use the enthalpy of coal, oil or natural gas to drive the chemical reactions. Several scenarios have been analyzed considering the future innovation of the CCU-ER technology as well as the future evolution of market prices, due to the application of instruments such as the European Union Emission Trading System or Power Purchase Agreements (PPAs). The scenarios analyzed in the study have suggested that the complete electrification of the integrated plants of soda ash through electric heat (EH) units is feasible from the environmental perspective, but it has major implications on the economics under current energy market prices. The use of inexpensive renewable energy is the key element to the future competitiveness of the electrification of heat and CCU integration in such a hard-to-abate production sector. Using low-cost electricity (*e.g.* using surpluses of renewable electricity or self-supplied electricity and/or PPAs) and a higher CO_2 price, which are expected in the short/mid-term, are required to ensure the future economic feasibility. The insights gained in this study may be of assistance in the sustainable implementation of CCU in energy-intensive manufacturing processes.

ASSOCIATED CONTENT

Supporting Information

General information: model description of carbon capture and utilization (CCU). Main and side electrochemical reactions. Mass and energy balances. Description of the distillation of MeOH model. List of hypotheses used in the mathematical model. Methodology used in the economic assessment.

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Author Contributions

Marta Rumayor, Antonio Dominguez-Ramos and Angel Irabien conceptualized this research work; Marta Rumayor carried out the investigation tasks and prepared the original draft. Antonio Dominguez-Ramos and Angel Irabien wrote, reviewed and edited the manuscript. Angel Irabien supervised the investigation and acquired the funding. All authors have given approval to the final version of the manuscript.

Funding Sources

This research has been supported by Spanish Ministry of Economy and Competitiveness (MINECO) through the project CTQ2016-76231-C2-1-R and the postdoctoral contract IJCI-2017-32621.

Notes

The authors declare no competing financial interest

ACKNOWLEDGMENT

Authors thank to Spanish Ministry of Economy and Competitiveness (MINECO) for the financial support through the project CTQ2016-76231-C2-1-R. We would like also to thank MINECO for providing Marta Rumayor with a Juan de la Cierva postdoctoral contract (IJCI-2017-32621).

ABBREVIATIONS

CCU, carbon capture and utilization; CO_2-MeOH, CO_2-based methanol; ER, electrochemical reduction; LCA, life cycle assessment; CF, carbon footprint; TEA, techno-economic assessment; electric-heat.

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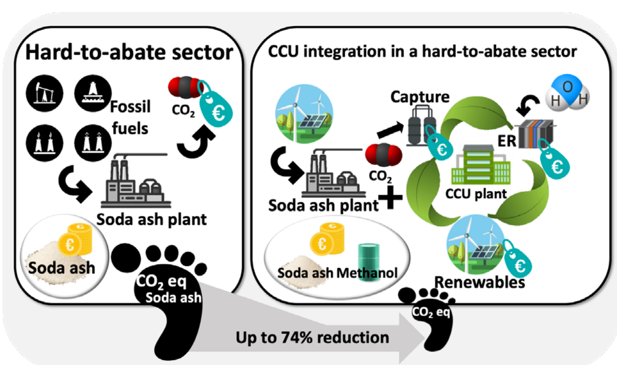

Synopsis:

The study demonstrated the possibilities of carbon footprint reduction of the synthetic soda ash at reasonable cost within medium/long-term developments.