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DOI
10.1016/j.apenergy.2017.10.123

Publication date
2018

Document Version
Final published version

Published in
Applied Energy

Citation (APA)
Schakel, W., Hung, C. R., Tokheim, L. A., Strømman, A. H., Worrell, E., & Ramirez Ramirez, C. A. (2018). Impact of fuel selection on the environmental performance of post-combustion calcium looping applied to a cement plant. *Applied Energy*, *210*, 75-87. https://doi.org/10.1016/j.apenergy.2017.10.123

Applied Energy 210 (2018) 75–87

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Impact of fuel selection on the environmental performance of post-combustion calcium looping applied to a cement plant

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HIGHLIGHTS

- The environmental performance of calcium looping applied to clinker production is studied.
- Replacing coal with natural gas or biomass improves the performance of calcium looping.
- Using biomass to drive calcium looping can lead to net negative life cycle CO_2 emissions.
- Using alternative fuels avoids environmental repercussions associated with coal production.

ARTICLE INFO

Keywords:
CO_2 capture
Cement plant
Calcium looping
Process modelling
LCA
Biomass

ABSTRACT

Calcium looping CO_2 capture is a promising technology to reduce CO_2 emissions from cement production. Coal has been seen as a logical choice of fuel to drive the calcium looping process as coal is already the primary fuel used to produce cement. This study assesses the impact of using different fuels, namely coal, natural gas, woody biomass and a fuel mix (50% coal, 25% biomass and 25% animal meal), on the environmental performance of tail-end calcium looping applied to the clinker production at a cement plant in North-western Europe. Process modelling was applied to determine the impact of the different fuels on the mass and energy balance of the process which were subsequently used to carry out a life cycle assessment to evaluate the environmental performance of the different systems. Using natural gas, biomass or a fuel mix instead of coal in a tail-end calcium looping process can improve the efficiency of the process, as it decreases fuel, limestone and electricity consumption. Consequently, while coal-fired calcium looping can reduce the global warming potential (life cycle CO_2 emissions) of clinker production by 75%, the use of natural gas further decreases these emissions (reduction of 86%) and biomass use could results in an almost carbon neutral (reduction of 95% in the fuel mix case) or net negative process (−104% reduction in the biomass case). Furthermore, replacing coal with natural gas or biomass reduces most other environmental impact categories as well, mostly due to avoided impacts from coal production. The level of improvement strongly depends on whether spent sorbent can be utilized in clinker production, and to what extent sequestered biogenic CO_2 can reduce global warming potential. Overall, the results illustrate the potential of using alternative fuels to improve the environmental performance of tail-end calcium looping in the cement industry.

1. Introduction

Carbon capture and storage (CCS) is an important technology to reduce greenhouse gas (GHG) emissions and mitigate climate change, and is considered essential in limiting the global temperature increase to 2 °C [1–4]. Although CCS is often associated with power plants, CCS is essential to achieve deep CO_2 emission reductions in industry as the effects of alternative climate change mitigation options e.g. energy efficiency improvement and the use of renewable fuels) are limited [5,6].

Global cement production accounts for about 1.4 Gt of CO_2 emissions per year [7], corresponding to roughly 5.8% of global anthropogenic emissions [8]. Established measures, such as improving energy

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http://dx.doi.org/10.1016/j.apenergy.2017.10.123
Received 24 July 2017; Received in revised form 27 September 2017; Accepted 29 October 2017

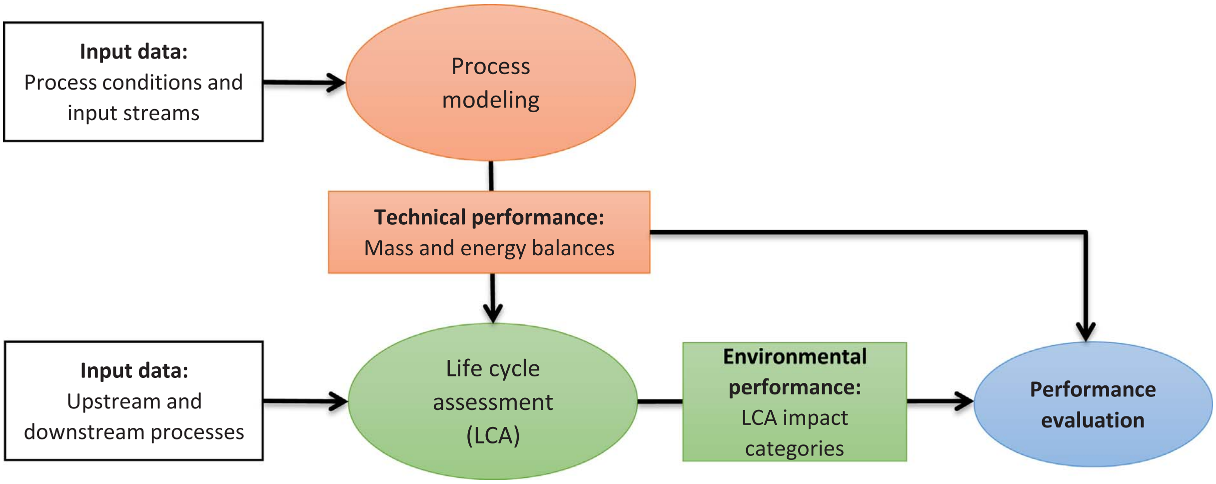

Fig. 1. Schematic overview of the general approach.

efficiency, using alternative raw materials and/or fuels, and reducing the clinker to cement ratio, are increasingly being used to lower CO_2 emissions from cement production [9]. However, these measures are expected to reduce the CO_2 emissions of cement production by only 20–25% by 2050 [10]. Deployment of CCS is thus necessary to achieve deeper emission reductions in the cement industry [11]. The main component of cement is clinker (usually over 90%), and clinker production is also the most energy- and CO_2 intensive process in cement manufacturing. Therefore, capturing the CO_2 emissions from clinker production is generally the point of focus when considering CCS in the cement industry.

Post-combustion CO_2 capture and oxy-fuel combustion are the preferred technologies for CO_2 capture in clinker production, as pre-combustion capture cannot capture the CO_2 from the calcination process [11]. Calcium looping is considered an especially favourable CO_2 capture technology for the cement industry, as cement plants already have experience with solids handling, have limestone handling infrastructure in place, and can potentially utilize the resulting spent solids in the cement production process [12–15]. Calcium looping CO_2 capture can be applied at the tail-end of the clinker production process post-combustion capture) or integrated with the calcination process. Integration of the calcium looping process with clinker production has been shown to be more efficient [16,17]. However, tail-end calcium looping can still be a valid retrofitting option for existing plants [18].

Traditionally, coal is used in the production of cement due to its high heating value, homogeneous composition, favourable radiative heat transfer characteristics, and relatively low costs. Although an increasing amount of cement plants has started to co-fire less carbon intensive fuels, such as waste streams and biomass to reduce CO_2 emissions, coal is still the most dominant fuel used in cement production [11]. Consequently, coal is generally selected as the fuel to also cover the heat demand of the calcium looping CO_2 capture processes. However, additional coal consumption can have significant repercussions for the environmental footprint of a cement plant as emissions associated with coal production and transport are reported to dominate the life cycle impact of calcium looping [19].

Other fuels than coal, e.g., natural gas or biomass, could also be used to deliver the heat demand of calcium looping. The performance of using natural gas for calcium looping has been studied for natural gas fired power plants [20,21] and natural gas fired industrial processes [22,23]. Besides, the feasibility to apply calcium looping to biomass fired power plants has been analysed [24]. To date, no publicly available literature addresses the environmental performance of other fuels driving the calcium looping CO_2 capture process at a cement plant. The required additional fuel input to drive tail-end calcium looping is in the same order of magnitude as the required fuel input for clinker production. Therefore, additional investments will be needed in clinker plants to increase fuel handling capacity, regardless of the type of fuel that is considered, and coal does not need to be selected as the fuel driving the calcium looping in the decision making process.

The possibility of using alternative fuels than coal for calcium looping can be interesting as environmental repercussions associated with coal production can be avoided. The goal of this study is to investigate whether, and if so by how much, using fuels with low carbon intensity might provide a low-hanging fruit to improve the environmental performance of calcium looping in cement plants.

Table 1
Kiln fuel mix of the clinker production process under study.

Fuel	Mass fraction (%)	Lower heating value (MJ/kg)	C content (%)
Coal	41.7%	27.2	72.9%
Refuse derived fuel	18.5%	10.3	43.1%
Solid hazardous waste, coarse	13.6%	14.7	35.9%
Solid hazardous waste, fine	1.1%	14.2	35.9%
Liquid hazardous waste	4.8%	14.2	43.7%
Waste carbon	10.6%	31.4	72.9%
Animal meal	4.5%	17.6	47.1%
Plastic	3.5%	27.2	58.7%
Waste oil	1.4%	39.8	86.5%
Fuel oil	0.3%	41.9	86.5%

Table 2
Cement plant flue gas characteristics.

Parameter	Unit	Average value	Wet/dry
Temperature	°C	165	–
Pressure	bar	1	–
Gas flow	Nm^3/h	330,000	Wet
Mole fraction O_2	%	7.5	Wet
Mole fraction H_2O	%	18.2	Wet
Mole fraction CO_2	%	17.8	Wet
Mole fraction N_2	%	56.5	Wet
Dust	mg/Nm^3	8.7	Dry
CO	mg/Nm^3	1470	Dry
NO_x	mg/Nm^3	250	Dry
SO_2	mg/Nm^3	25	Dry
HCl	mg/Nm^3	10	Dry

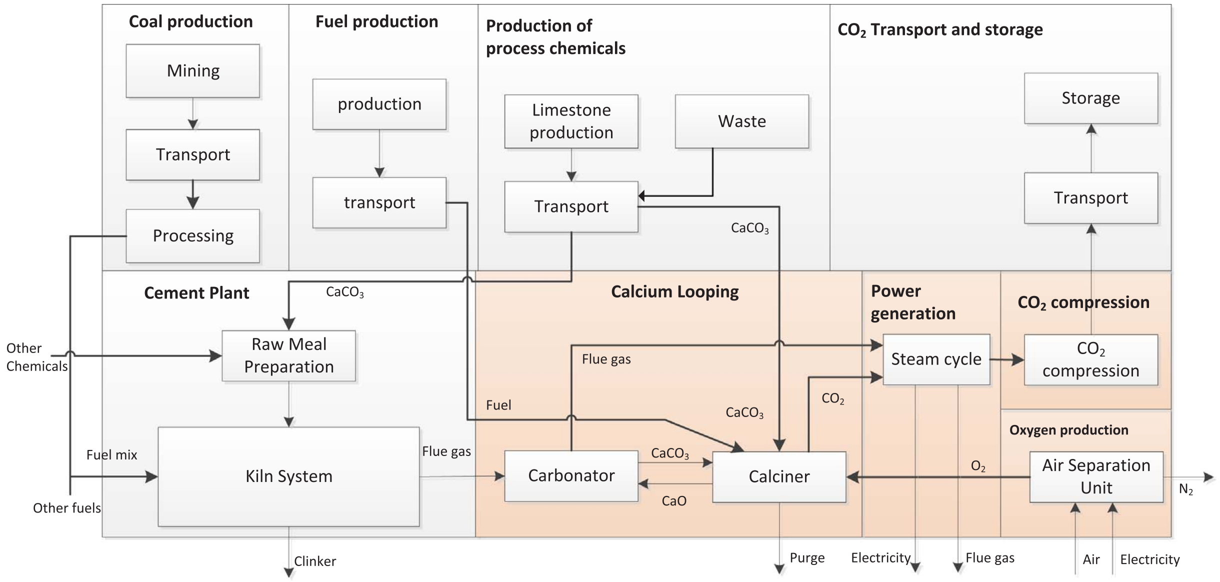

Fig. 2. Simplified flowsheet of the different systems assessed within the boundaries of this study. The coloured area represents the CO_2 capture processes which are included in the technical assessment.

2. Methodology

2.1. General approach

The environmental performance of tail-end calcium looping applied to a cement plant was studied by conducting a life cycle assessment (LCA). A technical assessment (see Section 2.3) was carried out by developing a preliminary process model for a tail-end calcium looping process for the different fuels under study. The mass and energy balance results from the process modelling together with input data of up- and downstream processes (e.g., fuel production and transport and CO_2 transport and storage) were the main basis to carry out the LCA to assess the environmental performance of the different cases (see Section 2.4), see Fig. 1.

2.2. System boundaries

The clinker production characteristics used in this study were based on a clinker production process at a real cement plant located in Northwestern Europe, producing 1 million tonnes of clinker. Due to data confidentiality, the clinker production characteristics are presented as a generic case. The clinker production process uses a mixture of ground limestone and additives (e.g. as quartzite, iron ore and bauxite), which is dried, ground and fed into a kiln to decarbonize the limestone in this mixture ($CaCO_3 \rightarrow CaO + CO_2$). The energy required for this endothermic process is provided by burning a fuel mixture containing coal and various types of (biogenic) waste. The fuel mixture used in the clinker production process is presented in Table 1. The major fuel input is coal, and more than half of the fuel input of the cement plant consists of waste, both of biogenic and non-biogenic origin. Biogenic waste fractions consist mainly of solid hazardous waste and animal meal. The solid hazardous waste is a mixture of wood chips purely biogenic), and hazardous materials such as glue, paint and solvent residues [25]. Non-biogenic waste includes waste carbon leftover stumps of anodes from the aluminium industry, plastic, refuse derived fuel RDF, liquid hazardous waste, and part of the solid hazardous waste fraction [25].

During clinker production, a total of 850,000 tonnes CO_2 are emitted per year. These emissions include CO_2 formed from calcination of the limestone, and CO_2 formed from fuel combustion. Key characteristics of the flue gas of the cement plant are presented in Table 2. Tail-end calcium looping CO_2 capture is applied to reduce CO_2 emissions from the clinker production by 85%.

Table 3
Fuel composition.

Component	Coal[a] mass %	Biomass (wood pellets)[b] mass %	Animal meal[c] mass %	Component	Natural gas[d] mass %
Water	1.2	3.5	4.4	CH_4	83.2
Ash	14.3	1.6	27.6	C_2H_6	3.7
C	71.7	47.0	40.9	C_3H_8	0.6
O	5.9	41.9	11.6	C_4H_{10}	0.2
H	3.9	5.6	6.0	C_5H_{12}	0.4
Cl	0.1	0.01	0.4	CO_2	1.0
N	1.7	0.4	0.4	N_2	10.9
S	1.2	0.04	0.5	S	0.0
LHV (MJ/kg)	25.6	18.6	15.3	LHV (MJ/kg)	46.5

[a] Based on the coal type used for clinker production [25].
[b] Based on the animal meal used for clinker production [25].
[c] Wood pellets produced from hard wood forest residues [47].
[d] Natural gas composition used by the European benchmarking task force [55].

Fig. 2 schematically presents the process diagram used in this study. The coloured area represents the CO_2 capture processes that are targeted in the technical process modelling. The flue gas from the clinker production is fed into a calcium looping consisting of a carbonator and a calciner. Fuel is burned in the calciner to produce the heat needed for decarbonizing the limestone via oxyfuel combustion, to generate a high-purity CO_2 stream. The required oxygen for this process is produced by an air separation unit. The captured CO_2 is compressed before transport and storage. The CaO reacts with the CO_2 in the flue gas in the carbonator, and the produced $CaCO_3$ is recycled back to the calciner. A small purge containing (spent) sorbents is extracted from the calciner to ensure continuous operation. The large amount of available waste heat is utilized for power production via a steam cycle. The design specifications and assumptions of the technical process modelling are presented in Section 2.3.

For the environmental assessment, upstream and downstream processes are included, such as the production of coal, fuel (for calcium looping) and chemicals, the clinker production itself, and the transport and storage of the captured CO_2. The key assumptions regarding these processes are described in Section 2.4.

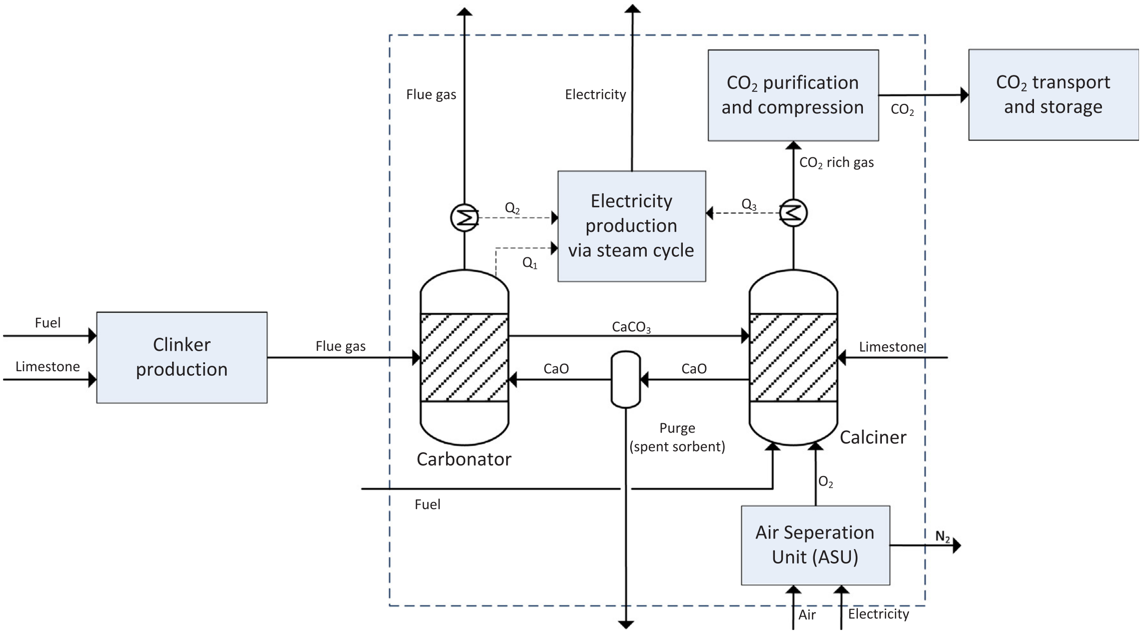

Fig. 3. Simplified process flow diagram of the calcium looping process. Details of the flows from the technical assessment are provided for each case in the supplementary information.

Different fuels are considered in this study to drive the calcium looping process. Coal is a straightforward option as it is also the most commonly used fuel in clinker production. Besides coal, natural gas, biomass (wood pellets) and a fuel mix comprising coal (50%), wood pellets (25%) and animal meal (25%) were selected as fuels to drive the calcium looping process. Natural gas was selected because this fuel has a significantly lower CO_2 emission factor than coal, and some cement kilns already use natural gas as their main fuel [26]. Biomass was included to investigate the potential of the combination of biomass and CCS (BioCCS), and the fuel mix case was included because this mix may be a more realistic alternative compared to 100% natural gas or biomass. The compositions of the fuels under study are presented in Table 3.

2.3. Technical assessment

2.3.1. Method selection

The purpose of the technical assessment was to generate the mass and energy balances required for carrying out the environmental assessment, and not to build a detailed process model taking into account all the complexities of the process. Therefore, a process model with low degree of resolution was considered sufficient for carrying out this study. As a result, the calcium looping process was not optimized or integrated with the cement plant providing a conservative scenario. Aspen Plus software [27] was used to carry out the technical modelling. The Peng-Robinson equation of state was selected as the thermodynamic model.

2.3.2. Process conditions

Fig. 3 presents a simplified flow diagram of the processes included in the technical modelling: an air separation unit, calcium looping, electricity production and CO_2 compression. The air separation was not modelled in Aspen Plus, but state of the art specifications obtained from literature were used, i.e., a specific energy demand of 180 kWh/t O_2 and an O_2 purity of 95% e.g. [28,29].

The calcium looping process includes a carbonator and a calciner. In the calciner, the fuel is burned with oxygen, and the limestone ($CaCO_3$) is calcined into CaO. The CaO is used to capture the CO_2 from the flue gas of the cement plant in the carbonator. The selected process conditions for the technical modelling are presented in Table 4. The calciner and carbonator were modelled using a Gibbs free energy reactor in Aspen Plus. The maximum conversion of limestone into CaO in the calciner was set at 100%, as the high operating temperature makes complete calcination feasible. The maximum conversion of CaO to $CaCO_3$ in the carbonator was set at 20%. This value is in line with values reported by experimental tests [12,30,31], although reported conversion rates of modelling studies are typically higher [16].

Table 4
Selected process conditions of the calcium looping process.

Parameter	Range in literature	Value in this study
Calciner operating temperature (°C)	800–930 °C[a,b,c,d]	900 °C[a]
Carbonator operating temperature (°C)	620–725 °C[a,b,c,d]	650 °C[a]
Carbonator capture efficiency[e]	90%[a,b]	85%
Carbonator sorbent conversion[f]	9–57%[a,b,d]	20%[g]
Purge ratio[h]	0.5–2%[i]	2.5% for coal and fuel mix case 1% for biomass and 0.5% for natural gas

[a] [18].
[b] [16].
[c] [12].
[d] [31].
[e] The percentage of CO_2 captured from the flue gas in the carbonator. Net amount of captured CO_2 is higher as this includes the CO_2 formed during fuel combustion.
[f] Maximum conversion of CaO into $CaCO_3$ in carbonator.
[g] This value is set for all cases as a conservative estimate within the range reported in literature[16,18,31].
[h] The amount of sorbent purged from the system per cycle.
[i] Reported ranges of coal based calcium looping processes [18].

The limestone sorbent activity degrades over time as repeated cycles cause sintering and thermal deactivation, and pollute the sorbent with e.g. ash and $CaSO_4$[1] [15,32,33]. The degradation caused by the formation of $CaSO_4$ (CaO sulphation) is considered to be a key aspect in the sorbent deactivation [34–36]. A periodic replacement is required to compensate the sorbent deactivation. This was modelled using a simple approach in which a purge extracting a small amount of the spent)

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[1] CaO easily reacts with sulphur components (sulphation) to form $CaSO_4$.

sorbent in every cycle is applied. Sorbent deactivation is especially present in the cases that use coal, due to the CaO sulphation resulting from the high sulphur content of the coal. Therefore, the purge ratio for the coal and fuel mix cases was set to 2.5%, which is a conservative estimate compared to values reported in similar modelling studies [18]. The need for purging in the natural gas and biomass cases can be decreased, as levels of sulphur and ash are much lower compared to the coal-fired cases. The purge ratio for the natural gas case was set to 0.5%. The use of biomass can lead to additional sorbent deactivation due to the reaction with alkali components of the biomass e.g. [37]. The levels of alkali components are, however, much lower than the levels of sulphur and ash. The additional sorbent deactivation is therefore considered to be minor compared to the sorbent deactivation caused by CaO sulphation. The purge level of the biomass case was assumed to be 1.0%, which is higher than the natural gas case but lower than the coal and fuel mix cases due to the substantially lower amounts of ash and sulphur content.

Because the calciner and carbonator operate at high temperatures, a substantial amount of waste heat is available from the carbonator (exothermic process) and the streams exiting the reactors (CO_2 and flue gas). This heat is utilized in a subcritical steam cycle for electricity production. The remaining (low temperature) waste heat is not utilized. The captured CO_2 is compressed to 110 bar to match conditions suitable for transport and storage. The compression train consists of five compressor steps to increase the pressure to 85 bar and a pump for the final compression step to 110 bar. Between every compression step, the CO_2 is cooled down and water is removed in knock-out vessels.

2.4. Environmental assessment

2.4.1. Life cycle assessment

A life cycle assessment (LCA) was performed for a reference case without CO_2 capture and for the four tail-end calcium looping CO_2 capture cases: coal, natural gas, biomass and mix. The life cycle inventory (LCI) included the outputs of the technical simulation and data from the e*coinvent 3.2* database [38]. The functional unit used in this study is the production of 1 kg clinker.

The full inventory, including input and emission factors and detailed assumptions, is provided in the supplementary information. This section contains a brief description of the LCI modelling of the system. The clinker production facility was assumed to have a 25 year lifetime and operation of 7000 hours per year. The fuel mix used in the clinker production (see Table 1) comprised coal, fuel oil and waste (both biogenic and non-biogenic). The coal and fuel oil were modelled using *ecoinvent* processes. The fuel fractions derived from waste products (i.e., RDF, hazardous waste, animal meal and plastic) are assumed to be "free" of upstream environmental impacts following existing LCA guidelines on waste use. Transport of these fuels to the cement plant, however, was included and estimated to be 10 km,[2] which is the average transport distance for municipal solid waste in *ecoinvent*. Animal meal was considered to be 100% biogenic while 50% of the solid hazardous waste fraction was assumed to comprise of wood chips. The upstream impacts of biomass residues (wood chips) include impacts from harvesting and collection processes.

The energy requirements for clinker production[3] were estimated from a technology description in IEA [39]. The raw meal was assumed to consist of limestone (84.9 wt%), quartzite (11.2 wt%), bauxite (1.3 wt%) and iron ore (2.6 wt%). Further raw meal additives were not modelled. In addition, ammonia was used in selective non-catalytic reduction of NOx emissions and lime slurry used in a gas suspension absorber technology applied for SOx control.

The results from the technical simulation used for the LCI comprise details of the mass and energy balance of the calcium looping process for the different cases. These outputs include fuel and limestone consumption, direct emissions, electricity balance including both production and consumption, cooling water consumption, and the amount of wastewater and purge of spent sorbent. The coal and natural gas fuels used in the calcium looping process were modelled using the Western European market mixes, as described in *ecoinvent*. The hardwood pellets were modelled using the *ecoinvent* process for wood pellets, modified to receive only hardwood chips as the biomass input. The animal meal used in the fuel mix case was modelled similar to the waste products used in the clinker production kiln fuel mix (considered "free" of upstream environmental impacts, only transport was accounted for). The fly ash produced during the calcium looping process was assumed to be recycled in cement production, and potential environmental impacts for fly ash treatment or utilization were not included. Produced electricity was consumed to replace grid electricity (see also Section 2.4.4). The *ecoinvent* medium voltage Dutch market electricity, (i.e., the Dutch consumption mix) was selected as proxy for North-western European electricity for the electricity consumption and production of the process. The compressed CO_2 (110 bar) is transported via pipeline and stored 95 km offshore in a 1000 m deep offshore well. Fugitive emissions during transport were assumed to be 0.6 wt% of the total gas transported.

Environmental impacts over eight impact categories[4] were evaluated using the ReCiPe 1.11 impact characterization method [40]. These impact categories were selected given their relevance to the system, and the quality of the characterization method [41,42].

2.4.2. Biogenic CO_2

In the majority of published carbon footprints and life cycle assessments that include biomass, the biomass is considered to be carbon neutral, and therefore the CO_2 emissions from biomass combustion do not contribute to climate change. However, it is increasingly recognized that this assumption may be incorrect due to the temporal mismatch between carbon uptake in biomass and its emission, as well as other climate-related effects arising from biomass harvesting [43–46]. The mismatch between carbon uptake and its emission, the so-called carbon debt, strongly depends on the type and amount of biomass harvested, and whether land-use change is accounted for [46]. Generally, the use of short-rotation biomass fast growing crops) is accompanied by a lower carbon debt than the use of long-rotation biomass forest biomass). For forest biomass, carbon payback times up to 200 years have been reported [43,46].

In this study, the wood pellets used in the biomass and fuel mix cases are considered to be produced from forest residues [47]. The relatively long rotation period of this biomass requires accounting for the carbon debt in the global warming potential (GWP) of the CO_2 that is formed by biomass combustion. Guest et al., [48] report GWP characterization factors of 0.44–0.61 kg CO_2 eq./kg CO_2 emitted for Norwegian long-rotation woody biomass assuming a 100 year time horizon, depending on whether changes in albedo are accounted for. In this study, the average global CO_2 GWP factor for biomass from forest residues of 0.49 kg CO_2 eq./kg CO_2 emitted was used, assuming a 100 year time horizon and 50% residue extraction [44]. For sequestered CO_2, the corresponding GWP factor used was −0.51 kg CO_2 eq./kg CO_2 sequestered.

For biomass with a rotation period of about one year, GWP characterization factors of 0 kg CO_2 eq./kg CO_2 emitted and −1 kg CO_2 eq./

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[2] Based on the average transport distance for municipal solid waste in the Netherlands in *ecoinvent* (2016).

[3] These include raw material grinding, homogenization, extraction and blending, conveying, packing and loading, and clinker production itself.

[4] Global warming potential (GWP), water depletion potential (WDP), fossil depletion potential (FDP), freshwater eutrophication potential (FEP), human toxicity potential (HTP), particulate matter formation (PMF), photochemical oxidant formation (POF), and terrestrial acidification potential (TAP).

kg CO_2 sequestered are reported when a 100 year time horizon is assumed [48]. Therefore, these values have been adopted for the CO_2 originating from the short-rotation biomass (i.e., animal meal) used for clinker. A sensitivity analysis on the GWP characterization factors was performed to assess the impact of the assumptions (see Section 3.3).

2.4.3. Purge of spent sorbent

The spent sorbent purge of the calcium looping system could potentially be utilized to replace limestone in the clinker production process [15]. The feasibility of using the spent sorbent in clinker production mainly depends on the composition of the purge, especially the sulphur ($CaSO_4$) content. The amount of sulphur that can be added to the clinker production is restricted, as high levels of sulphur compromise clinker quality. Therefore, the potential of utilizing a purge with high sulphur content is limited. In this study, the potential gains of using the purge to replace limestone in the cement production process were not included, thus providing a conservative estimate. Therefore, a sensitivity analysis is performed to investigate how potential utilization of the purge stream in clinker production can affect the results (Section 3.4).

2.4.4. Co-production of electricity

The waste heat of the calcium looping process was utilized for the production of electricity. As a result, electricity is added as a co-product of the cement plant. There are several approaches to deal with the multi-functionality of systems in LCA, namely, allocation by partitioning, "classic" system expansion, "alternate activity" substitution and "product" substitution [49].

In this study, the alternate activity substitution approach is adopted, where the complete amount of produced electricity in the calcium looping process was assumed to substitute electricity from the grid. The emissions and impacts associated with this electricity were assumed to be avoided and deducted from the total emissions and impacts in the calcium looping cases. By doing so, contributions from the different processes within the calcium looping process are clearly distinguished.

3. Results

A technical assessment and LCA was carried out to assess the environmental performance of tail-end calcium looping. The main objective of the technical assessment was to provide input to the life cycle assessment inventory for the environmental assessment. Nevertheless, the technical performance results also provide insights into the effect of fuel changes in the tail-end calcium looping process. Both the technical and environmental performance results are presented and discussed in this section.

Table 5 presents the main performance indicators of the tail-end calcium looping process modelling for the different cases. The circulating lime molar ratio Fr/FCO_2 (kmol CaO in circulating solids/kmol CO_2 in flue gas) is equal in all cases, as the maximum carbonator efficiency was kept constant for all cases. The fresh lime ratio $F0/FCO_2$ (kmol $CaCO_3$ in fresh limestone make up/kmol CO_2 in flue gas). Consequently the fresh limestone consumption is substantially reduced in the natural gas and biomass cases due to the lower purge ratio. The oxygen consumption is also reduced, especially in the biomass case, as the biomass selected in this study has a relatively high oxygen content compared to the other fuels (see Table 3). The reduction in oxygen consumption lowers the calciner duty, and consequently the fuel use (MJ/kg clinker) is reduced in the biomass case by 15% compared to coal. Fly ash is produced in the calciner in the coal case and in the fuel mix case due to the ash content of coal and animal meal. Replacing coal with the fuel mix does not substantially improve the calcium looping performance, first because the biomass used in the fuel mix (animal meal) has a lower heating value compared to the wood pellets used in the biomass case, and second because the purge ratio is equal to the coal case. However, the use of fuel mix instead of coal reduces the $CaSO_4$ content of the spent sorbent.

Table 5
Mass and energy balance of tail-end calcium looping process.

	Coal	Natural gas	Biomass	Fuel mix
Calcium looping performance				
$F0/FCO_2$[a]	0.11	0.02	0.04	0.11
Fr/FCO_2[b]	4.25	4.25	4.25	4.25
Fuel consumption (MJ/kg clinker)	5.82	5.69	4.95	5.60
Limestone consumption (kg/kg clinker)	0.22	0.04	0.09	0.22
Oxygen consumption (kg/kg clinker)	0.49	0.43	0.34	0.46
Fly ash production (g/kg clinker)	27	0	4	31
Purge (CaO and $CaSO_4$) (kg/kg clinker)	0.13	0.02	0.05	0.13
$CaSO_4$ ratio in purge	8.1%	0.0%	0.9%	5.6%
Ash ratio in purge	2.5%	0.0%	0.4%	3.0%
CO_2 balance				
CO_2 captured from flue gas (kg/kg clinker)	0.74	0.74	0.74	0.74
CO_2 captured from fuel combustion (kg/kg clinker)	0.59	0.32	0.45	0.55
CO_2 captured from limestone (kg/kg clinker)	0.10	0.02	0.04	0.10
Total CO_2 captured (kg/kg clinker)	1.43	1.07	1.23	1.38
CO_2 purity (mole based)	97.1%	97.0%	97.8%	96.7%
Nominal CO_2 capture ratio (by default)	85.0%	85.0%	85.0%	85.0%
Real CO_2 capture ratio	91.7%	89.2%	90.4%	91.4%
Electricity balance				
Gross electricity production (MW)	0.40	0.38	0.38	0.40
Electricity consumption Ca-looping (MW)	0.01	0.01	0.01	0.01
Electricity consumption CO_2 compression (MW)	0.15	0.11	0.13	0.15
Electricity consumption O_2 production (MW)	0.09	0.08	0.06	0.08
Net surplus electricity production (MW)	0.16	0.19	0.19	0.17

[a] Fresh limestone molar ratio (kmol $CaCO_3$ in limestone make up/kmol CO_2 in flue gas).

[b] Circulating lime molar ratio (kmol CaO in circulating solids/kmol CO_2 in flue gas).

The tail-end calcium looping process captures CO_2 from the flue gas from clinker production, but also co-captures all CO_2 formed in the calciner by fuel combustion and limestone calcination. As the CO_2 reduction target was set at 85%, the CO_2 captured from the flue gas is equal in all cases (0.74 kg/kg clinker). Note that the amount of co-captured CO_2 is substantial, almost approaching the amount of CO_2 from the flue gas of clinker production in the coal case (0.69 kg/kg clinker) and the fuel mix case (0.65 kg/kg clinker). In the natural gas and biomass cases, the reduced limestone consumption lowers the CO_2 formed by the limestone calcination, and less CO_2 is formed by fuel combustion due to reduced fuel consumption and lower carbon intensity of the fuels (compared to coal). As a result, the amount of co-captured CO_2 is substantially lower in the natural gas case and biomass cases, namely 0.34 kg/kg clinker and 0.49 kg/kg clinker, respectively. Overall, replacing coal with natural gas, biomass or the fuel mix decreases the total amount of CO_2 captured by 25%, 14% and 3%, respectively.

The electricity balance shows that less electricity is produced in the natural gas and biomass cases compared to the coal and fuel mix cases, as less waste heat is available in these cases due to reduced fuel consumption. On the other hand, less electricity is consumed by the calcium looping process, the compression of CO_2 and the production of O_2 in these cases. The electricity consumption of the calcium looping process includes the parasitic load of the process and is slightly lower in the natural gas and biomass cases, as lower volume of materials are circulated. The electricity consumption of the CO_2 compression process is directly related to the total amount of CO_2 captured in the different

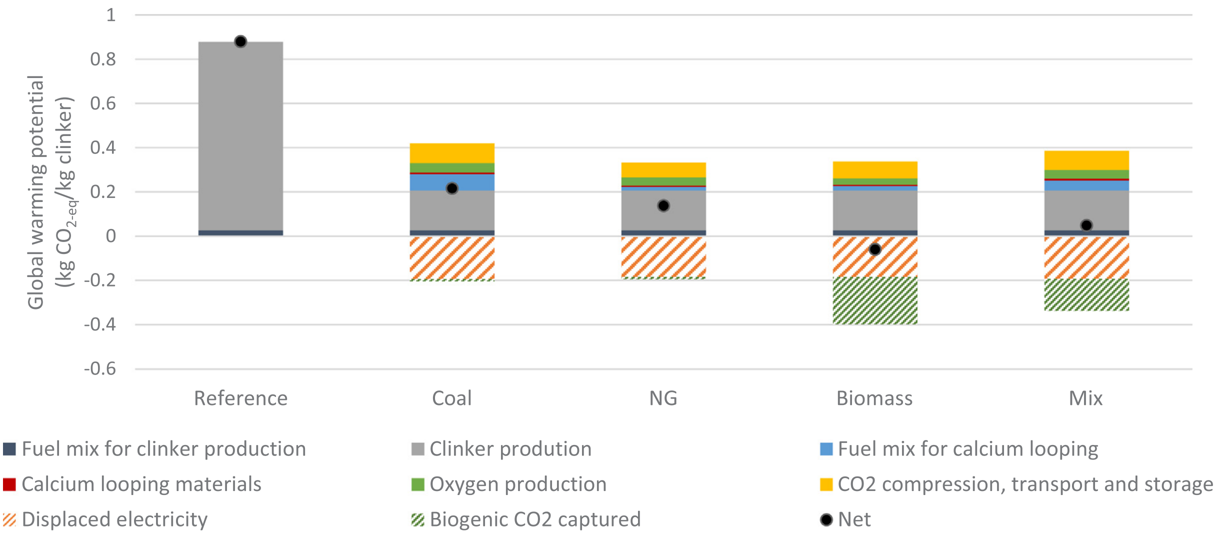

Fig. 4. Global warming potential results of the calcium looping cases compared to the reference case without CO_2 capture. The total net global warming potential values are represented by the black circles.

cases. As less CO_2 is captured in the cases where coal is replaced, the electricity consumption of CO_2 compression is reduced by 25%, 14% and 3% in the natural gas, biomass and fuel mix cases, respectively. The lower consumption of oxygen consequently decreases the electricity consumption of oxygen production by 13%, 32% and 8% in the natural gas, biomass and fuel mix cases, respectively, compared to the coal case. In total, the electricity production covers the electricity consumption in all cases and using natural gas, biomass or the fuel mix instead of coal increases the net electricity produced by 29%, 31% and 11%, respectively. The net amount of produced electricity is more than sufficient to cover the electricity consumption of clinker production 0.07 kWh/kg clinker [39] in all cases.

3.1. Global warming potential

Fig. 4 presents the GWP for the reference case and the different calcium looping cases. The addition of CO_2 capture reduces the net global warming potential by 76% and 84% for coal fired and natural gas fired calcium looping, respectively. The increased amount of biogenic CO_2 captured further reduces the total net GWP by 95% in the fuel mix case and leads to a negative total net GWP (reduction of 107%) in the biomass case.

The calcium looping process reduces the direct CO_2 emissions from clinker production by 85% in all cases, as 85% was the CO_2 capture target. A small part of the captured CO_2 originated from biogenic (waste) fuel components (wood chips and animal meal) of the clinker kiln fuel mix, and was therefore included in the biogenic CO_2 captured. The electricity produced from the waste heat of the calcium looping process was assumed to displace grid electricity, and the GWP associated with this product substitution is thus avoided and included as a negative contribution. The production and transport of the different fuels used for the calcium looping process, the combustion of additional fuel, impacts associated with the production of oxygen, and downstream emissions and processes during CO_2 compression, transport and storage contribute to global warming potential. The GHG emissions associated with these processes partly offset the global warming potential reduction from CO_2 capture and electricity substitution.

The replacement of coal with natural gas further reduces GWP mainly due to the avoided upstream emissions (CO_2 and methane) from coal mining. Besides, the reduction in electricity consumption of CO_2 compression and oxygen production also contributes to some extent to the lower GWP of natural gas fired looping compared with coal fired looping. In the biomass and mix cases, the stored CO_2 captured from the wood pellets and animal meal used to drive the calcium looping process was included in the biogenic CO_2 sequestered, and further reduces the GWP of these cases compared to the coal or natural gas cases. Although twice as much biomass was used in the biomass case (100% wood pellets) than in the fuel mix case (25% wood pellets, 25% animal meal), the GWP reduction from biogenic CO_2 captured is only slightly higher, because sequestered CO_2 from animal meal was assigned a GWP factor of −1.00 (animal meal was considered short-rotation biomass), compared to −0.51 for wood pellets. The impact of the GWP factor of sequestered biogenic CO_2 is discussed further in Section 3.3. In general, the increased amount of biogenic CO_2 captured and avoided upstream emissions from coal mining, and lower electricity consumption due to reduced oxygen consumption resulted in a lower GWP for the biomass case than for the fuel mix case (−0.06 kg $CO_{2\ eq.}$/kg clinker versus 0.05 kg $CO_{2\ eq.}$/kg clinker).

3.2. Other environmental impacts

Fig. 5 presents the results of the six other environmental performance indicators for the different calcium looping cases relative to the reference case. Results are divided into contributions from the production of fuel for the clinker production, the clinker production process, production of fuel for calcium looping process, the calcium looping process, production of oxygen, substitution of grid electricity and CO_2 compression, transport and storage. The total net impacts are represented by the black circles.

The main drivers for *water depletion potential (WDP)* in the value chain are the (cooling) water consumption of thermoelectric power plants and the water use during limestone mining. The avoided use of grid electricity due to the net electricity production in the calcium looping cases results in a net negative WDP in these cases. WDP is reduced by 108%, 145%, 119% and 116% in the coal, natural gas, biomass and fuel mix cases, respectively. The additional decrease in the natural gas case is mainly caused by reduced electricity consumption of CO_2 compression. Although more water is consumed during biomass production than during coal mining, the WDP is lower in the biomass and fuel mix cases than in the coal case, due to a reduction in water and electricity consumption for O_2 production, and lower CO_2 compression duty.

Fossil fuel depletion (FDP) measures the amount of fossil feedstock that is required over the total life cycle. The use of fossil fuel to (partly) drive the calcium looping process in the coal, natural gas and fuel mix cases, increases the FDP by 178%, 148% and 89%, respectively. These

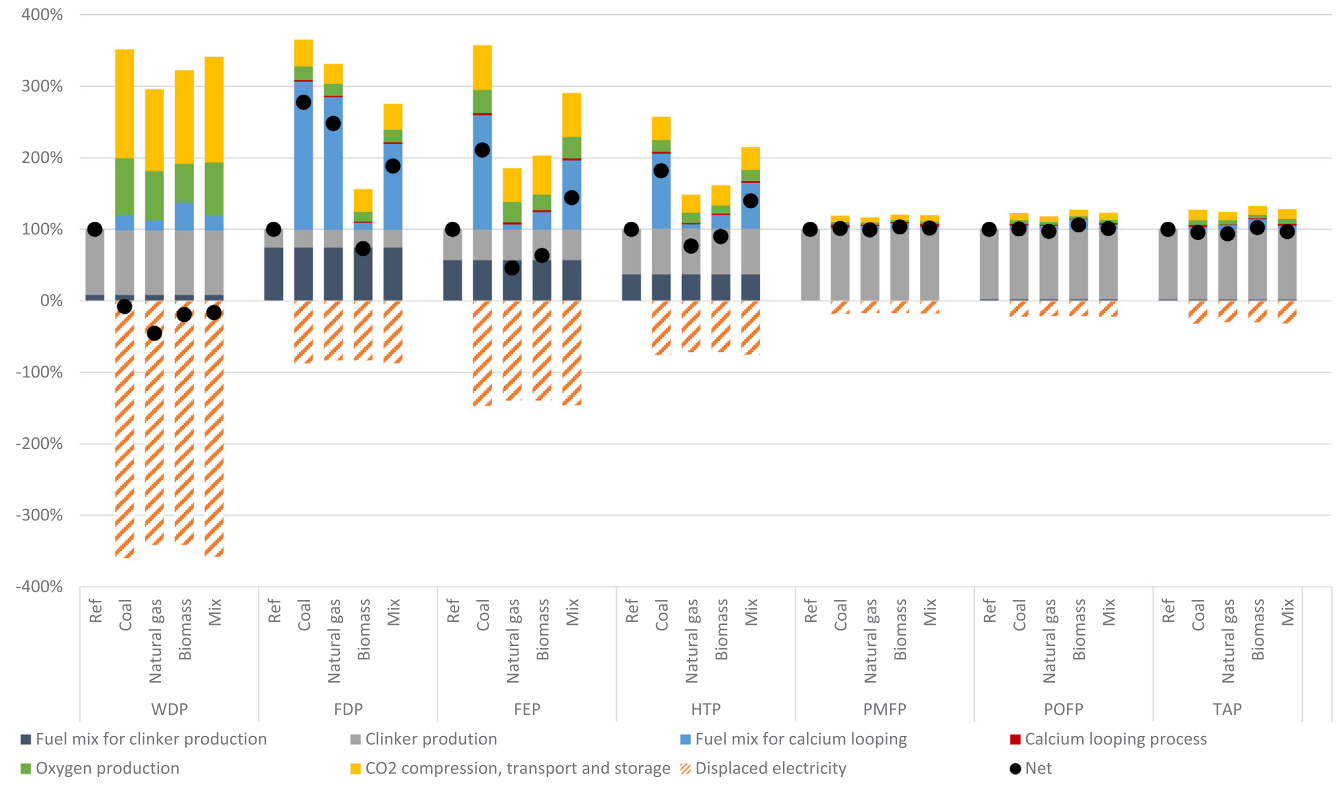

Fig. 5. Results of the calcium looping cases relative to the reference case without CO_2 capture for the other environmental impacts categories: water depletion potential (WDP), fossil depletion potential (FDP), freshwater eutrophication potential (FEP), human toxicity potential (HTP), particulate matter formation (PMF), photochemical oxidant formation (POF), and terrestrial acidification potential (TAP).

increases are solely caused by an increased use of fossil fuels, and are only partly compensated by the net production of electricity that displaces grid electricity. There is a lower increase in FDP when natural gas is used instead of coal, as a result of the lower calciner duty and carbon intensity of natural gas. In the fuel mix case, the FDP increase is approximately halved compared to the coal case as 50% of the coal is replaced by biomass (25% animal meal, 25% wood pellets). In the biomass case, the FDP caused by the use of fossil-based energy during biomass production and transport, oxygen production and CO_2 compression, transport and storage is more than compensated by the FDP of the displaced electricity. As a result, driving the calcium looping process with 100% biomass actually reduces the fossil fuel depletion by 27% compared to the reference case. The FDP reduction is essentially the result of using part of the biomass to generate electricity, which replaces electricity partially produced by fossil fuelled power plants.

The use of coal for tail-end calcium looping increases the *freshwater eutrophication potential (FEP)* in the coal and fuel mix case compared to the reference case by 111% and 44%, respectively. Eutrophication is mainly caused by sulfidic tailings from the mining and waste disposal of coal production. The total net production of electricity positively contributes to FEP due to the displacement of grid electricity. As no FEP is associated with the production of natural gas, the FEP in the natural case is reduced by 54% compared to the reference case. The production of wood pellets requires electricity, which is partially supplied from coal powered plants accompanied by sulfuric tailings. Nevertheless, due to the avoided coal use, the FEP of the biomass case is substantially lower than that of the coal and fuel mix case, and it is reduced by 37% compared to the reference case.

Human toxicity potential (HTP) is mainly caused by toxic emissions to air and toxic leakages to groundwater. The toxic leakages (e.g., arsenic, barium and selenium) and emissions during coal production lead to an increase in the HTP in the coal and fuel mix case of 82% and 40%, respectively. Negligible toxic emissions and leakages are associated with natural gas production, and the avoided emissions from displaced electricity results in a decrease on the HTP of natural gas fired calcium looping by 23% compared to the reference case. The toxic leakages to water during wood pellet production are considerably less severe than those of the coal value chain. As a result, the HTP for biomass is considerably lower compared to the coal and fuel mix case and even 10% lower than to the reference case, due to avoided toxic emissions associated with electricity production.

Particulate matter formation (PMF) is dominated by direct NOx and particulate matter emissions from clinker production. As the NOx emissions unaffected by the calcium looping capture process, changes in the PMF are only minor for all cases. A minor increase is noticed in the coal and fuel mix cases compared to the reference case, as a result of emissions of particulates from increased demand of limestone quarrying. As significantly less limestone is used in the natural gas and biomass case, the majority of particulate emissions are avoided in these cases. Therefore, the PMF of the natural gas case is on par with the reference case. In the biomass case, the PMF marginally increased by 3% compared to the reference case, mainly due to NOx emission from diesel during wood harvesting and pellet production.

Photochemical oxidant formation (POFP) and *terrestrial acidification potential (TAP)* are dominated by direct NOx and SOx (only for TAP) emissions of clinker production. The addition of tail-end calcium looping insignificantly affects the TAP in all cases. The NOx and SOx emissions during upstream processes (from e.g. diesel burning and electricity use) are compensated by the avoided emissions of grid electricity production.

3.3. Biogenic CO_2

A key aspect in the climate change reduction potential of BioCCS is the GWP characterization factor of sequestered biogenic CO_2. The assumption that biomass is carbon neutral and that sequestered biogenic

Table 6
GWP characterization factors for emitted and sequestered CO_2 from biogenic origin used in sensitivity analysis.

GWP characterization factor	Base case	Worst case scenario	Best case scenario
Emitted CO_2 from wood pellets (kg $CO_{2\ eq.}$/kg $CO_{2,bio}$)	0.49[a]	0.76[b]	0.02[c]
Sequestered CO_2 from wood pellets (kg $CO_{2\ eq.}$/kg $CO_{2,bio,sequestered}$)	−0.51[a]	−0.24[b]	−0.98[c]
Characterization factor emitted CO_2 from animal meal (kg $CO_{2\ eq.}$/kg $CO_{2,bio}$)	0.00[d]	0.16[e]	0.00[d]
Sequestered CO_2 from animal meal (kg $CO_{2\ eq.}$/kg $CO_{2,bio,sequestered}$)	−1.00[d]	−0.84[e]	−1.00[d]

[a] Based on the global average GWP factor for woody biomass assuming 50% residue extraction and a time horizon of 100 years [44].

[b] Based on woody biomass assuming a time horizon of 20 years [48].

[c] Based on woody biomass assuming a time horizon of 500 years [48].

[d] Assuming CO_2 neutrality of short-rotation biomass.

[e] Based on short-rotation biomass 6 years) assuming a time horizon of 20 years [48].

CO_2 "removes" an equal amount of CO_2 from the atmosphere has increasingly been debated, especially for long-rotation biomass [43–46]. The extent to which sequestered biogenic CO_2 actually removes CO_2 from the atmosphere depends on many factors, such as the type of biomass, rotation period, time horizon, land use change and albedo change.

The selected GWP characterization factors for the long-rotation woody biomass used in the biomass and fuel mix cases were based on global average values for a time horizon of 100 years [44]. However, wide ranges have been reported in literature for different types of biomass or time horizons. Therefore, a sensitivity analysis was performed in which these GWP characterization factors were varied (see Table 6). The worst case scenario assumed factors based on a 20 year time horizon, in which only a small part of biogenic CO_2 can contribute to climate change mitigation. In the best case scenario, biogenic CO_2 is considered almost climate neutral as a result of assuming a 500 year time horizon. For short-rotation biomass (animal meal) used in the clinker production, the climate neutrality assumption of the biomass in the base case already represented the best case scenario. In the worst case scenario, a rotation period (6 years) and 20 year time horizon were assumed.

Fig. 6 presents the GWP results of the base case, worst case and best case scenarios. The impact of changing the GWP characterization factors on the GWP of biogenic CO_2 emitted or sequestered from clinker production is negligible, due to the minor share of biogenic fuels in the kiln fuel mix. However, the different GWP factors for biogenic CO_2 significantly affect the biomass case (in which 100% long-rotation woody biomass is used) and, to a lesser extent the fuel mix case (in which 25% long-rotation woody biomass and 25% short-rotation animal meal is used). The higher factors in the worst case scenario avoid a total net negative GWP in the biomass case, though the total GWP of the biomass and fuel mix cases clearly remains below the coal and natural gas cases. In the best case scenario, the GWP reduction associated with biogenic CO_2 sequestered completely compensates the GWP contributions of all other processes. As a result, total net GWP is reduced to −0.25 kg $CO_{2\ eq.}$/kg clinker, a reduction of 129% compared to the base reference case.

3.4. Utilization of spent sorbent

In the environmental assessment, utilization of the spent sorbent (purge) of the calcium looping process in the clinker production was not considered providing a conservative estimate of the environmental impacts of tail-end calcium looping. However, the possibility to utilize the spent sorbent in clinker production is one of the arguments that supports the feasibility of tail-end calcium looping [15]. Therefore, the effect of utilizing the spent sorbent on the environmental performance is explored in this section.

The utilization of spent sorbent can lead to a decrease in limestone

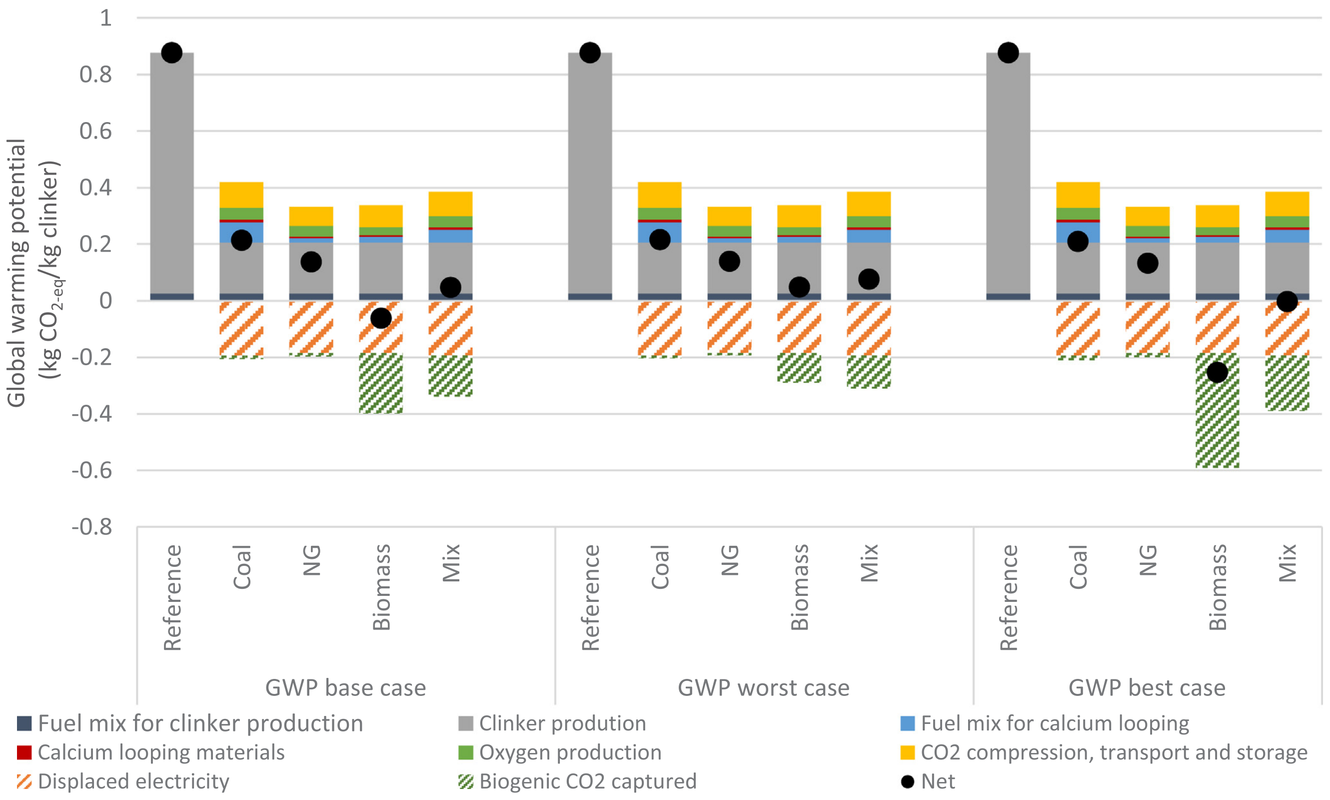

Fig. 6. Sensitivity of GWP characterization factors of biogenic CO_2 on GWP of the cases under study.

Table 7
Effects of utilization of spent sorbent in all the calcium looping cases on the mass and energy balance of clinker production.

	Coal case	NG case	Biomass case	Fuel mix case
Spent sorbent (kg/kg clinker)	0.13	0.02	0.05	0.13
CaO in spent sorbent (kg/kg clinker)	0.12	0.02	0.05	0.12
Limestone replacement (kg/kg clinker)[a]	0.22	0.04	0.08	0.22
Primary energy savings calcination process (MJ/kg clinker)[b]	0.37	0.07	0.14	0.37
Less CO_2 formed by calcination (kg/kg clinker)	0.09	0.02	0.04	0.09
Less CO_2 formed by fuel combustion (kg/kg clinker)[c]	0.02	0.00	0.01	0.02

[a] Assuming that one mole CaO in spent sorbent can replace one mole $CaCO_3$ in clinker production.

[b] Based on calcination reaction enthalpy of 1.7 MJ/kg $CaCO_3$

[c] Calculation based on the kiln fuel mix LHV of 21.8 MJ/kg and the CO_2 intensity factor of 1.40 kg CO_2/kg fuel.

and fuel consumption in the clinker production process. The CaO content of the spent sorbent reduces the consumption of limestone, and lowers the duty of the calcination process as less limestone needs to be calcined. Furthermore, CO_2 emissions from fuel combustion and limestone are also reduced. Finally, if the sensible heat of the spent sorbent (900 °C) can effectively be utilized, further energy savings could be possible.

A sensitivity analysis was performed on the life cycle GWP to assess the effect of utilizing the spent sorbent in all calcium looping cases. In this analysis, the spent sorbent was completely utilized in clinker production in all cases. The spent sorbent could be added to the raw mill department or directly to the kiln system. The latter option allows utilization of the sensible heat of the spent sorbent. However, feeding the spent sorbent directly into the kiln system is considered infeasible, firstly because the particle size of the spent sorbent is probably too large, secondly because homogenization of the raw meal is required, and thirdly because careful control of the raw material rates is needed to ensure the right chemical composition of the raw meal. Consequently, the spent sorbent was assumed to be added to the raw meal before milling, and the potential energy savings from the heat content were not taken into account.

Table 7 presents the effect of utilizing the spent sorbent on the mass and energy balance of the clinker production. The larger amount of spent sorbent in the coal and fuel mix cases, due to the higher purging, provides substantially more limestone replacement, energy savings and CO_2 formation reduction compared to the natural gas and biomass case. The utilization of spent sorbent in clinker production could lower CO_2 emissions and consequently the amount of CO_2 that needs to be captured in the tail-end calcium looping process. Ideally, an integrated model of clinker production and calcium looping would allow optimizing the size of both processes. However, as the focus of this study was on the tail-end calcium looping process, the clinker production unit was not modelled. The effects of utilizing the spent sorbent on the life cycle CO_2 emissions and other impacts are, therefore, not quantified.

Nevertheless, the changes in CO_2 emissions shown in Table 7 indicate that utilization of the spent sorbent could drastically improve the performance of the high purge cases (coal and fuel mix). The potential CO_2 emission reduction achieved when utilizing the complete amount of spent sorbent in these cases (ca. 0.11 kg/kg clinker) exceeds the GWP difference between these cases and the natural gas case (0.08 kg/kg clinker). Consequently, the possibility of utilizing the spent sorbent in clinker production might nullify the relative advantage of the natural gas case over the coal and the fuel mix cases. Yet, high levels of $CaSO_4$ in the spent sorbent can lead to an excessive amount of sulphur in the kiln system, causing operational problems [50] and compromising the quality of the produced clinker [51]. Therefore, the amount of spent sorbent that can be utilized in clinker production is limited, and utilization of the complete amount of spent sorbent in the coal and fuel mix cases might be infeasible.

3.5. Fly ash disposal

The fly ash that is produced during the calcium looping process was

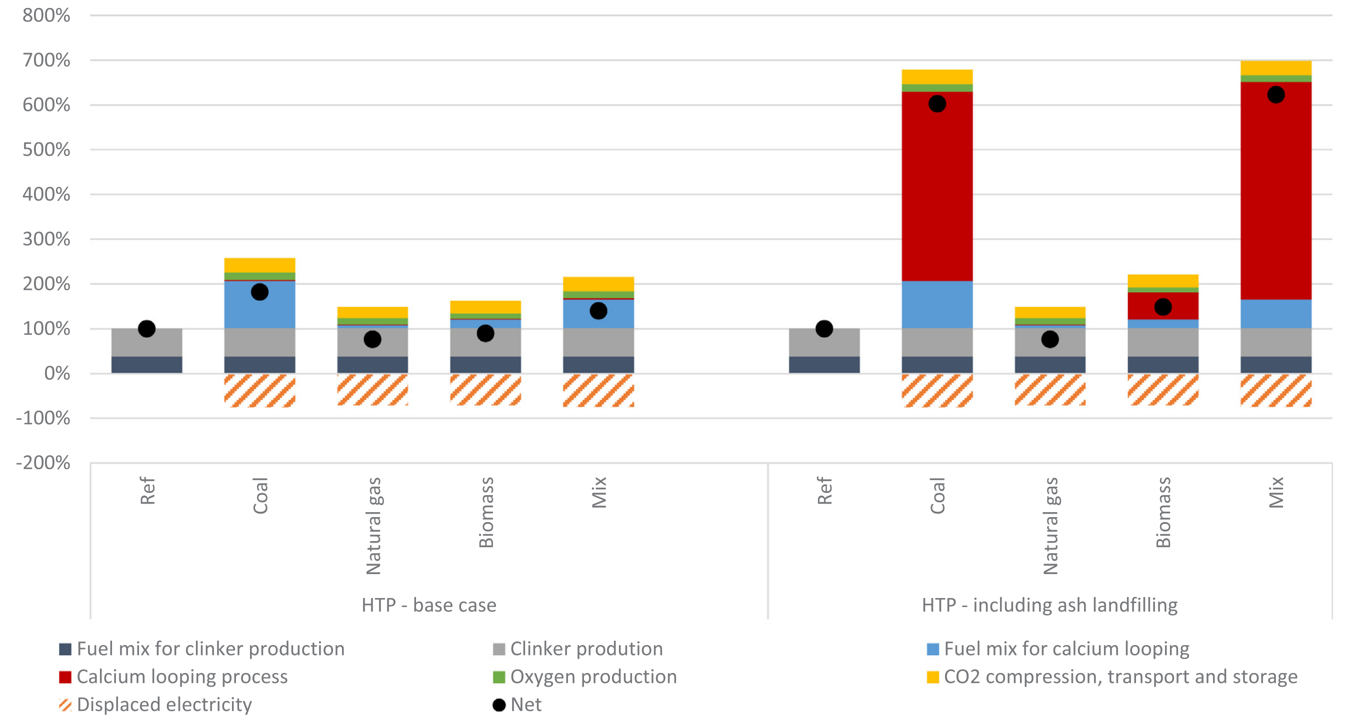

Fig. 7. Sensitivity of disposal of fly ash instead of utilization of the ash on the human toxicity potential (HTP) of the calcium looping cases.

assumed to be utilized in cement production. However, if utilization of the fly ash would not be possible, the ash might need to be disposed through landfilling. The fly ash landfilling, especially ash from coal, can result in severe toxicity impacts due to the leaching of heavy metals [52,53]. Fig. 7 shows the effect in the environmental assessment when the ash is landfilled instead of utilized. Evidently, the potential leakage of toxic materials to groundwater of the disposed ash massively increases the life cycle HTP of the calcium looping cases that produce fly ash. For the coal and fuel mix cases, total HTP rises by a factor of seven compared to the reference case, whereas the increase in the biomass case is less severe due to the lower ash content of the biomass. The natural gas case remains unaffected because no ash is produced when combusting natural gas. Although the need to dispose (all of) the produced fly ash is considered unrealistic, the sensitivity analysis shows that the utilization of fly ash is vital to minimize HTP impacts of tail-end calcium looping.

4. Discussion and conclusion

4.1. Technical assessment

The main objective of the technical assessment was to calculate the mass and energy balances required to conduct the life cycle assessment of the various calcium looping cases. A technical model with a relatively low degree of resolution was developed as this was considered sufficiently fit for purpose. Consequently, the calcium looping model did not include the full kinetics of the calciner and carbonator and simplifying assumptions were used for these two processes. To avoid overestimating the technical performance of the process, conservative estimates regarding the CaO conversion in the carbonator and purge ratio were applied. Besides, process optimization or heat integration with the clinker production process was not considered in this study. Potential integration advantages were therefore not taken into account, and the development of an optimized integrated model of the calcium looping process and clinker production process is recommended if a more detailed analysis on the technical performance of calcium looping is desired.

A key assumption in the technical modelling was the purge ratio. Purging of sorbent is applied to the calcium looping process to maintain low levels of impurities of mainly $CaSO_4$ and ash. The assumed purge ratio directly affects the technical performance of the calcium looping process, as lower purging decreases limestone consumption, fuel consumption and CO_2 formation (amount of CO_2 captured). For the cases in which the used fuel has a relatively high sulphur and/or ash content (the coal and fuel mix case), a considerably higher purge ratio (2.5%) was applied than for the natural gas case (0.5%) and biomass case (1.0%). The lower purge ratio of the natural gas and biomass cases substantially contributes to the observed technical performance advantages over the coal and fuel mix cases. The purge ratio for the coal and fuel mix case was set at 2.5% as a conservative estimate to keep $CaSO_4$ and ash levels low in the circulating sorbent. When a lower purge ratio ($< 2\%$) was used in the model, the concentration of inert substances accumulated, decreasing the capture efficiency of the process. For the natural gas and biomass case, such challenges were not observed due to the lower sulphur and ash content of these fuels. The effect of sorbent deactivation as a result of reactions with alkali components of the biomass was not accounted for in the model. However, the alkali content is much lower than the ash and sulphur content of biomass and the sorbent deactivation is expected to be minor compared to the sorbent deactivation caused by CaO sulphation. Nevertheless, the sorbent deactivation could be higher than considered in the biomass case studies, and the applied purge ratios might therefore underestimate the purge requirement in these cases. The technical performance of the case studies that use biomass could be negatively affected when sorbent deactivation as a result of alkali components is taken into account. As the purge ratio is identified as a key parameter in the model, a more elaborate approach would be recommended if the technical performance of the system needs to be analysed with a greater level of detail and accuracy.

The technical assessment showed that using natural gas or (co-)firing biomass instead of coal significantly improves the performance of tail-end calcium looping. The lower sulphur and ash content of biomass, and especially natural gas, increases the efficiency of the looping process. As a result, fuel and limestone consumption are reduced. The reduction in fuel consumption in combination with a lower carbon intensity of natural gas and biomass compared to coal, decreases the total amount of captured CO_2 while still avoiding 85% of the CO_2 emissions from clinker production. The corresponding electricity consumption of CO_2 compression is, therefore, also lowered and the total net electricity generation increases. The illustrated technical improvements provide incentive to further investigate the technical feasibility of using alternative fuels in tail-end calcium looping processes.

4.2. Environmental assessment

A life cycle assessment (LCA) was conducted to compare the environmental performance of tail-end calcium looping of the different fuels under study. The LCA results showed that he global warming potential (GWP) is substantially reduced by the calcium looping process compared to the reference process for all fuels. The use of natural gas or biomass instead of coal further reduces GWP, mainly driven by avoided upstream GHG emissions from coal mining and reduced electricity consumption for oxygen consumption and CO_2 compression. The sequestered biogenic CO_2 in the biomass and mix cases was assumed to be (partly) removed from the atmosphere, leading to an additional decrease in the total net GWP, namely almost zero total life cycle GHG emissions in the fuel mix case and slightly negative life cycle GHG emissions in the biomass case.

The extent to which the use of biomass lowers the GWP depends on how the sequestered biogenic CO_2 contributes to climate change reduction. Sequestering CO_2 from long-rotation biomass is considered to limitedly contribute to climate change reduction due to the temporal difference between CO_2 uptake in the biomass and emission or storage of that CO_2 carbon debt). Carbon debt strongly depends on the type of biomass and time horizon considered, and consensus on appropriate methodologies is limited [43]. The sensitivity analysis performed in Section 3.3 showed that the GWP characterization factors applied in this study can significantly affect the GWP of the cases that use biomass, especially long-rotation biomass, for the calcium looping process. Long-rotation biomass is used to drive the calcium looping process in the biomass case (100%) and in the fuel mix case (25%). When a pessimistic scenario is considered, the total GWP of the biomass case is positive, although still considerably lower than the coal and natural gas case. On the other hand, a best case scenario further reduces the GWP substantially. The effect of alternative GWP characterization factors for the short term biomass used in this study biogenic waste used in the clinker production and animal meal used (in the fuel mix case) is less substantial. The results of the sensitivity analysis align with reported conclusions that the carbon debt associated with the use of long-rotation biomass, such as forest residues, requires methodology improvements and improved consensus in scientific literature to support GWP calculations and policy decisions [43,46].

Replacing coal with natural gas or biomass to drive tail-end calcium looping reduces the freshwater eutrophication potential and human toxicity potential of the system, mainly due to avoided toxic emissions and sulfidic tailings from coal mining. The fossil fuel depletion is only slightly reduced when coal is replaced with natural gas, but substantially reduced when biomass is considered. The effect of replacing coal with natural gas or biomass on particulate matter formation, photochemical oxidant formation and terrestrial acidification is insignificant as these environmental impact categories are dominated by direct NOx and SOx emissions from the clinker production process.

Utilization of the spent sorbent of the calcium looping process in the clinker production was not considered in this study. However, when all of the spent sorbent purged from the calcium looping system is used in the clinker production process, limestone consumption, fuel consumption and the corresponding CO_2 emissions are considerably lower (see Section 3.4). As more spent sorbent is available in the coal and fuel mix case due to the higher purge ratio selected, potential gains when utilizing the spent sorbent are most prevalent in these cases. Using the spent sorbent could compensate part of the observed advantages of replacing coal with natural gas or biomass, especially for the GWP as direct CO_2 emissions are considerably lower.

The produced fly ash during the calcium looping process is considered to be used in cement production and potential environmental impacts are not accounted for. However, the performed sensitivity analysis in Section 3.5 showed the importance of this assumption with respect to the human toxicity potential HTP) results. When the fly ash cannot be used, and needs to be disposed of instead, the HTP of the ash producing cases coal and fuel mix) substantially increases, mainly due to toxic leakages that accompany ash landfilling. Although the utilization of fly ash in cement production is considered realistic and feasible e.g. [54], significant effects on HTP arise if utilization is not possible; accounting for these effects is important when evaluating the environmental performance of the tail-end calcium looping system.

4.3. Impact of fuel selection on calcium looping performance

The results of this study illustrated considerable advantages of using natural gas or biomass instead of coal to drive the tail-end calcium looping process. The use of natural gas or biomass improves the technical performance of the looping system, as lower sulphur and ash levels reduce the need to purge and as a result decrease the limestone and fuel consumption. The LCA results indicated that these improvements positively affect the environmental performance as well. Coal-fired calcium looping already substantially reduces GWP, but the GWP is further lowered when using natural gas or especially biomass, as the captured biogenic CO_2 accounts for additional removal of CO_2 from the atmosphere. The impact of other environmental categories, e.g., freshwater eutrophication potential and human toxicity potential, is also lowered when using natural gas or biomass instead of coal, mainly due to avoided emissions from coal production.

This study also explored the sensitivity of assumptions and model simplifications. To improve the reliability and robustness of the results, the following recommendations are proposed:

- Develop an integrated model of clinker production and calcium looping that would allow the investigation of potential heat integration and spent sorbent utilization options.
- Include kinetics when an integrated model is used for process optimization
- Develop a more comprehensive method that allows a consistent assessment of the climate change mitigation potential of sequestration of biogenic CO_2.

The goal of this study was to explore whether replacing coal with natural gas or biomass provides low-hanging fruit for improving the environmental performance of tail-end calcium looping. Even when taking uncertainties into account, the results of this study showed that replacing coal with natural gas or biomass to drive tail-end calcium looping can provide interesting benefits to the environmental performance of the system. It is therefore worthwhile and recommended to consider the use of alternative fuels when pursuing tail-end calcium looping deployment in the cement industry.

Acknowledgements

This research has been carried out as part the EDDiCCUT project (www.eddiccut.com). EDDiCCUT was a 4 year research project (2012–2016) aiming to assess the environmental performance of carbon capture and utilization technologies. The project was led by the Industrial Ecology Programme at Norwegian University of Science and Technology in collaboration with the Copernicus institute at Utrecht University and Tel-Tek in Porsgrunn. The project was supported by Gassnova and industrial partners (Bharat Petroleum, Norske Shell and Uniper).

We also like to thank Gabriel Orreggioni for his contributions during the early stage of the assessment conducted in this paper.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apenergy.2017.10.123.

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