Integrated Carbon Capture and Utilization in the Cement Industry: A Comparative Study

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ABSTRACT: This study analyzes a novel carbon capture and utilization pathway that has been proposed for the decarbonization of the cement sector and compares its performance in terms of carbon dioxide (CO_2) emissions to business as usual (BAU) and a carbon capture and storage (CCS) alternative. In the proposed integrated carbon capture and utilization (I-CCU) solution, methanol is produced with hydrogen from an electrolysis plant and with CO_2 captured at an oxyfuel cement plant; the oxygen delivered to the oxyfuel cement plant comes from the same electrolysis plant that provides hydrogen, which eliminates the need for an air separation unit (ASU). Due to the high energy demand for electrolysis, the carbon footprint of the solution depends on the carbon intensity of the power grid; any advantage from avoiding an ASU is overshadowed by the energy requirements of I-CCU. Consequently, BAU outperforms I-CCU in geographical regions with specific electricity emissions larger than 0.2 kg_{CO_2}/kW h, which corresponds to most of Europe. Furthermore, CCS is practically always a better alternative to I-CCU; only when there is renewable electricity available in abundance, I-CCU is better. Finally, it should be highlighted that using additional low-carbon electricity sources to drive I-CCU is not the most efficient use in terms of emission reductions per unit of low-carbon electricity. While the pursuit of (energy) integration and circularity should always be considered, our work emphasizes the necessity of conducting a comparative analysis, such as that presented here, to guarantee the achievement of the desired objectives.

KEYWORDS: CCU, cement, methanol, integration, electrolysis, hydrogen, oxygen
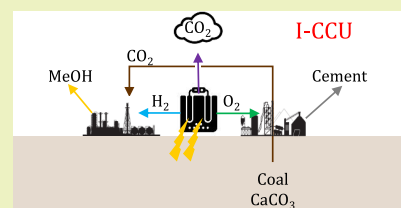
■ INTRODUCTION

Background. Cement is one of the key ingredients of concrete, along with water and sand, and it has a global annual production of around 4 Gt,[1] with further growth expected in the future.[2] Although cement comprises only around 10% of the total weight of concrete, it contributes to approximately 70% of the greenhouse gas emissions associated with concrete production.[3] Cement production has a typical carbon footprint between 600 and 900 kg of carbon dioxide (CO_2) per ton of cement[4−6] and is responsible for 7% of all global CO_2 emissions.[2] There are two main contributors for the CO_2 emissions during cement manufacturing, which are (i) the burning of fuel for heat generation (one-third) and (ii) calcination, i.e., the decomposition of $CaCO_3$ into CaO and CO_2 (around two-thirds). The emissions from calcining are referred to as hard-to-abate emissions as they are intrinsic to the chemistry of cement manufacturing. The industry has considered various strategies for reducing its carbon footprint by changing the cement recipe, improving energy efficiency, or using biofuels.[3,7] However, fully mitigating the emissions from cement manufacturing requires the implementation of CO_2 capture technologies,[3,8,9] coupled with permanent disposal of the captured CO_2 carbon capture and storage (CCS). Alternatively, captured CO_2 may be utilized as a feedstock, which may lead to partial mitigation of carbon capture and utilization (CCU). Several capture technologies have been developed for separating CO_2 with high purity from the cement-making process, of which oxyfuel combustion is a promising candidate according to the literature,[10,11] while it has also been advocated by the cement sector itself.[12] In this process, pure oxygen, separated from the air with an air separation unit (ASU), is used for combustion instead of air for clinker production, creating a process stream very high in CO_2 content; this drastically simplifies the capture of CO_2 in preparation for transport and storage, or utilization.

Several barriers to the implementation of CCS in the cement industry have been identified,[13] with the major one being its cost. The low profit margin on cement sales makes it extremely difficult for the industry to add technology elements such as CO_2 capture, which would increase its market price, thus hampering competitiveness. Nevertheless, it has been shown that the increase in cement costs stemming from the implementation of CCS may be absorbed along the value
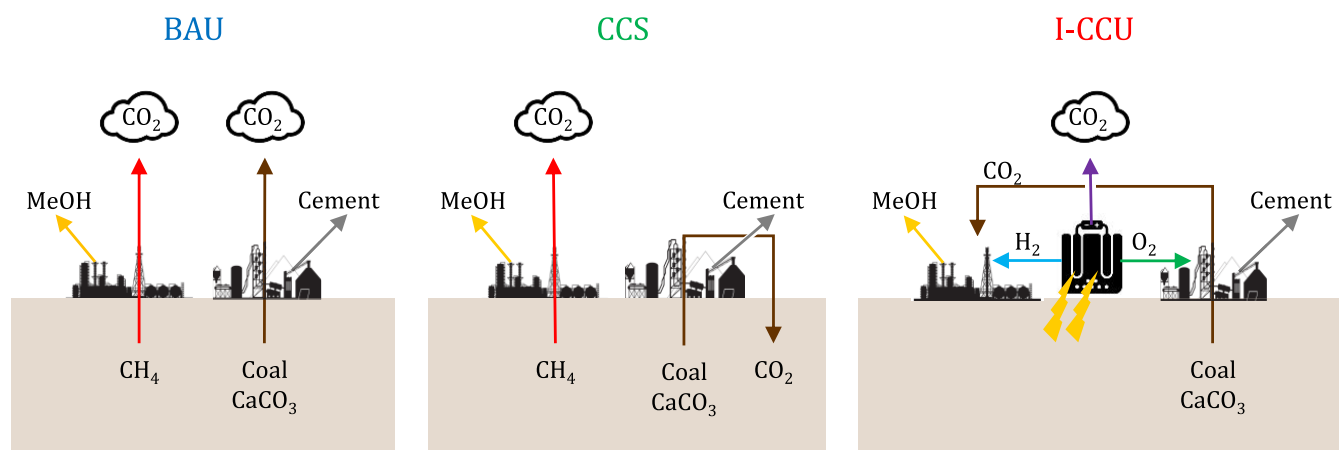
Figure 1. Illustration of the three concepts considered for the production of cement and methanol, from left to right: BAU, CCS, and I-CCU. Only the arrows ending in the clouds indicate emissions into the atmosphere.

chain leading to the final cement-based product, e.g., a major infrastructure like a bridge. A major fraction of CO_2 produced upon cement making can be captured and stored with an increase of the final price of ca. 1% only.[14,15] Furthermore, the competitiveness of companies offering low-carbon footprint products is expected to be enhanced through policy mechanisms such as the Carbon Adjustment Border Mechanism that the European Union is introducing,[16,17] aimed at offering a fair market for companies that wish to invest early in clean solutions.

A second large barrier to the full-scale deployment of CCS is the availability of the infrastructure necessary for CO_2 transport and storage. Although many technological aspects regarding transport and storage have a high technology readiness level, their deployment requires political will and public acceptance.[18] At the time of writing, the availability of CO_2 transport capacity and operational storage capacity is low (although developments are accelerating) compared to the CO_2 emissions generated by the cement industry,[19] hampering the investments for the deployment of CO_2 capture technology.

To cope with the barriers associated with the deployment of CCS, some advocate that captured CO_2 should be exploited as an asset, e.g., as a feedstock for the chemical sector, turning CO_2 into valuable chemicals via CCU technologies. The obvious objection that such transformation requires energy, in fact, a lot of clean energy (CO_2 to carbonates is the only exothermic pathway leading to valuable materials, for instance, for construction),[20,21] is commonly addressed by assuming the utilization of affordable surplus renewable energy.[22,23] Unfortunately, the availability of such cheap excess renewable energy is neither a reality at this time,[24] nor is this expected in the coming decades.[25]

In this admittedly challenging context for the cement sector, a new proposal has emerged, and it has found institutional support and financial means, namely, the taxpayer money distributed, for instance, by the European Commission through the Innovation Fund.[26] This approach consists of combining CO_2 captured via the oxyfuel technology with CCU, whereby CO_2 from the cement plant and hydrogen from an electrolyzer are combined to synthesize methanol, i.e., an important chemical commodity. Since oxyfuel requires pure oxygen, which is a side product of hydrogen synthesis via electrolysis, the goal is to realize a double circularity, where

CO_2 is recycled from the cement plant to the methanol synthesis and oxygen is recycled from the electrolyzer to the calciner of the cement plant. At first glance, this appears to be a promising solution that combines (1) energy integration, (2) sector coupling, and (3) circular economy. Although some work has been done in investigating similar integrated approaches in other contexts,[27−30] we are not aware of a simple analysis of the material and energy balances involved (in the spirit of other analyses[31−34]) nor of a rigorous life cycle analysis for this type of integration in the cement industry (similar to other works[20,35]). This work aims to fill this gap through a study of the first type of integrated CCU (I-CCU) pathway.

Investigated Pathways for the Cement Sector. Figure 1 illustrates the business as usual pathway and the two potential decarbonization pathways, which are defined as

1. Business as usual (BAU), relying on conventional production of clinker and on fossil-based methanol synthesis.
2. CCS, consisting of the production of fossil-based methanol (as in the BAU pathway) and of "decarbonized" cement, is achieved by capturing CO_2 via the oxyfuel process and then storing it permanently in the underground.
3. I-CCU, whereby methanol is produced with hydrogen from water electrolysis and with CO_2 captured at an oxyfuel cement plant; the oxygen delivered to the cement plant comes from the same electrolysis plant that supplies hydrogen.

For the sake of a valid comparison, unless specified otherwise, the three pathways are assessed based on the same functional unit: the emissions for the production of 1000 kg of clinker, m_{clk} [kg], and a related mass of methanol, m_{MeOH} [kg]. The latter, which is typically around 500 kg, is determined in the I-CCU pathway, as its process integration fixes the ratio m_{MeOH}/m_{clk} (see eqs 15 and 19 in Appendix A). The underlying assumption is that there is an existing, fixed market demand for both clinker and methanol, and producing them through the decarbonization pathways reduces production via the BAU pathway. Clinker is chosen for this purpose instead of cement, as different types of cement produced by using the same clinker may have different amounts of additives and thus vary in their carbon footprint. Furthermore, although the usage of biogenic fuels has an impact on the overall

emissions, the impact is similar for all pathways; hence, for the sake of simplicity without the loss of generality, the analysis of their use is out of scope here.

In the (Appendix A), the pathways are described in more detail in terms of process steps, relevant material flows, and electricity demands. The following section analyzes and discusses the main outcomes of the computations, provides a thermodynamic comparison between the strategies (extending the analysis beyond methanol as a product), and debates a special case that assumes dedicated investments in renewable electricity for I-CCU. Afterward, in the conclusions, a summary of the findings and general guidelines for decision-making are outlined.

COMPARATIVE ASSESSMENT OF THE BAU, CCS, AND I-CCU PATHWAYS

The three pathways are analyzed and assessed in the following sections; the outcome of the calculations presented in the Appendix A in detail is summarized in Table 1. First, the overall emissions generated by each pathway are broken down into process emissions, methanol utilization, electrolysis, and auxiliary emissions. They are analyzed for two carbon intensities of electricity, as well as considering a functional unit of 1 ton of clinker only. Then, the overall emissions for the three pathways as a function of the carbon intensity of electricity are analyzed while considering several fossil feedstocks in conventional MeOH production. After that, the main thermodynamic differences between the BAU and the I-CCU pathway are discussed, thus extending the analysis to other feedstock-product combinations for I-CCU. Finally, we analyze the implications of using new renewable electricity generation to power the I-CCU pathway or for reducing emissions by using this renewable electricity to drive e-mobility.

Breakdown of Overall Emissions. Figure 2 shows the breakdown of the overall emissions for the three pathways,

Table 1. Computed Material Amounts and Electricity Demands for the Three Considered Pathways and the Functional Unit of 1000 kg of Clinker Plus 522 kg of Methanol

$m_{fuel}^{clk} = 112$ kg	$m_{CO_2}^{CPU,loss} = 85$ kg	$P^{clk} = 132$ kW h
$m_{RM} = 1600$ kg	$m_{CO_2}^{CPU,out} = 765$ kg	$P^{conv} = 38$ kW h
$m_{O_2}^{clk} = 231$ kg	$m_{CO_2}^{TS} = 107$ kg	$P^{CPU} = 100$ kW h
$m_{O_2}^{clk} = 850$ kg	$m_{MeOH} = 522$ kg	$P^{ASU} = 30$ kW h
$m_{CO_2}^{conv} = 363$ kg	$m_{CO_2}^{novel,loss} = 46$ kg	$P^{elec} = 5217$ kW h
$m_{CO_2}^{util} = 719$ kg	$m_{H_2} = 88$ kg	$P^{novel} = 104$ kW h

split into process emissions, methanol utilization, electrolysis, and auxiliary-related emissions (defined as all emissions due to electricity consumption excluding electrolysis) for the following cases:

(a) For the European average carbon intensity of electricity, $e_{EL} = 0.375$ kg/kWh; this case represents the deployment of the pathways, for example, in Germany.

(b) For the French energy mix, $e_{EL} = 0.1$ kg/kWh; this case represents the deployment of the pathways in regions with a relatively low carbon intensity of electricity.

The figure shows that for the European average carbon intensity of electricity, I-CCU is inferior to BAU and CCS, as
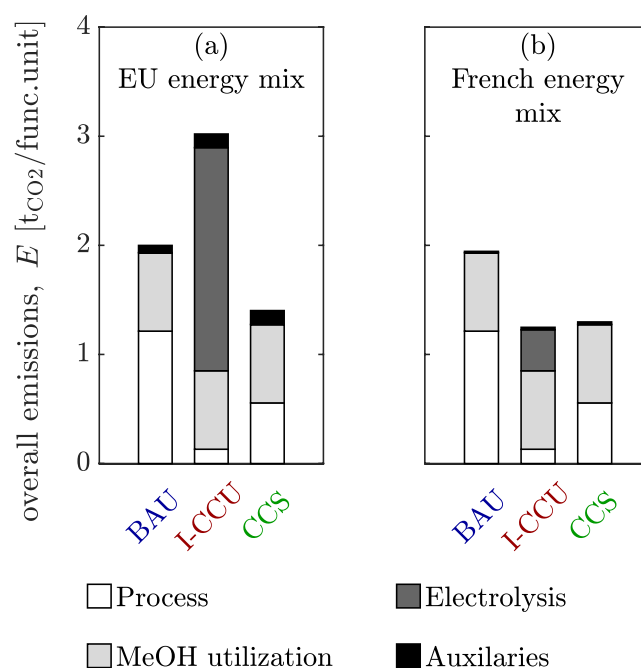

Figure 2. Breakdown of the CO_2 emissions for the three pathways for (a) deployment in Europe and (b) deployment in France, split into process, methanol utilization, electrolysis, and auxiliary-related emissions.

these pathways emit 36 and 55% less CO_2, respectively. For the French-specific electricity emissions, I-CCU is competitive with CCS, and both reduce emissions by almost 40% compared to BAU. The auxiliary emissions, which in the CCS pathway include the ASU, are very small relative to the emissions caused by electrolysis in the I-CCU pathway. This implies that the anticipated benefit of process integration, i.e., the elimination of the ASU for oxyfuel operations within the CCU pathway, is insignificant due to the major energy demand associated with electrolysis, even within a region with favorable conditions, such as France. When comparing the performance of the I-CCU pathways in cases (a) and (b), we note that electrolysis production has by far the largest impact for case I, with its contribution to the overall emissions decreasing from 68% to 30% for case II. This indicates a large sensitivity of the environmental performance of the I-CCU pathway, as will be further discussed in the next subsection. For case II, where I-CCU becomes competitive with CCS, the utilization of methanol contributes 37 and 58% to the overall emissions in the BAU and CCS pathways, respectively, while it is only slightly affected by the carbon intensity of the electricity.

Finally, it should be mentioned here that the excess of O_2, $m_{O_2}^{excess}$, is not part of the functional unit. However, including $m_{O_2}^{excess}$ would not change the outcome of the analysis, as the emissions associated with producing this amount of oxygen with an ASU (as would be the case for the BAU and CCS pathways when included in the functional unit) are insignificant.

Effect of Electricity Mix and of Feedstock in Conventional MeOH Production. A sensitivity analysis (see Appendix B) reveals that the parameters having the largest influence on the emissions of the three pathways are the specific emissions of the electricity mix, e_{EL}, and the direct emissions related to conventional methanol synthesis, c_{MeOH}^{conv}.

Figure 3 shows the overall CO_2 emissions, E, of the three pathways as a function of e_{EL}. The bands for the CCS and I-
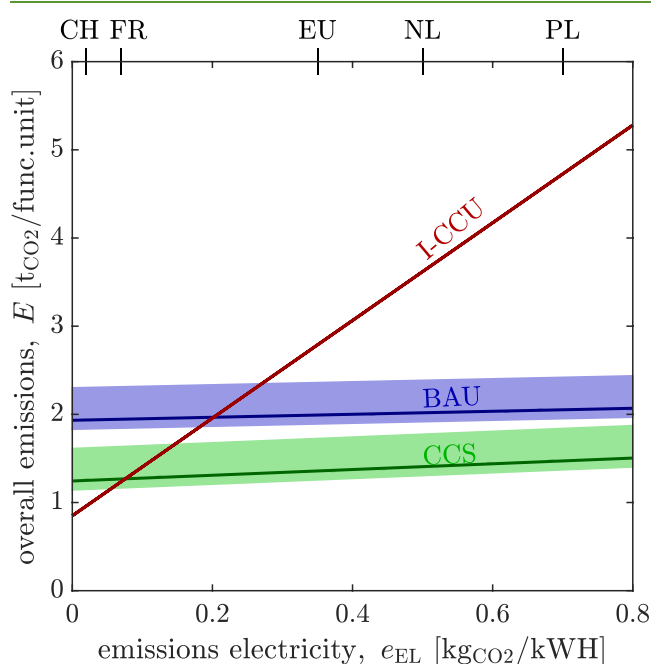

Figure 3. Overall CO_2 emissions of BAU, I-CCU, and CCS pathways as a function of e_{EL}.

CCU pathways relate to ranges of values for c_{MeOH}^{conv}, which represent the usage of different feedstocks for conventional methanol production; the lines refer to the use of a mixed feedstock based on natural gas (70%) and oil (30%), corresponding to European production. On the top horizontal axis, the specific emissions of the electricity mix for different countries and for the European mix are reported, for reference.

The I-CCU pathway is highly dependent on the specific electricity emissions (unlike BAU and CCS) and performs better than BAU in terms of overall emissions when $e_{EL} \lesssim 0.2$ kg_{CO_2}/kWh. For many European countries,[36] e.g., The Netherlands, Poland, or Germany, producing clinker and methanol via the I-CCU pathway would be worse than releasing the emissions of the clinker production to the atmosphere and producing and utilizing fossil methanol (i.e., the BAU pathway). This stems from the large amount of power required to generate the hydrogen for the I-CCU pathway, with its associated emissions (see Table 1, the comparison of the pathways from a thermodynamic perspective is elaborated further down below). The intersection point of the I-CCU and BAU pathways is defined by the condition that $E_{BAU} = E_{CCU}$, neglecting the impact of the auxiliaries, this may be written as (see eqs 14 and 23)

$$m_{CO_2}^{conv} + m_{CO_2}^{util} = e_{EL} P^{elec} \quad (1)$$

Therefore, the I-CCU and BAU pathways yield equivalent emissions when the emissions generated by electrolysis are equal to those generated by producing and using fossil methanol.

The CCS pathway can reduce the overall emissions compared to BAU by only around 40% because emissions from methanol utilization are not reduced with this approach. Nonetheless, CCS outperforms I-CCU in nearly all European

regions, unless the specific emissions of electricity are practically zero.

Thermodynamic Considerations. To further understand the nature of the differences in emissions among the considered pathways, it is worth inspecting the enthalpy changes due to the chemical conversions. Figure 4 illustrates
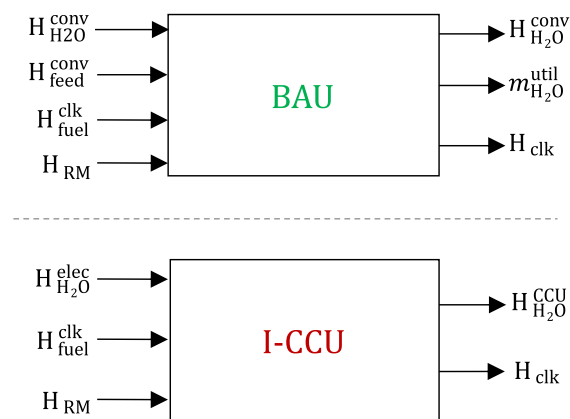

Figure 4. Material inflows and outflows involved in chemical conversions for (top), the BAU pathway and (bottom), the I-CCU pathway, only materials flows with $h \neq 0$ are drawn.

the BAU and I-CCU pathways as simple boxes with the material inflows and outflows involved in the chemical reactions. Only those with nonzero enthalpies of formation are drawn, i.e., O_2 and CO_2 are omitted. Furthermore, it is assumed that natural gas is used as a feedstock for conventional methanol production, and coal is used as a fuel for clinker production.

The first observation is that both pathways have commonalities, namely, the inflows m_{fuel}^{clk} and m_{RM}, and the outflows m_{clk} and $m_{H_2O}^{conv}$. It is convenient to group those related to the clinker production and to introduce a new variable, ΔH_{kiln}, for their enthalpy difference

$$\Delta H_{kiln} = m_{fuel}^{clk} h_{coal} + m_{RM} h_{RM} - m_{clk} h_{clk} \quad (2)$$

Here, h is the enthalpy of material flows at standard conditions in kJ/kg. Now for the enthalpy change for BAU, ΔH_{BAU}, we can write

$$\Delta H_{BAU} = \Delta H_{kiln} + m_{feed}^{conv} h_{NG} + m_{H_2O}^{conv,in} h_{H_2O}$$
$$- m_{H_2O}^{conv,out} h_{H_2O} - m_{H_2O}^{util} h_{H_2O} \quad (3)$$

For I-CCU, the water flow in and out of this system is the same; hence, their enthalpies cancel, thus

$$\Delta H_{CCU} = \Delta H_{kiln} \quad (4)$$

From this simple analysis, it becomes evident that the I-CCU pathway introduces less chemical energy into the system with respect to the BAU pathway; therefore, this lack of energy inputs must be compensated by another energy, more specifically, that provided by electrical energy. This amount, given by $\Delta H_{CCU} - \Delta H_{BAU}$, cor-

$$= m_{feed}^{conv} h_{NG} + m_{H_2O}^{conv,in} h_{H_2O} - m_{H_2O}^{conv,out} h_{H_2O}$$

responds in fact to the heat of combustion provided by the natural gas used as carbon feedstock in the BAU and CCS pathways.
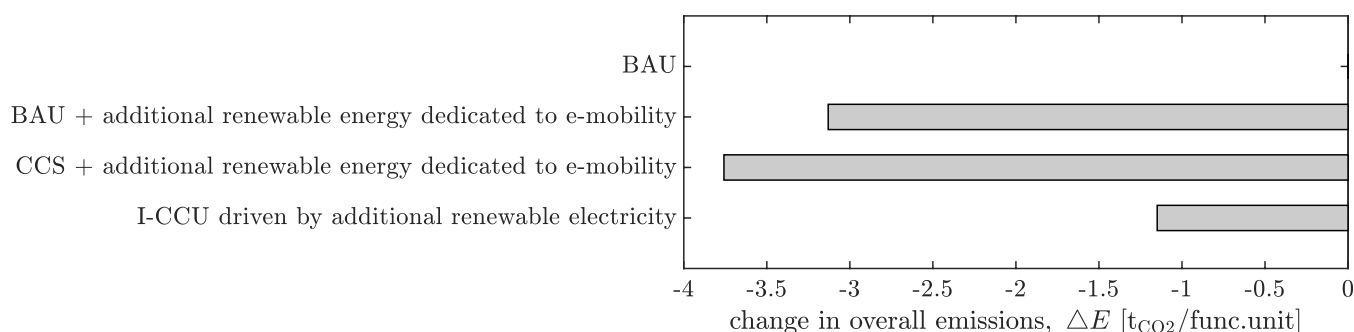
Figure 5. Change in emissions relative to BAU when additional power infrastructure is dedicated to e-mobility in the BAU or CCS pathway or used to drive the I-CCU pathway. Calculations are based on the European average methanol production and specific electricity emissions.

The outcome of the analyses in previous subsections is rooted in the energy balances presented here, which have natural gas and methanol as a feedstock/product combination. However, any fossil feedstock/product combination with similar enthalpy differences results in similar thermodynamics and consequently also in similar results. Hence, the analyses presented are relevant and representative for other fossil-based products, e.g., methane, ethanol, or jet fuels.[31,33,34]

Alternative Case: Renewable Power Infrastructure. This analysis has assumed so far that electricity is sourced from the existing power grid, entailing an associated carbon footprint. An alternative perspective involves establishing a supplementary renewable energy source to power electrolysis within the I-CCU pathway, thereby minimizing the overall emissions. Nonetheless, this investment could also be leveraged to concurrently reduce emissions by driving other processes or services in the BAU or CCS pathway. Recently,[20] it was established that using renewable energy for e-mobility, i.e., replacing gasoline or diesel in transport, reduces emissions by about 0.6 kg CO_2 per kW h of renewable energy. Hence, including this approach in the BAU and CCS pathways would result in the following emission savings

$$E_{savings} = 0.6 P^{elec} \tag{5}$$

Figure 5 shows the change in emissions relative to BAU when additional power infrastructure is built and used for powering e-mobility in the BAU and CCS pathways or for driving the I-CCU pathway.

The figure illustrates that the reductions in emissions from the allocation of renewable resources toward augmenting e-mobility are more than double the emission reductions achieved by employing these resources for the I-CCU pathway. Worth mentioning is that e-mobility is chosen as an illustrative example; other examples, like the replacement of natural gas boilers, driving heat pumps, or simply replacing coal-fired power plants, result in a similar view. Thus, the rationale for establishing supplementary power infrastructure to drive I-CCU only becomes justifiable under conditions of abundant renewable energy availability and exhausted more efficient applications (this conclusion is not novel, as established in previous research[20,34]). Whether more efficient applications for renewable energy are available is a regional consideration, depending on economic, geographic, and political circumstances. However, it can be said that in advanced economies, the development of e-mobility[37,38] (and also other electrification strategies[39,40]) has not been exhausted. Put in simpler terms, at this moment, in most geographical regions (although exceptions may exist), the allocation of resources toward

renewable energy for I-CCU should not be pursued to achieve emissions reduction but rather for other motivations, such as diminishing reliance on fossil fuels or realizing economic benefits.

◼ CONCLUSIONS

This work analyzed two pathways for the decarbonization of the cement sector, namely, a newly proposed I-CCU pathway and a CCS pathway; both pathways have been compared to the BAU scenario. In the proposed I-CCU pathway, methanol is produced with hydrogen from an electrolysis plant and with CO_2 captured at an oxyfuel cement plant; the oxygen delivered to the cement plant is produced by the same electrolysis plant that provides hydrogen. The main comparative analysis considering energy and emissions balances (performed based on a functional unit of 1 ton of clinker plus 522 kg of methanol) has led to the following conclusions.

- The main contributor for I-CCU is the electrical energy requirement for electrolysis, which makes this pathway sensitive to the carbon footprint of the electricity grid.
- I-CCU outperforms BAU only when the specific electricity emissions are below about 0.2 kg_{CO_2}/kWh; in most European regions, I-CCU performs worse than BAU.
- CCS is practically always a better alternative to I-CCU, only when the specific electricity emissions are nearly zero, I-CCU is a better alternative.
- The benefit of the process integration in the I-CCU pathway, i.e., the elimination of the ASU for oxyfuel operations, is insignificant relative to the substantial energy demand associated with electrolysis.
- The electricity requirements for I-CCU are much larger due to the lack of fossil energy brought into the system; a typical I-CCU system requires around 1 GW of electrical power, and it is not trivial that such an amount of electricity will be available without building new power generation infrastructure.
- Unless there is renewable energy in abundance and its utilization is exhausted, investing in renewable energy to drive e-mobility or other services is much more advantageous than investing in renewable energy to drive I-CCU.

In conclusion, our analysis highlights several crucial considerations for the implementation of decarbonization strategies in the cement sector.

While the pursuit of energy integration is essential, it is fundamental to distinguish the sources of energy and
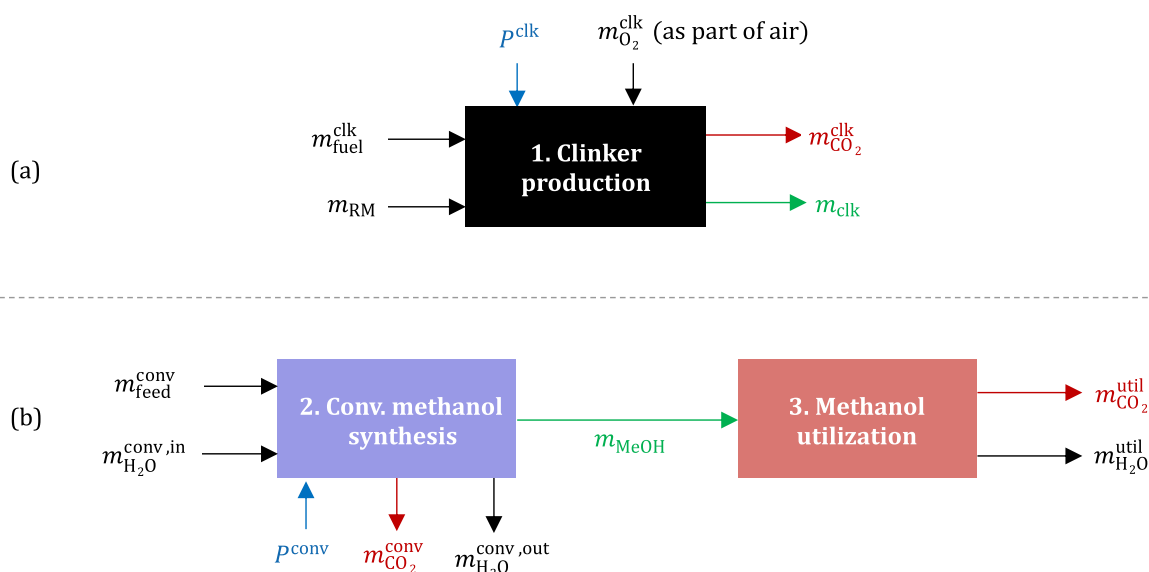
Figure 6. Material flow and electricity demand scheme of the BAU pathway with (a) conventional clinker production and (b) conventional methanol synthesis.

comprehend their environmental impacts. Specifically, the transition from conventional fossil feedstock to CO_2 for methanol synthesis requires a careful consideration. The energy previously contributed by fossil feedstock must now be provided through alternative means, such as electrolysis. Consequently, the assumed positive effects of integration and sector coupling in the I-CCU concept cannot be assumed and must be evaluated in comparison with alternative concepts on a case-by-case basis to justify their pursuit. Finally, amidst the enthusiasm surrounding the circular economy, it is essential to recognize that achieving circular material cycles alone is not sufficient. The circularity of energy cycles must also be considered to fully realize the objectives of a circular economy within a specific value chain. Our work emphasizes the necessity of conducting the type of analysis presented here to ensure a holistic evaluation of circular economy objectives.

■ APPENDIX A

Detailed Description of the Pathways

BAU. Figure 6 shows a high-level process scheme and the material and electricity requirements associated with the conventional productions of (a) clinker and (b) fossil-based methanol, which are described in detail in the following.

Conventional Clinker Production. As outlined in the introduction, the production of 1 ton of clinker requires certain amounts of raw meal, m_{RM} [kg], and fuel, $m_{F,clk}$ [kg], as established by the following equations

$$m_{RM} = c_{RM} m_{clk} \tag{6}$$

$$m_{fuel}^{clk} = D/l_{fuel} \tag{7}$$

where c_{RM} [kg_{RM}/kg_{clk}] is the mass of raw meal required per mass of clinker, whose value depends on the $CaCO_3$ content of the raw meal, which in turn depends on the materials' origin and process conditions. Here, we assume c_{RM} to have a constant value of 1.6, which corresponds to a $CaCO_3$ mass fraction in the raw meal, z_{CaCO_3}, of 0.78, i.e., typical for most cement plants. The parameter D represents the specific energy demand required for the clinker production, i.e., the energy required to drive the decomposition of $CaCO_3$ and the

formation of the cementitious phases. Besides the heat requirements dictated by the chemistry, the energy demand also depends on the plant efficiency and operational circumstances. Here, we assume a constant value of $D = 3.025$ GJ/t_{clk}, which is considered representative. Furthermore, l_{fuel} is the low-heating value of the fuel used, which is assumed to be coal, with $l_{fuel} = 27.15$ MJ/kg_{coal}.

The mass of oxygen required for combustion, $m_{O_2}^{clk}$ [kg], depends on the carbon, hydrogen, and oxygen content of the fuel and is given by

$$m_{O_2}^{clk} = m_{fuel}^{clk}\left(\frac{M_{O_2}}{M_C}x_C + \frac{M_{O_2}}{4M_H}x_H - x_O\right) \tag{8}$$

where x_i refers to the mass fraction of the specific element in the fuel and M_i is the molar masses. The total mass of CO_2 generated in the process, i.e., due to the combustion and $CaCO_3$ decomposition, is

$$m_{CO_2}^{clk} = \frac{M_{CO_2}}{M_C}x_C m_{fuel}^{clk} + \frac{M_{CO_2}}{M_{CaCO_3}}z_{CaCO_3}m_{RM} \tag{9}$$

The total electricity demand, P^k, for production step k is determined by the multiplication of a specific electricity demand, p_l^k, and a material mass, m_l

$$P^k = p_l^k m_l \tag{10}$$

Hence, the total electricity demand for driving auxiliary systems like pumps, motors, etc., in clinker manufacturing, P^{clk}, is specified through the specific parameter, p_{clk}^{clk} [kW h/kg_{clk}] and the mass of clinker, m_{clk}. In clinker manufacturing, the total electricity consumption is typically only a fraction ($\sim$15%) of the heat supplied by the fuel. This electricity demand is assumed to be satisfied via the existing power grid, which has associated specific emissions of electricity, e_{EL} [kg_{CO_2}/kWh]. The parameters and values assumed for the calculations related to the conventional clinker production are reported in Table 2.

Conventional Methanol Synthesis. The methanol production, m_{MeOH} [kg], is specified by the functional unit, which is

Table 2. Parameters and Values Used for the Calculations Relative to Conventional Clinker Production and Those for Conventional Methanol Synthesis[41a]

c_{RM}	$1.6\ kg_{RM}/kg_{clk}$
D	$3.025\ MJ/kg_{clk}$
l_{fuel}	$27.15\ MJ/kg_{coal}$
x_C	0.69
x_H	0.04
x_O	0.09
z_{CaCO_3}	0.78
p_{clk}^{clk}	$0.132\ kWh/kg_{clk}$
c_{MeOH}^{conv}	$0.695\ kg_{CO_2}/kg_{MeOH}$
p_{MeOH}^{conv}	$0.073\ kWh/kg_{MeOH}$

[a]The values for methanol synthesis correspond to a weighted average between using natural gas (70%) and oil (30%) as feedstock.[42,43]

determined through the I-CCU pathway (see Appendix A). The synthesis of conventional methanol uses a fossil feedstock, in Europe either natural gas (70%) or oil (30%), which is converted into syngas via steam reforming or partial oxidation, respectively, which requires water. The mass of fossil feedstock required, m_{feed}^{conv} [kg], depends on its nature, namely, three-fourths of m_{MeOH} in the case of natural gas, while approximately equal to m_{MeOH} for oil; the amount of water required, $m_{feed}^{H_2O}$, varies, but in general, more water is required for oil than for natural gas. In the next step, the syngas is transformed into methanol at high pressure and temperature over a catalyst. Overall, this is an endothermic process; hence, a small fraction of the carbon feedstock is burned and used for heat generation, causing direct CO_2 (and H_2O) emissions. Furthermore, the conversion of the reaction is not 100%,

which causes another small amount of direct CO_2 (and H_2O) emissions. The total direct CO_2 emissions of the conventional methanol production process, $m_{CO_2}^{conv}$ [kg], is determined through the specific parameter c_{MeOH}^{conv} [kg_{CO_2}/kg_{MeOH}]

$$m_{CO_2}^{conv} = c_{MeOH}^{conv} m_{MeOH} \tag{11}$$

The value of c_{MeOH}^{conv} depends on the carbon feedstock used and corresponds to 0.5 or 1.4 kg_{CO_2}/kg_{MeOH} for natural gas or oil, respectively. The total direct H_2O emissions of the conventional methanol production process, $m_{H2O}^{conv,out}$ [kg], varies significantly, and is not relevant for our analysis here. Conventional methanol production requires minor amounts of electricity, which is specified by the parameter p_{MeOH}^{conv} [kWh/kg_{MeOH}] using eq 10. Finally, upon methanol utilization, an additional amount of CO_2 and H_2O is generated, $m_{CO_2}^{util}$ and $m_{H_2O}^{util}$, which are disposed of in the atmosphere

$$m_{CO_2}^{util} = \frac{M_{CO_2}}{M_{MeOH}} m_{MeOH} \tag{12}$$

$$m_{H_2O}^{util} = \frac{2M_{H_2O}}{M_{MeOH}} m_{MeOH} \tag{13}$$

The corresponding values used in this analysis are reported in Table 2.

Overall Emissions of the BAU Pathway. The BAU pathway results in the production and utilization of given amounts of clinker and methanol, m_{clk} and m_{MeOH}, respectively, and causes a total amount of CO_2 emissions E_{BAU} given by

$$E_{BAU} = e_{EL}(P_{clk} + P_{conv}) + m_{CO_2}^{clk} + m_{CO_2}^{conv} + m_{CO_2}^{util} \tag{14}$$
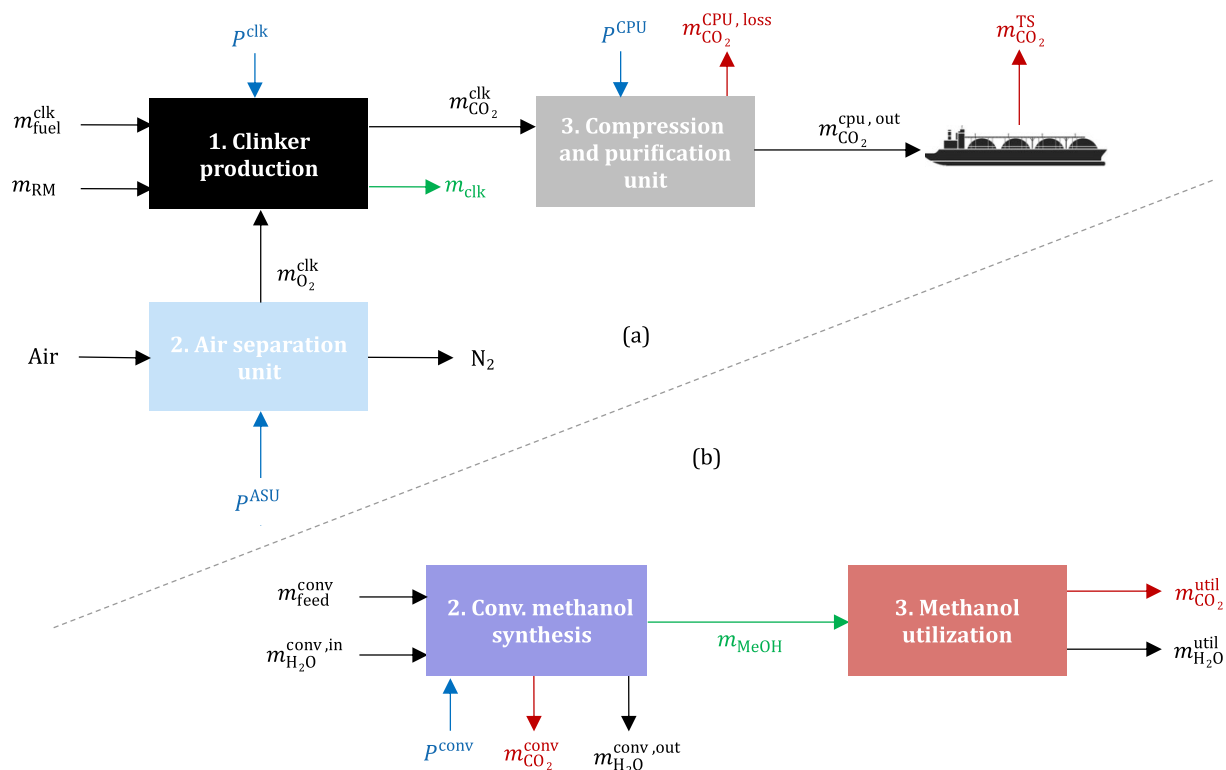

Figure 7. Material flow and electricity demand diagram of the CCS pathway with separate (a) oxyfuel clinker production and (b) conventional methanol production.
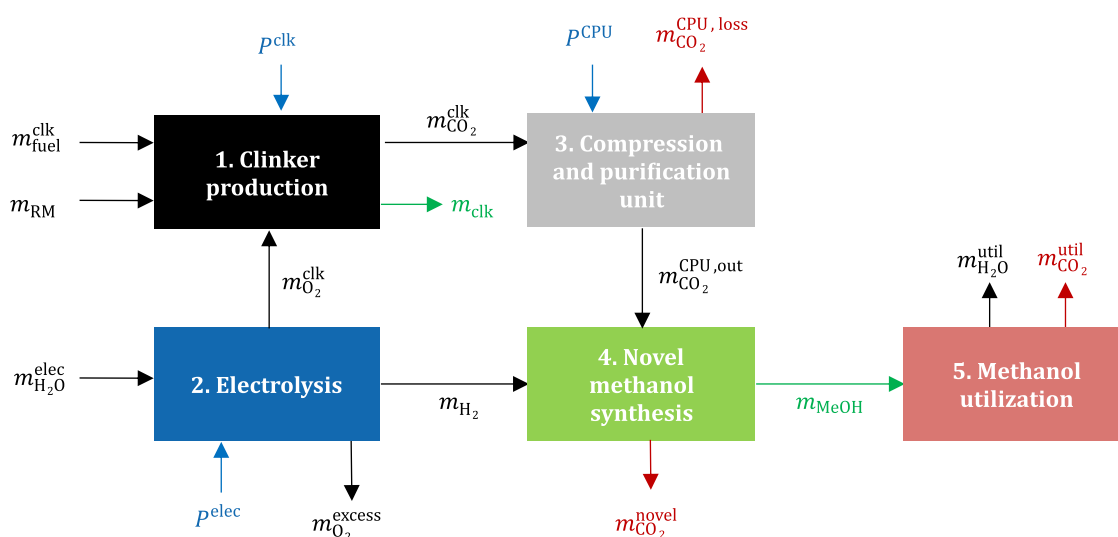
Figure 8. Material flow and electricity demand diagram of the CCU pathway, which integrates hydrogen, cement, and methanol production.

The emissions caused by clinker utilization are not considered, as those emissions are the same for all pathways studied, hence their consideration is unnecessary.

Carbon Capture and Storage. Figure 7 shows a high-level process scheme and the relevant material and electricity requirements for the CCS pathway, consisting of two uncoupled production processes: (a) oxyfuel-based clinker production and (b) conventional methanol synthesis. The latter is the same as for the BAU pathway.

As to process (a), the oxygen demand, m_{O_2}, the CO_2 generation $m_{CO_2}^{clk}$, and the electricity requirements, P^{clk}, of the clinker production process are assumed to be the same as those of the BAU pathway. Due to differences in the total gas flows throughout the oxyfuel plant compared to BAU, there are in principle minor differences in the power consumption,[11] which are neglected here for simplicity but without the loss of generality. Pure oxygen is delivered by an ASU, which separates oxygen from air using cryogenic distillation, whose power requirement is defined through the specific power requirement, $p_{O_2}^{ASU}$ [kWh/kg$_{O_2}$].

The compression and purification unit (CPU) required to separate CO_2 from the process stream has a separation efficiency of η_{CPU} [—], which defines the fraction captured and purified from what is generated in the clinker production

$$m_{CO_2}^{CPU,out} = \eta_{CPU} m_{CO_2}^{clk} \quad (15)$$

the fraction not captured is released to the atmosphere

$$m_{CO_2}^{CPU,loss} = (1 - \eta_{CPU}) m_{CO_2}^{clk} \quad (16)$$

The CPU requires electricity to operate, which is specified by the parameter $p_{CO_2}^{CPU}$ [kW h/kg$_{CO_2}$].

Finally, the captured CO_2 is transported and stored, with an associated specific emission penalty given by the constant $c_{CO_2}^{TS}$ [kg$_{CO_2}$/kg$_{CO_2}$], hence

$$m_{CO_2}^{TS} = c_{CO_2}^{TS} m_{CO_2}^{CPU,out} \quad (17)$$

In this work, a conservative value of 0.14 is used, which refers to the transport of CO_2 via trucks and barges over 2000

km.[44] In the future, when pipelines become operational, this value will drop drastically,[45] i.e., with orders of magnitude.

Finally, for the CCS pathway, the overall emissions, E_{CCS}, are

$$E_{CCS} = e_{EL}(P^{ASU} + P^{clk} + P^{CPU} + P^{conv}) + m_{CO_2}^{conv}$$
$$+ m_{CO_2}^{util} + m_{CO_2}^{TS} + m_{CO_2}^{CPU,loss} \quad (18)$$

The values used in the calculation for the CCS pathway are reported in Table 3.

Integrated Carbon Capture and Utilization. Figure 8 shows a high-level process scheme and the relevant material flows and electricity requirements for the I-CCU pathway, which integrates the production of hydrogen, clinker, and methanol. This pathway utilizes pure oxygen, obtained from the electrolysis of water, as the oxidizing agent for the

Table 3. Parameters and Values Used in the Calculations Related to the CCS Pathway[10,11,44]

$p_{O_2}^{ASU}$	0.240 kWh/kg$_{O_2}$
η^{CPU}	0.9
$p_{O_2}^{CPU}$	0.130 kWh/kg$_{CO_2}$
$c_{CO_2}^{TS}$	0.14 kg$_{CO_2}$/kg$_{CO_2}$

Table 4. Parameters Used in the Calculations for the CCU Pathway[42,46,47]

η^{novel}	0.94
p_{MeOH}^{novel}	0.136 kWh/kg$_{MeOH}$
$p_{H_2}^{elec}$	50 kWh/kg$_{H_2}$

combustion in the clinker production as in the CCS pathway. Electrolysis also produces hydrogen, which is combined with the CO_2 generated in the oxyfuel combustion to synthesize methanol.

It is assumed that the fuel, m_{fuel}^{clk}, raw meal, m_{RM}, and oxygen, $m_{O_2}^{clk}$, fed to the kiln, as well as the CO_2 generated in the kiln, $m_{CO_2}^{clk}$, are the same to those of the CCS and BAU pathways, i.e., given by eqs 6−10; similarly, the power requirement for
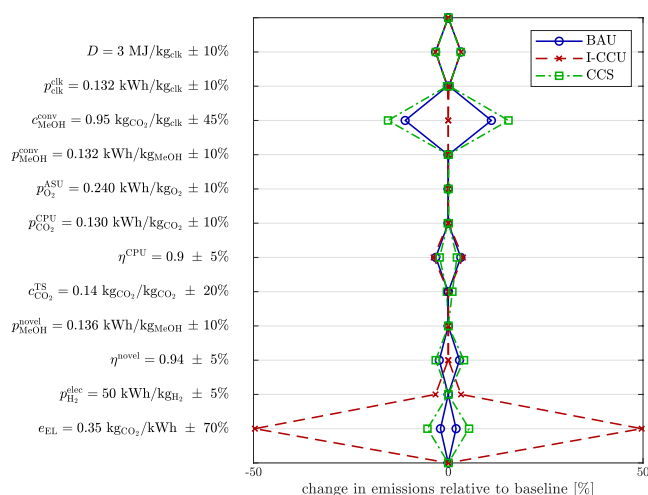
Figure 9. Sensitivity analysis of the emissions for the three pathways when varying the parameters in the calculations.

the clinker production, P_{clk}, is assumed to be the same to that of the previous pathways. The CPU operates in the same manner as in the CCS pathway, i.e., the CO_2 flows, $m_{CO_2}^{CPU,out}$ and $m_{CO_2}^{CPU,loss}$, and power consumption, P_{CPU}, are given by eq 15.

The novel methanol production process is characterized by η_{novel}, which represents the fraction of the CO_2 fed to the process that is converted into methanol. Therefore, the resulting carbon-based material outputs from the process, i.e., methanol, m_{MeOH}, and CO_2, $m_{CO_2}^{novel}$, are

$$m_{MeOH} = \frac{M_{MeOH}}{M_{CO_2}} \eta_{novel} m_{CO_2}^{CPU,out} \tag{19}$$

$$m_{CO_2}^{novel} = (1 - \eta_{novel}) m_{CO_2}^{CPU,out} \tag{20}$$

When the methanol is utilized, $m_{CO_2}^{util}$ and $m_{H_2O}^{util}$ are released into the atmosphere, see eq 12. The integrated CCU pathway produces two services, namely, clinker and a related amount of methanol, which is reflected in the functional unit of the main analysis. Equations 6–9, 15, and 19 define the amount of methanol that is part of the functional unit, which depends on $m_{CO_2}^{clk}$, η_{CPU}, and η_{novel}. Furthermore, the specific electricity required to drive the novel methanol process is given by p_{MeOH}^{novel} [kWh/kg$_{MeOH}$].

The hydrogen requirement, m_{H_2}, is defined through the reaction stoichiometry[42]

$$m_{H_2} = \frac{3M_{H_2}}{M_{CO_2}} m_{CO_2}^{CPU,out} \tag{21}$$

Consequently, the corresponding excess of oxygen, i.e., the amount not required in the kiln is

$$m_{O_2}^{excess} = \frac{M_{O_2}}{M_{H_2}} m_{H_2} - m_{O_2} \tag{22}$$

In the analysis presented, this excess oxygen is not part of the functional unit and is assumed to be disposed of in the atmosphere; this will be further elaborated in the breakdown analysis.

The power required to run the electrolysis is determined by $p_{H_2}^{elec} = 50$ kWh/kg$_{H_2}$; it is worth noting that this specific power requirement is orders of magnitude larger than the specific power requirements of the other steps (see Tables 2–4).

Finally, realizing that $m_{CO_2}^{CPU,loss} + m_{CO_2}^{novel,loss} + m_{CO_2}^{util} = m_{CO_2}^{clk}$, the overall emissions of this system, E_{CCU}, can be written as

$$E_{CCU} = e_{EL}(P^{clk} + P^{CPU} + P^{novel} + P^{elec}) + m_{CO_2}^{clk} \tag{23}$$

It is worth mentioning that in this system, the direct emissions from clinker manufacturing are not avoided but merely moved toward after the methanol production.

■ APPENDIX B

Sensitivity Analysis

Figure 9 shows the relative change in total emissions of the three pathways when changing one of the model parameters, compared to a baseline scenario; the parameters' baseline values and the applied variations to them are listed on the vertical axis. The baseline values and the magnitudes of the applied variations are based on what is typically observed throughout Europe.

The figure shows two outliers where the change in outcome is very large and is very different between the pathways, i,e., the process emissions in conventional methanol synthesis, c_{MeOH}^{conv}, and the specific emissions of electricity, e_{EL}. Therefore, the effects of these two parameters are analyzed and discussed in detail in the electricity mix analysis.

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Notes

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