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Effect of mitigation technologies on the total cost and carbon dioxide emissions of a cement plant under multi-objective mixed linear programming optimisation

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A B S T R A C T

With the increase of industrial activities in past decades, climate change has been a challenge worldwide. The cement industry is considered one of the industries that generate high carbon dioxide (CO_2) emissions. With an imminent increase in CO_2 emissions due to increased cement demand, this study proposed a systematic model for a cost-optimal cement plant that fulfils carbon limitations without compromising product specifications. This study considered three mitigation methods for cement manufacturing: co-processing, kiln system improvements, and carbon capture. The mixed integer linear programming model was executed in GAMS. From the optimisation model, it was found that a cement plant with co-processing, kiln improvements, and carbon capture managed to reduce more than 90 % CO_2 emissions with USD 135.96/tonne clinker.

1. Introduction

About 8 % of current global man-made carbon dioxide (CO_2) emissions is contributed by cement production (Olivier et al., 2015). According to an estimation by the US Geological Survey (2022), China, with an output of 2.5 Gtonnes of CO_2 in 2021, continues to be the biggest cement producer by far (56.82 %) and exceeded the second largest cement manufacturer, India, by about 7.58 times. In general, Asia produced the majority of cement globally even when considering the exclusion of cement production from China and India. Globally, 4.4 Gtonnes of cement were produced in 2021. With an estimated world population of 9.8 billion by 2050 (GCCA, 2021), cement production is forecasted to increase by 12–23 % by 2050 in reference to 2014 global cement production (IEA, 2018). The CO_2 emissions from cement production increased by 1.8 % annually between 2015 and 2020. Thus, to achieve net zero emission by 2050, a 3.3 % annual CO_2 reduction until 2030 is required (IEA, 2021a). With a new deal affirmed at COP26 in Glasgow, five participating nations (Canada, Germany, India, the United Arab Emirates, and the United Kingdom) pledged to achieve net zero in concrete and steel production by 2050 (Brownell, 2021).

The biggest CO_2 emission contributor during cement manufacturing is cement clinker production. During the

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Nomenclature

a	Alkalis.
c	Carbon capture and storage.
fg	Flue gases.
h	Heavy metals.
j	Raw materials.
k	Fossil fuels.
l	Nonfossil fuels.
o	Oxides.
p	Clinker phases.
r	Kiln improvements.
s	Sulphurs.

Parameters

A	Availability in kg/t clinker.
B	Bogue value.
C	Unit cost in USD/kg.
CEF	Carbon emission factor in kg CO_2/kg.
CO_{2Base}	Current CO_2 emission without mitigation method in kg CO_2/t clinker.
FCO_2	CO_2 reduction target in %.
FCI	Capital investment in USD/t clinker.
M	Big M constant.
MB	Amount of p^{th} clinker phases in clinker product in %.
$M_{clinker}$	Mass of clinker produced in kg.
MW	Molecular weight in kg/kmol.
N_c	Effects when oxyfuel capture is selected.
NCV	Net calorific value in GJ/kg.
OM	Operating and maintenance cost in USD/t clinker.
OM_l	Operating and maintenance cost in USD/kg of fuels.
ST	Stoichiometric for O_2 required for fuel combustion in kg O_2/kg.
TED	Thermal energy demand in GJ/t clinker.
TDI_r	Thermal energy improvement in GJ/t clinker.
TSR	Thermal substitution rate in %.
Ø	GHG impact when fuels are selected.
ϑ	Carbon capture and storage efficiency in %.
ω	Mass fraction in wt%.

Binary variables

x	Technology selections.

Continuous variables

m	Mass in kg/t clinker.
ϵ	ϵ-constraint in kg/t clinker.
v	Volumetric gas flow in Nm^3/t clinker under normal condition.
α, β, ψ	Linearisation variables for *mX* in kg/t clinker.
z_1	Economic objective function in USD/t clinker.
z_2	Environmental objective function in kg/t clinker.

production, fuels are combusted and raw materials are subjected to the calcination process (decomposition of calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$) to calcium oxide (CaO) and magnesium oxide (MgO)). Lower CO_2 emissions during cement manufacturing are from electrical usage and transportation. Carbon dioxide emission is expected to increase with the increasing demand for cement production. Environmental issues in the cement industry are caused by the manufacturing of an intermediate cement product called clinker. Reduction strategies are mainly aimed at reducing emissions per tonne of clinker rather than by a cement plant as a whole. During the production of clinker, the decomposition of raw materials and the combustion of fuels to provide heat in a cement kiln leads to high CO_2 emissions and can yield nitrogen oxides (NO_x), sulphur oxides (SO_x), heavy metals, volatile organic compounds (VOCs), and particulate matter (PM).

There is an urgent need to mitigate carbon emissions from industrial processes. It is especially important in the cement industry as the majority of carbon emissions in cement is not only contributed by fuel combustion but also from the main reaction process, hence making thermal improvement alone insufficient to combat emissions (Scrivener et al., 2018). The following section reviews some relevant studies on carbon mitigation measures that can be applied in cement plants. The mitigation measures reviewed are co-processing, cement kiln system improvements, and also carbon capture and storage technologies. The measures are reviewed to understand the general idea of how they work and to give an overview of some research that has been done on the measures. Then, the literature review of optimisation studies focusing on mitigating carbon emission in cement plants is presented. The gap between the optimisation studies and this study is also explained to highlight the novelty of this study.

1.1. *Mitigation measures*

Co-processing aims to replace the use of fossil fuels that emit a large amount of CO_2 by burning with less carbon-intensive alternative fuels. Approximately 40 % of carbon emissions can be reduced ideally if an almost zero carbon alternative fuel is to be used as a substitute for fossil fuel. Different countries have different substitution rates of alternative fuels for cement production. On average, 4.3 % of alternative fuel is used globally (Nidheesh and Kumar, 2019). Several studies have been performed to find suitable alternative fuels in cement plants. Schuhmacher et al. (2009) studied a mixture of petroleum coke and sewage sludge (80 %:20 %) as a fuel mixture for a cement plant operated in Spain and concluded that the amount of pollutants could be slightly reduced when less carbon intensive fuels (sewage sludge) were partially used. Georgiopoulou and Lyberatos (2018) evaluated the effect of alternative fuel usage in a dry cement kiln on the environment using the life cycle assessment method. They introduced seven different scenarios with different types of fuels (coal, petroleum coke, refuse-derived fuel (RDF), TDF, and biological sludge) to be used in the dry cement kiln, where they considered a 10 % substitution of fossil fuels by alternative fuels. The assessment concluded that the scenario with RDF is the most environmentally beneficial, while the least beneficial alternative fuel is biological sludge. Although almost 40% of carbon emissions can be abated ideally, full substitution might not be suitable as stated by Ishak and Hashim (2015). Thus, smaller CO_2 reduction is anticipated from co-processing.

Higher CO_2 reduction could be achieved by reducing fuel consumption. In order to reduce fuel consumption, the thermal energy demand of a cement kiln needs to be improved. Cement production requires high thermal energy due to the endothermic reaction of the main cement constituent, $CaCO_3$. The high temperature of 1600 °C needed for the burning stage also contributes to the higher energy demand (Ige et al., 2021). Wu et al. (2019) highlighted that heat is lost through the kiln shell in a cement kiln and suggested that kiln refractories/lining need to be improved to avoid or reduce heat loss. The efficiency of a lined cement kiln depends heavily on the selection of refractory materials. The use of alternative fuels in cement plants, however, has rigorously affected cement kiln refractories, according to Ren et al. (2018). Dominguez et al. (2010) suggested a dense material with components that can withstand corrosive matter as a refractory material to avoid penetration. The energy lost within a cement kiln can also be experienced through non-optimal process conditions or management. This situation can be prevented by improving process control. Fuel and raw feed can be improved by process control through physical and chemical properties analyses. Process conditions, such as air and mass flow rate, and temperature distribution within a cement kiln can also be controlled to optimise the kiln operation. For example, a model predictive control (MPC) system of a cement rotary kiln was proposed by Zanoli et al. (2015). The system showed improvements in energy efficiency, environmental impact, and product quality. Teja et al. (2016) proposed an MPC model for a six-stage preheater with three strings to achieve specified product quality, production target, and stable operating conditions, and simultaneously increase brick lifetime and lower fuel usage. These targets were achieved by maintaining the burning zone and calciner at the desired temperature, maintaining kiln feed, and maintaining the oxygen level required for fuel combustion. Another improvement that can be applied to improve thermal demand in a cement kiln is by upgrading the preheater/precalciner stage of a cement kiln. This upgrade increases the plant capacity and reduces fuel usage, and consequently, reduces emissions. This reduction is contributed by the lower combustion temperature required from the installed precalciner chamber (ECRA, 2017).

If higher CO_2 emission mitigation is desired, carbon capture and storage (CCS) will be able to substantially reduce the CO_2 produced in cement plants. Carbon capture and storage is a technology that captures CO_2 and then transports it to storage. Commonly discussed capture technologies suitable for cement plants are post combustion and oxyfuel combustion. Post combustion captures CO_2 from the exhaust gases at the end of the manufacturing line. Exiting flue gas goes through several treatment processes before CO_2 is captured to avoid solvent degradation. The treatment processes include denitrification, desulphurisation, dust removal, and cooling (Wu et al., 2020). When discussing post-combustion capture, it must be noted that chemical absorption has a technology readiness level of 9, indicating a high maturity level (Bui et al., 2018) and at this time, chemical absorption using monoethanolamine (MEA) is the only commercially used post-combustion technology (Coleman, 2018). In oxyfuel combustion, instead of combustion air being fed to a cement kiln, pure oxygen is used to make sure that the exhaust gas will be rich with CO_2 for the capture process. Gerbelová et al. (2017) compared the feasibility of retrofitting a post-combustion capture plant and an oxyfuel capture plant to an existing cement plant. The techno-economic study suggested that an oxyfuel capture plant to be retrofitted due to the plant's lower cost and high carbon removal.

Decarbonisation of cement manufacturing can be limited by challenges, such as cost, technology maturity, approval within the industry, and other unpredictable factors (Fransen et al., 2021). Table 1 summarises the discussed strategies as well as some other abatement strategies that can be applied to the cement industry, such as using alternative raw materials as opposed to limestone, alternative binders as opposed to the usual Portland cement, waste heat recovery, and substituting or upgrading older equipment to newer and more efficient technology.

1.2. *Research gap in optimisation studies*

Mathematical programming or optimisation for sustainable cement production or processes has been used by several researchers to study the potential of reducing emissions from industrial activities. Cao et al. (2016) developed a non-linear multi-objective proportioning optimisation model that correlates sensitivities of CO_2 emissions to clinker quality. Genetic algorithm optimisation was used by Zhang et al. (2019) to minimise the heat required to produce one kilogram of clinker with different product qualities. Although the studies reviewed discussed the potential of carbon mitigation, these studies did not consider the economic aspect of the studied mitigation strategies, which is one of the important factors in environmental decision-making.

Optimisation is also a powerful tool to study the selection of alternative technologies in an economical way (Gao and You, 2017). A supply chain study covering environmental and economic factors was conducted by Nurjanni et al. (2017). The supply chain study includes multi-objective optimisation of cement production, where minimal solutions for overall costs and carbon emissions are desired. This study, however, focused on the transportation of product alternatives instead of the manufacturing process itself. The optimisation studies in cement plants mostly discussed the possibility of implementing alternative fuels as one of the burning fuels (co-processing). Carpio et al. (2008) and Oyepata and Obodeh (2015) focused on achieving minimal clinker production costs by having product specification as the limiting factor. Dinga and Wen (2021) proposed a multi-objective non-linear model that considers alternative raw materials, fuels, and energy-efficient equipment as mitigation strategies. The models proposed by Carpio et al. (2008), Oyepata and Obodeh (2015), and Dinga and Wen (2021) are non-linear programming (NLP). However, according to Liu et al. (2014), NLP is generally harder to solve using standard commercial solvers compared to linear programming. Therefore, this study considers linear programming to avoid this problem. Klanšek (2015) suggested that linear programming is suitable for small- and medium-sized problems with enough input data.

Several mitigation methods have been discussed by Ba-Shammakh et al. (2008), Ogbeide (2010), and Adebiy et al. (2015) with the aim to minimise cement production costs while satisfying carbon constraints. Referring to the previous section, strategies considered by Ba-Shammakh et al. (2008), Ogbeide (2010), and Adebiy et al. (2015) can be categorised into co-processing, post-combustion capture installation, and installation of energy-efficient equipment, while Adebiy et al. (2015) only discussed the selection of energy-efficient technologies. Understanding the full potential of mitigation methods is essential to operate cement plants sustainably. In finding optimal production cost with sets of selected mitigation methods, these studies, however, did not consider how the selected

Table 1 – Summary of selected mitigation strategies.

Mitigation Strategies	Improvement	Cost	Practice[a]
Co-processing	Up to 40% CO_2 reduction depending on the fuel substitution rate[b]	Depending on the types of fuel[b]	Early adoption[b]
Kiln improvements	Up to 7% improvement[b]	Cost of retrofitting equipment[b]	N.A.
Kiln refractory improvement	About 19% energy savings[c,d]	0.25 USD/t clinker[c,d]	Early adoption
Process control improvement	About 6% energy savings[c,d]	1.70 USD/t clinker[c,d]	Early adoption
Increasing preheater stage	About 3% energy savings[c,d]	0.88 USD/t clinker[c,d]	Early adoption
CCS			
Post combustion	> 90% CO_2 captured[e]	205.96 USD M[e] 23.99 USD M/yr[e]	Demonstration[f]
Oxyfuel combustion	61% CO_2 captured[e]	50.04 USD M[e] 8.49 USD M/yr[e]	Prototype[f]
Alternative raw materials	2.3–95.6 kcal/kg clinker energy savings[g]	Depending on raw materials	Early adoption
Alternative binders			
Magnesium-based cement	Has not been scaled up sufficiently to make it possible to be assessed		Research[h]
Low-carbonate clinkers with pre-hydrated calcium silicates	Has not been scaled up sufficiently to make it possible to be assessed		Demonstration[h]
Waste heat recovery from exhaust streams	7 × 10^5 kW/t clinker could be saved annually[i]	N.A.	N.A.
Energy-efficient technologies			
Improved ball mills to vertical roll mills for the grinding process	11–15 kWh/t cement energy savings (raw material preparation) 6–25 kWh/t cement energy savings (product finishing)	33 USD/t cement (raw material preparation) 35 USD/t cement (product finishing)	Early adoption
High efficiency fans	0.9 kWh/t cement energy savings	0.46 USD/t cement	Early adoption
Lighting system efficiency	12–50% energy improvement depending on specific changes made	N.A.	Early adoption

Adapted from EPA (2010) unless mentioned
[a] Practicality adapted from the technology readiness level scale applied by the IEA
[b] The citation is Bataille, C. (2019). Low and zero emissions in the steel and cement industries: Barriers, technologies and policies. Issue Paper: Conference Version. Greening Heavy and Extractive Industries. 26 – 27 November, 2015. OECD, Paris. Bataille, C. (2019)
[c] Worrell et al. (2008), ECRA (2009)
[d] Worrell et al. (2008), ECRA (2009)
[e] IEAGHG (2008)
[f] IEA (2021b)
[g] Balsara et al. (2019)
[h] Lehne and Preston (2018)
[i] Benhelal et al. (2021)

technologies will affect the selection of raw materials and fuels consumed, which will directly relate to emissions in addition to the total cost as no material balance for clinker production is introduced to the programming. As the strategies are inter-related, contributions from every strategy should affect the material flows depending on the way that they are selected (Miller et al., 2021). To address this issue, this study considers the effects of technology selection on these constraints.

A linear integer optimisation model developed by Kookos et al. (2011) for a cement plant with the implementation of co-processing is the basis of this study. The model includes thermal energy demand, product specification, and thermal substitution rate with an aim to minimise production costs. As a 100 % substitution rate of alternative fuels (zero carbon emission from fuels) is unattainable due to operational constraints, the proposed model is expanded in this research to include other mitigation methods (i.e., kiln improvements and carbon capture) to overcome low carbon reduction from co-processing. Among the key differences of this study compared to Kookos et al. (2011) include:

- The model in this study is presented as a multi-objective mixed linear programming (MILP) model.
- The inclusion of kiln improvements and carbon capture technologies for carbon mitigation into the optimisation model in order to achieve higher mitigation at an optimal condition.
- In a post-combustion capture technology, the flue gas stream upon entering the capture system is cited to include water vapour (H_2O) and cooled air (Moullec and Neveux, 2016). The presence of H_2O formed during fuel combustion in the flue gas exiting the cement kiln is included in this study.
- Due to the highly alkaline atmosphere in the cement kiln, the SO_3 formed in the cement kiln is retained in clinker instead of partially purged.
- For a clearer distinction between the differences in fuel and process-based CO_2 emissions, CO_2 emissions in this study are classified as CO_2 emissions from decarbonation of raw materials and CO_2 emissions from fuel combustion. With this distinction, it will be easier to identify which area of emissions to be further improved for future study.

Table 2 summarises the measures, optimisation objectives, constraints, and studies of model types reviewed in this section. It can be seen that there is no multi-objective

Table 2 – Summary of optimisation studies.

Mitigation measures	Authors	Optimisation objective	Constraints	Model type
Clinker/cement Quality	Cao et al. (2016)	Minimise lime saturation ratio (KH), silicic ratio (SM), and aluminium ratio (IM)	Material balances, product specifications, and CO_2 emission	Multi-objective NLP
	Zhang et al. (2019)	Minimise heat needed for clinker production	Material balances, energy balances, and flue gas analysis	Single-objective NLP
Supply chains	Nurjanni et al. (2017)	Minimise total cost and total emission of CO_2 throughout supply chains	Product demand, and product deployment	Multi-objective NLP
Co-processing	Kookos et al. (2011)	Clinker production cost	Material balances, product specifications, thermal energy demand, and thermal substitution rate	Single-objective MILP
	Carpio et al. (2008)	Minimise clinker production cost	Product specification and thermal energy demand	Single-objective NLP
Kiln improvements	Oyepata and Obodeh (2015)	Minimise clinker production cost	Product specification and thermal energy demand	Single-objective NLP
Various strategies/ integrated strategies	Ba-Shammakh et al. (2008)	Minimise cement production cost	Product demand, technology selection, and CO_2 emission constraint	Single-objective MILP
	Ogbeide (2010)	Minimise cement production cost	Product demand, technology selection, and CO_2 emission constraint	Single-objective MILP
	Adebiy et al. (2015)	Minimise cement production cost	Product demand, technology selection, and CO_2 emission constraint	Single-objective MILP
	Dinga and Wen (2021)	Minimise energy consumption, emissions, and total cost	Technology selection and technology penetration rate	Multi-objective NLP

linear optimisation study that discusses the possibility of integrating various mitigation strategies environmentally and economically. Thus, this study offers novelty in a simple multi-objective MILP model that considers both environmental and economic aspects of cement manufacturing subjected to various technology selections, material selections, material balances, and product specifications for a more holistic view of optimal cement manufacturing. Furthermore, the combination of keyword search of cement, optimisation, MILP, and emission is used to quantitatively establish the novelty of this study. From the keywords search on Scopus, there has been no overlapping of studies done based on the keywords.

The remainder of this article is organised as follows. Section 2 describes the overall methodology in this work. Section 3 presents the case study to illustrate the applications of the model. Section 4 presents the analysis of the optimal study along with a sensitivity analysis of the model. Finally, Section 5 concludes the findings of this study.

2. Overall methodology

First, a preliminary study was carried out where process flowsheeting was developed and all data related to cement production were obtained. Various data related to cement manufacturing were obtained from official reports and published journals. In solving a real life optimisation problem, problem statement was described first (Section 2.1). Secondly, due to the complexity of chemical properties and reactions during clinker production, the lack of technological information, and the need to simplify the model description, several limitations and assumptions would be required (Section 2.2). From these limitations and assumptions, superstructure was then constructed to explain the flow of the cement kiln system (Section 2.3). Then, the optimisation model based on the superstructure was formulated (Section 2.4). The developed model was then coded into an optimisation tool to generate optimal results (Section 3) for further analysis (Section 4).

2.1. *Problem statement*

About 90 % of CO_2 emissions from a cement plant is generated in a cement kiln (IPCC, 2014), while about 10 % of CO_2 emissions is accounted for other processes, such as electricity (Benhelal et al., 2012), grinding, and transportation (Bosoaga et al., 2009). Therefore, the optimisation part of this study focused on the cement kiln area and the resulting problem was then defined as follows.

Given.

- Sets of potential mitigation technology data: efficiency, etc.
  - o r = {improved kiln refractories, improved process control, increased preheater stage}
  - o c = {oxyfuel combustion capture, post-combustion capture}
- Sets of raw material data: chemical composition of oxides, etc.
  - o j = {limestone, sand, clay, iron source}
- Sets of fuel data: chemical composition, emission factor, etc.
  - o k = {coal, petroleum coke}
  - o l = {refuse -derived fuel, sewage sludge, tyre-derived fuel, meat bone meal}
- Solid in clinker product: oxides, alkalis, sulphurs, and heavy metals.
  - o o = {SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO}
  - o a = {K_2O, Na_2O}
  - o SO_3 = {SO_3}
  - o h = {Hg, Tl, Cd, As, ...}
- Parameters on clinker phases based on bogue calculation
  - o p = {C_3S, C_2S, C_3A, C_4AF}
- Parameters on production data: energy demand, production capacity, etc.
- Parameters on cost data

To determine

- Technological pathway
- Flue gas
  - o fg = {N_2, O_2, H_2O, CO_2}
- Mass of clinker phases
- Raw material and fuel consumption

2.2. *Assumptions and simplifications*

Several assumptions and simplifications were made for the optimisation study due to the complexity of chemical reactions during clinker production, its chemical properties, and the lack of technological information. The assumptions applied would be able to simplify the model description and to obtain model parameters. Note that the assumptions in this study cannot be compromised. The obtained optimal results would only be applicable if all the listed assumptions are satisfied.

Process-related assumptions:

- Full incorporation of fuels' ashes into clinker is assumed.
- Sulphur content in fuels also contributes to the SO_3 formation in the clinker. Sulphur is assumed to react with oxygen to form SO_2. However, the highly alkaline (Na and K) condition and excess O_2 in the cement kiln further oxidise SO_2 into alkali sulphates (alkali-SO_3) in clinker.
- Given that CO_2 accounts for about 98 % of pollutants emitted from cement plant flue stack, only CO_2, combustion air (O_2 and inert N_2), and inert water vapour (H_2O) are considered in the flue gas analysis.
- O_2 leaving the production line is maintained at a level of 10% by optimising the shape of the flame, efficient mixing of fuel, and combustion air. This is to ensure that complete combustion is achieved (Environmental Quality (Clean Air) Regulations, 2014).
- Clinker is mainly composed of four phases as described by the Bogue method (C_3S, C_2S, C_3A, and C_4AF). They are formed by oxides contributed by raw materials and ashes of fuels. The method helps to calculate the amount of raw feed needed (raw feed proportioning) to achieve the estimated product specification of the clinker's four main minerals (Kookos et al., 2011).
- If oxyfuel combustion carbon capture technology is selected, air for combustion is separated in an air separation unit prior to entering the cement kiln so that pure O_2 (97 % O_2) is fed into the kiln (Stanger et al., 2015).

Parameter-related assumption:

- CEM I Portland cement is the cement product, where 95 % of the total cement produced is composed of clinker (CEMBUREAU, 2013).

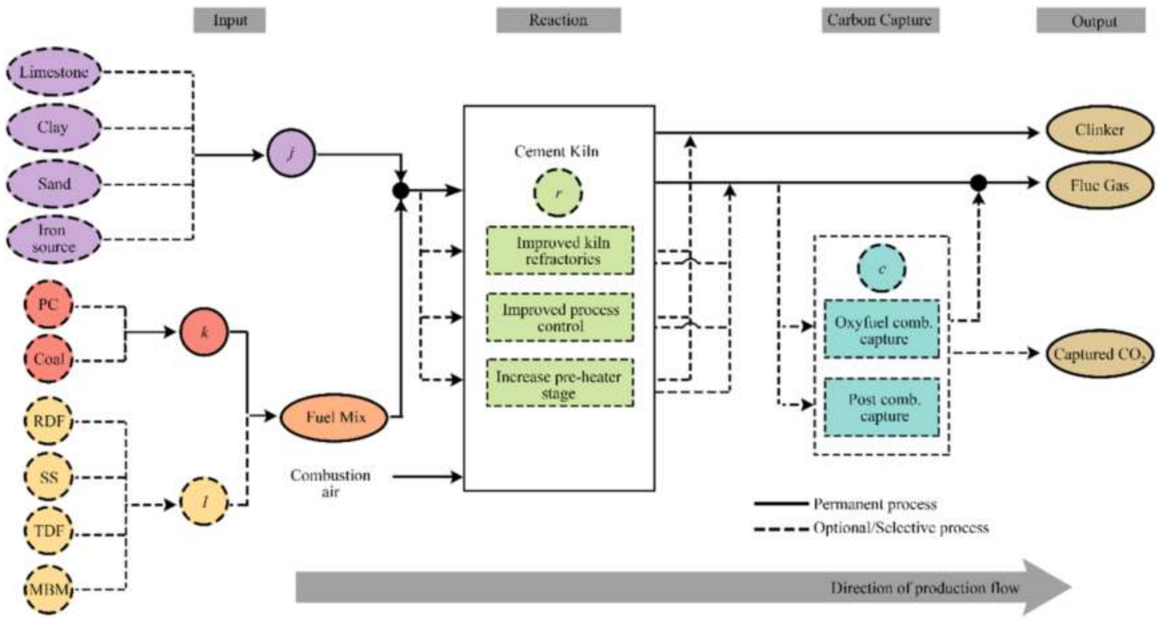

Fig. 1 – Superstructure representation of cement production. *j* denotes the raw materials, *k* denotes the fossil fuels, *l* denotes the non-fossil fuels, *r* denotes the kiln improvement technologies, and *c* denotes the capture technologies.

- Partial substitution of alternative fuel is assumed as opposed to full fuel substitution.
- All kiln improvement measures considered can be applied simultaneously where the effect of these technologies is assumed to be additive.
- This study focuses on CO_2 capture process. The costs of transport and storage of captured CO_2 have not been considered in this study.

2.3. *Superstructure representation*

Based on the problem definition, Fig. 1 presents the superstructure of this study. For a holistic view, this superstructure involves the possible connections among all the manufacturing decisions in this study that could determine which raw materials and fuels to be consumed, which energy-efficient technologies to be used for thermal energy demand improvement, and which capture technology is suitable when substantial carbon mitigation is required.

The manufacturing starts from raw meal preparation that should meet specified clinker phase composition and thermal heat demand. Raw meal mix comprises raw materials and fuels. There are four raw materials selection: limestone, clay, sand, and/or iron (Fe) source. While fuels in cement manufacturing mainly provide thermal energy, they also contribute to the quality of the product due to the incorporation of their ashes in the final product. Fuel mixture is obtained from co-processing where primary fuel (i.e., petroleum coke and/or coal) is partially substituted with secondary fuel (i.e., RDF, SS, TDF, and/or meat bone meal (MBM)). The selection of secondary fuel with lower C content compared to primary fuel will lower the amount of CO_2 produced from the cement kiln during fuel combustion. Air is fed into the cement kiln for fuel combustion.

For clinker to be produced, the raw materials in the cement kiln are heated to certain temperatures for chemical reactions (decarbonation) to take place. The heat is provided by fuel combustion. Improving cement kiln thermal energy demand directly reduces the amount of fuels needed and eventually the CO_2 from fuel combustion. This can be achieved by improving kiln refractories, improving process control, and/or increasing preheater stage.

Exiting the cement kiln are clinker with specific clinker phase mass and flue gas consists of O_2, N_2, H_2O, and CO_2. The decarbonation of raw materials and combustion of fuels in a cement kiln produces CO_2. For substantial carbon mitigation, CO_2 is separated from the flue gas stream at a specific capture facility. Possible capture facilities in this study are oxyfuel combustion capture technology or post-combustion capture technology. Fig. A.1 shows an example of technical pathways that can be obtained from the constructed superstructure.

2.4. *Model formulations*

2.4.1. *Objective functions*

The proposed model considers a multi-objective MILP approach, in which the objective function consists of the minimisation of the total cost and CO_2 emission. The presented problem that corresponds to a multi-objective problem was solved using ϵ-constraint method (Section 2.4.3).

2.4.1.1. Economic objective function. The economic objective function minimises the total cost of cement manufacturing. The objective consists of capital and maintenance costs, material costs, and technology costs. The model also includes various installation and operational costs, such as the costs of handling, storage, facilities, installation cost of non-fossil fuels, and installation cost of kiln improvements.

minimise total cost,

$$\begin{aligned} z_1 = {} & FCI + OM + \sum_{j \in Rawmaterials} C_j m_j + \sum_{k \in Fossil} C_k m_k \\ & + \sum_{l \in Nonfossil} C_l m_l + \sum_{l \in Nonfossil} [FCI_l x_l + OM_l m_l] \\ & + \sum_{r \in Kiln} [FCI_r x_r] + \sum_{c \in Carbon\ capture} [FCI_c x_c + OM_c x_c] \end{aligned} \tag{1a}$$

Binary variables x_k, x_l, x_r, and x_c were introduced to consider the selection of fuels for co-processing, selection of kiln improvement system, and selection of carbon capture and storage technology, where:

$$x_k \begin{Bmatrix} 1\text{if fuel k is used} \\ 0\text{otherwise} \end{Bmatrix}$$

$$x_l \begin{Bmatrix} 1\text{if alternative fuel l is used} \\ 0\text{otherwise} \end{Bmatrix}$$

$$x_r \begin{Bmatrix} 1\text{if kiln improvement r is used} \\ 0\text{otherwise} \end{Bmatrix}$$

$$x_c \begin{Bmatrix} 1\text{if carbon capture c is used} \\ 0\text{otherwise} \end{Bmatrix}$$

2.4.1.2. *Environmental objective function.* The environmental objective function minimises CO_2 emissions from cement manufacturing. This objective function was formulated by subtracting the total of CO_2 emitted from the cement kiln from the CO_2 captured from the implementation of carbon capture technology.

$$\text{minimise}CO_2\text{emission}, \quad z_2 = m_{CO_2}(1 - \sum_{c\in Carbon\ \ capture} \vartheta_c x_c) \tag{1b}$$

2.4.2. *Constraints*

Simple input-output model of constraints in a cement plant were used in this study as shown in Appendix B.

2.4.2.1. *Mass balance of solid materials.* Mass balance of solid materials describes the chemical components in cement clinker. The components that exist in cement clinker are oxides, alkalis, sulphurs, and heavy metals. Ashes from both fossil and alternative fuels are fully incorporated in the clinker product as assumed. The total of solid produced is the sum of all oxides, alkalis, heavy metals, and sulphurs (Eqs. 2–5). Eqs. 2–4, and Eq. 6 are adapted from Kookos et al. (2011). Eq. 5 is slightly different from Kookos et al. (2011), as no SO_3 is purged as flue gas and sulphur content in fuels contributes to the SO_3 formation in clinker due to the highly alkaline nature in the cement kiln and the availability of excess O_2, as they react with alkalis to form alkali sulphates in clinker. Fig. B.2 illustrates the mass balance of solid material constraint. Full incorporation from fuels is assumed to be contributed by their ashes as previously stated, where the mass fractions of fuels are multiplied by their respective ash mass fraction.

Oxides:

$$m_o = \sum_{j\in Raw\ \ materials} \omega_{o,j} m_j + \sum_{k\in Fossil} \omega_{o,k} m_k + \sum_{l\in Nonfossil} \omega_{o,l} m_l \tag{2}$$

Alkalis:

$$m_a = \sum_{j\in Raw\ \ materials} \omega_{a,j} m_j + \sum_{k\in Fossil} \omega_{a,k} m_k + \sum_{l\in Nonfossil} \omega_{a,l} m_l \tag{3}$$

Heavy metals:

$$m_h = \sum_{j\in Raw\ \ materials} \omega_{h,j} m_j + \sum_{k\in Fossil} \omega_{h,k} m_k + \sum_{l\in Nonfossil} \omega_{h,l} m_l \tag{4}$$

Sulphurs:

$$m_{SO_3} = \sum_{j\in Raw\ \ materials} \omega_{SO_3,j} m_j + \sum_{k\in Fossil} \omega_{SO_3,k} m_k + \sum_{l\in Nonfossil} \omega_{SO_3,l} m_l + \sum_{k\in Fossil} \left(\omega_{S,k} \times \frac{80}{32}\right) m_k + \sum_{l\in Nonfossil} \left(\omega_{S,l} \times \frac{80}{32}\right) m_l \tag{5}$$

It must be noted that $\omega_{S,k}$ and $\omega_{S,l}$ are not multiplied by their respective ash mass fraction as specified in the assumption. To quantify the amount of SO_3 that comes from the sulphur content in fuels, the fuels' sulphur wt% is multiplied with the molar mass ratio of SO_3:S (80 kg SO_3/mol:32 kg S/mol). During fuel combustion, the production of 1 mol of SO_3 requires 1 mol of sulphur as shown below:

$$S + \frac{3}{2} O_2 \rightarrow SO_3$$

Therefore, the total of solid components to produce clinker is:

$$M_{clinker} = \sum_{o\in Oxides} m_o + \sum_{a\in Alkalis} m_a + \sum_{s\in Sulfurs} m_s + \sum_{h\in Heavy\ \ metals} m_h \tag{6}$$

2.4.2.2. *Flue gas analysis.* Exhaust gases from cement manufacturing consist of CO_2, H_2O, O_2, and N_2. Under the assumption of an ideal gas law, with normal conditions, with a molar volume of 22.414 Nm^3/kmol, the volumetric flow rate of exhaust gases can be quantified as follows (Kookos et al., 2011):

$$v_g = 22.414 \sum_{g\in Flue\ \ gases} \frac{m_g}{MW_g} \tag{7}$$

Complete combustion is achieved from the controlled 10% O_2 released, as shown in Eq. 10 (Kookos et al., 2011). Air is composed of 23.2 mass% O_2 and 76.8 mass% N_2. When the carbon capture mitigation method is considered as the mitigation method, changes in the flue gas mass balance, namely N_2 and O_2, are included in the model of this study to show the effect of applying carbon capture based on post-combustion and oxyfuel combustion configurations. This study also accounts for H_2O in the flue gas stream formed during fuel combustion. Fig. B.3 illustrates the input-output model of the flue gas constraint.

The exiting flue gas constraints are then gathered as follows:

$$m_{N_2} = 76.8\% \times m_{air} - \sum_{c\in Carbon\ \ capture} 76.8\% \times N_c \times \beta_c + \sum_{c\in Carbon\ \ capture} 3\% \times N_c \times \beta_c \tag{8}$$

$$m_{O_2} = (23.2\% \times m_{air}) - \sum_{c\in Carbon\ \ capture} (23.2\% \times N_c \times \beta_c) + \sum_{c\in Carbon\ \ capture} 97\% \times N_c \times \beta_c - \left(\sum_{k\in Fossil} ST_k m_k + \sum_{l\in Nonfossil} ST_l m_l\right) \tag{9}$$

$$m_{O_2} = v_{fg}\left(\frac{32}{22.414}\right)(10\%) \tag{10}$$

$$m_{H_2O} = \sum_{k\in Fossil}\left(\omega_{H,k} \times \frac{18}{2\times 1}\right) m_k + \sum_{l\in Nonfossil}\left(\omega_{H,l} \times \frac{18}{2\times 1}\right) m_l \tag{11}$$

To calculate m_{O2}, the mass of O_2 in air fed is subtracted from the mass of O_2 that is used for combustion. ST_k and ST_l denote the stoichiometric O_2 for complete combustion of k^{th} fossil fuels and l^{th} alternative fuels (Green and Perry, 2008).

Binary x_c is introduced for the selection of c^{th} carbon capture technology. To include the effect of the selected capture technology, constant N_c is introduced. Once oxyfuel combustion is selected, pure O_2 (97 %) will be fed into the kiln instead of the usual combusting air. Thus, to account for this condition, the terms 76.8 %$N_c \beta_c$ and 3 %$N_c \beta_c$ are introduced in Eq. 8. Similarly, two terms are introduced in Eq. 9 (23.2 %$N_c \beta_c$ and 97 %$N_c \beta_c$) to include O_2-rich input air. Clear difference between these two input-output model can be seen from the general configuration of the two capture system as shown in Fig. C.1 and C.2. β_c is a linearised variable for the multiplication of continuous variable m_{air} and binary variable x_c. As suggested by Wei and Wang (2020), to linearise continuous binary term, two inequalities should be introduced as follows:

$$0 \le \beta_C \le Mx_C \quad (12)$$

$$m_{air} - M(1 - x_C) \le \beta_C \le m_{air} \quad (13)$$

This linearisation process is also applied to Eq. 16 subjected to Eqs. 17–20, and Eq. 30 subjected to Eqs. 31–32. The selection of M values is discussed in Appendix D.

CO_2 emissions (m_{CO2}) are contributed by decarbonation and fuel combustion. From the decarbonation of $CaCO_3$ and $MgCO_3$ into their oxides, CO_2 is also formed. As for the combustion process, the carbon content in fuels reacts with the O_2 provided by combustion air to produce CO_2. Kookos et al. (2011) classified the total CO_2 emissions into biogenic and non-biogenic emissions to account for greenhouse gas impact, which this study classified the CO_2 emissions into the emission produced during decarbonation and combustion. The mass of CO_2 emitted in kg/t clinker from decarbonation (m_{cb}) and combustion (m_{cm}) is then formulated as Eqs. 14–16:

$$m_{CO_2} = m_{cb} + m_{cm} \quad (14)$$

$$m_{cb} = \frac{44}{56}\sum_{j\in Raw\ materials}\omega_{CaO,j}m_j + \frac{44}{40}\sum_{j\in Raw\ materials}\omega_{MgO,j}m_j \quad (15)$$

$$m_{cm} = \sum_{k\in Fossil}CEF_k\alpha_k + \sum_{l\in Nonfossil}CEF_l\alpha_l \quad (16)$$

The CaO mass% from j^{th} raw materials is multiplied by a molar mass ratio of 44 kg CO_2/kmol:56 kg CaO/kmol while the MgO mass% from j^{th} raw materials is multiplied by a molar mass ratio of 44 kg CO_2/kmol:40 kg MgO/kmol, which is similar to Eq. 5.

Similar to Eqs. 8 and 9, using exact linearisation, the model is simplified to avoid the complexity of solving a non-linear model. Eq. 16 is subjected to these constraints:

$$0 \le \alpha_k \le Mx_k \quad (17)$$

$$m_k - M(1 - x_k) \le \alpha_k \le m_k \quad (18)$$

$$0 \le \alpha_l \le Mx_l \quad (19)$$

$$m_l - M(1 - x_l) \le \alpha_l \le m_l \quad (20)$$

Alternatively, when reporting for greenhouse gas impact, CO_2 emissions can be classified as biogenic and non-biogenic. In greenhouse gas reporting, the impact of CO_2 produced from biogenic sources is not recorded as biogenic CO_2 is assumed to be carbon neutral. To account for this, $\varnothing_l$ is a factor introduced to present the effects of l^{th} fuels on the environment. The biogenic CO_2 emitted (m_{bio}) by alternative fuels is formulated as (Kookos et al., 2011):

$$m_{bio} = \sum_{l\in Nonfossil}CEF_l\varnothing_l\alpha_l \quad (21)$$

2.4.2.3. *Raw feed proportioning using Bogue equation (Product specification)*. The raw feed required for clinker production is determined based on the clinker analysis suggested by Bogue (1955). According to the method, four major phases in clinker are formed from the oxides contributed by raw materials and ashes of fuels. These phases exist in clinker within the defined ranges (Kookos et al., 2011):

$$MB_p{}^{L}m_{clinker} \le \sum_{j\in Raw\ materials}(B_{p,o}m_{o,j}) + \sum_{k\in Fossil}(B_{p,o}m_{o,k}) + \sum_{l\in Nonfossil}(B_{p,o}m_{o,l}) \le MB_p{}^{U}M_{clinker} \quad (22)$$

2.4.2.4. *Thermal energy*. The thermal energy required by a cement kiln is provided by fossil and non-fossil fuels. NCV_k and NCV_l are the net calorific values of k^{th} fossil fuels and l^{th} non-fossil fuels in GJ/kg of fuels, respectively. Slight changes to the models suggested by Kookos et al. (2011) are applied in Eqs. 23–24, where binary x_r is included for the selection of r^{th} kiln improvements. Fig. B.4 shows the thermal energy constraint in this study.

The thermal energy demand can be formulated as:

$$TED\sum_{r\in Kiln}\left(1 - x_r\frac{TDI_r}{100}\right) = \sum_{k\in Fossil}m_kNCV_k + \sum_{l\in Nonfossil}m_lNCV_l \quad (23)$$

For co-processing, the thermal substitution rate (TSR) expressed in % is introduced as the use of non-fossil fuels is subjected to a limit. As mentioned previously, realistically, a fully functioning burner cannot be achieved with 100 % non-fossil fuel usage. Thus, the limitation is expressed as follows:

$$\sum_{l\in Nonfossil}m_lNCV_l \le \left(\frac{TSR}{100}\right)TED\sum_{r\in Kiln}\left(1 - x_r\frac{TDI_r}{100}\right) \quad (24)$$

The additive effect of thermal energy improvement is applied in Eqs. 23–24, where the improvement is linearly added.

2.4.2.5. *Fuel availability*. Mass of k^{th} and l^{th} fuels are subjected to the availability of each respective fuel (Kookos et al., 2011).

$$m_k \le A_kx_k \quad (25)$$

$$m_l \le A_lx_l \quad (26)$$

Where A_k and A_l denote the k^{th} primary fuel and l^{th} alternative fuel availability in kg/t clinker, respectively.

2.4.2.6. *Technology selection*. The number of fuels selected must not be more than the allowed number of fuels (F_{max}) that can be combusted in the burner.

$$\sum_{k\in Fossil}x_k + \sum_{l\in Nonfossil}x_l \le F_{max} \quad (27)$$

Since it is assumed that all kiln improvements can be applied simultaneously as suggested in the assumption, the maximum number of kiln improvement selections can be achieved (K_{max}).

$$\sum_{r\in Kiln}x_r \le K_{max} \quad (28)$$

At most, one c^{th} carbon capture is installed. Therefore:

$$\sum_{c\in Carbon\ capture}x_c \le 1 \quad (29)$$

2.4.3. *Solving multi-objective optimisation through ϵ-constraint method*

The ϵ-constraint method proposed by Haimes et al. (1971) was used to obtain a set of Pareto optimal solutions to show trade-offs between the environmental and economic objectives in the analysis. The solutions were obtained for different values of ϵ parameter. In the ϵ-constraint method, one

Table 3 – Optimisation study conditions for increasing CO_2 reduction target.

Variables and scalars	Condition
Thermal substitution rate, TSR (%)	30
Current CO_2 emission, CO_{2Base} (kg/t clinker)	[a]
CO_2 reduction target, FCO_2 (%)	+ 10
Fuel selection: $\sum_{k\epsilon Fossil} x_k + \sum_{l\epsilon Nonfossil} x_l$	2
Kiln improvement selection: $\sum_{r\epsilon Kiln} x_r$	3
Carbon capture selection: $\sum_{c\in Carbon\ capture} x_c$	1

[a] m_{CO2} value was obtained from the optimised base-case scenario

of the objective functions was optimised while the other objectives were treated as constraints such as follows:

minimisez_1

Subjected to

$$z_2 \le \epsilon$$

$$\epsilon_L \le \epsilon \le \epsilon^U \quad (30)$$

From Eq. 30, z_2 was expressed so that the amount of carbon released into the atmosphere would not exceed the ϵ parameter. In this study, ϵ denotes the targeted emission reduction in kg/t clinker. Fig. B.5 illustrates this constraint.

$$m_{CO_2} - \sum_{c\in Carbon\ capture} \vartheta_c \psi_c \le \left(1 - \frac{FCO_2}{100}\right) CO_{2Base} \quad (31)$$

Where FCO_2 is the targeted emission reduction in % that will be in the range of [0100], and CO_{2Base} is the current mass of CO_2 emissions gained from the optimised base-case scenario. Eq. 30 is subjected to:

$$0 \le \psi_c \le Mx_c \quad (32)$$

$$m_{CO_2} - M(1 - x_c) \le \psi_c \le m_{CO_2} \quad (33)$$

3. Case study

3.1. *Scenario I: Base-case (Benchmark)*

A cement plant operating with a five-stage preheater/precalciner cement kiln required thermal energy of 3.25 GJ/t clinker. The plant had an FCI of USD 285.12 M and OM of USD 25.55 M/y (IEAGHG, 2008). An interest rate of 10 % for 25 years of life was applied. CEM I Portland cement was the cement product where 95 % of the total cement produced comprised of clinker (CEMBUREAU, 2013). For benchmark, a cement plant with no mitigation method and no CO_2 reduction target was assumed. For base-case optimisation, the selection for fossil fuels involved coal or petroleum coke (PC). The m_{CO2} value obtained in this scenario was used as CO_{2Base} for optimisation analysis.

3.2. *Scenario II: Cement manufacturing with increasing carbon emission reduction target*

After obtaining benchmark result, scenario with increasing carbon emission reduction applied to the optimisation model was carried out next. Fuel selection for this scenario included coal or PC as primary fuels, with SS, RDF, MBM, or TDF as secondary fuels. A maximum 30 % substitution rate was allowed according to ICR research (2015). This is also in accordance with the average substitution rate of alternative fuels in cement plants across Europe (30.5 %) (IEAGHG, 2013). Mitigation measures in kiln improvements and carbon capture are also considered in this scenario. To study the effects of CO_2 reduction target on the total cost of clinker production, flue gas emissions, raw material and fuel consumption, clinker phase and fuel selection, and several conditions were applied to the model. Table 3 shows the conditions applied to the model for the optimisation study. The increment of 10% reduction target was repeated until infeasible results were achieved in order to find the range for the highest CO_2 reduction.

3.3. *Sensitivity analysis*

Sensitivity analysis was carried out to obtain insights on the optimisation of model behaviour and structure so that the response to changes in model inputs can be gained. From the analysis, the competency of process models and also the areas with significant and negligible effects on the objectives were identified. Table 4 summarises the parameters evaluated for this study. Base CO_2 emission was chosen as it was anticipated to directly affect the total cost and CO_2 released into the atmosphere through technology selection. Capture technologies were both high in cost and efficiency, which are attractive for substantial emission reduction but detrimental economically. As the maturity of capture technologies in cement plant applications is ever evolving (Plaza et al., 2020), it is of interest to study the significance of capture efficiency and cost parameter deviations on the objectives.

The sensitivity analysis for each parameter was performed separately to identify the impact of each parameter on the total cost and emission from the cement plant at a constant 30 % TSR and 65 % reduction target. The values applied for the TSR and reduction target allowed the selection of mitigation technologies during optimisation. When evaluating parameter $CO_{2Base,}$ for example, + 30 % increase of the value was applied to the optimisation model while other parameters remained constant. After the results were generated, the impact of + 30 % in CO_{2Base} on the total cost and total CO_2 emissions was observed. Next, the impact of –30 % in CO_{2Base} was observed. These steps were repeated for other parameters.

3.4. *Data usage*

Fuel prices and chemical analysis were obtained from Kookos et al. (2011) and Díaz et al. (2011); clay, sand, and Fe source prices from the US Geological Survey (2014); limestone price from Willett (2011); and plant capital cost and operating cost values from IEAGHG (2008). The Retrofitting cost for new facilities and the price of fossil fuels were obtained from Kookos et al. (2011), the FCI values for kiln improvement were obtained from ECRA (2009) and Worrell et al. (2008), and carbon capture data that include the costs for each carbon capture system and CO_2 captured from each carbon capture system were obtained from IEAGHG (2008) and Chen et al. (2004). The data used in this study can be found in Appendix D.

4. Results and discussion

The multi-objective ϵ-constraint MILP optimisation model in this study was performed using CPLEX solver in GAMS 23.5.1. The model consisted of 133 single equations, 98 single variables,

Table 4 – Parameters evaluated for sensitivity analysis.

Parameters	Fluctuation (± %)*
Current CO_2 emission, CO_{2Base}	30[a]
System removal/absorption rate, ϑ_c	25[b]
Carbon capture capital and operating cost, FCI_c and OM_c	20[c]

* Panell (1997) suggested that the deviations of each parameter must be approximately in a reasonable range. Thus:
[a] Adapted from IEA (2018), which aims to reduce direct CO_2 emissions by 24 % below the current emission level by 2050.
[b] A common range of sensitivity analysis deviations adapted from Hemmati et al. (2019). The same range was applied for oxyfuel capture efficiency.
[c] Adapted from Tzimas (2009). While only + 20 % was applied in Tzimas (2009), this study applied –20 % to the costs for comparison purposes.

11 discrete variables, and was solved in 0.070 s. The model was solved on an Intel(R) Core(TM) i7–3520 M CPU @ 2.90 GHz, RAM 8 GB, 64-bit operating system, Windows 7 computer.

Optimisation analysis was carried out to determine the effects of increasing CO_2 reduction target on the technological pathway, the total cost of clinker production, flue gas emissions, raw material and fuel consumption, clinker phase, as well as to find the highest CO_2 reduction target that can be achieved by the selected technologies, and then compared with Kookos et al. (2011). Subsequently, sensitivity analysis was carried out. Sensitivity analysis may be conducted for a number of reasons, as per Hamby (1994). The sensitivity analysis in this study was conducted on several input parameters to identify the parameters with a significant impact on the output/objectives.

4.1. *Analysis of optimal solutions*

As mentioned, the mass of CO_2 emission (880.89 kg CO_2/t clinker) where no mitigation method and no CO_2 reduction target was applied was used as the current CO_2 emissions from the cement plant for further optimisation study. From Table 5, the maximum CO_2 reduction reached between 90 % and 100 %. At 0 % CO_2 reduction target and 30 % TSR, the

Table 5 – Effects of CO_2 reduction target on the total cost of clinker production, flue gas emissions, raw material and fuel consumption, clinker phase, and fuel and technology selection.

TSR (%)	0	30	30	30	30	30
Scenario	I	II				
CO_2 reduction target, FCO_2 (%)	Base	0	10	20	70	100
CO_2 reduction from optimisation (%)	–	9.52	10.64	64.71	98.19	IS
Total cost, z_1 (USD/t clinker)	94.52	91.62	92.23	104.92	135.96	IS
Final thermal energy demand (GJ/t clinker)	3.50	2.82	2.71	2.82	2.82	IS
CO_2 emissions (kg CO_2/t clinker)						
Total CO_2 produced, m_{CO2}	880.89	797.04	787.12	797.04	797.04	IS
CO_2 released from fuel combustion, m_{cm}	350.00	265.23	255.10	265.23	265.23	IS
Fossil fuel, $\sum_{k \in Fossil} CEF_k \alpha_k$	350.00	197.51	189.97	197.51	197.51	IS
Alternative fuel, $\sum_{l \in Nonfossil} CEF_l \alpha_l$	0.00	67.72	65.13	67.72	67.72	IS
CO_2 released from raw material decarbonation, m_{cb}	530.89	531.82	532.02	531.82	531.82	IS
CO_2 captured, $\sum_{c \in Carbon\ capture} \vartheta_c \psi_c$	0.00	0.00	0.00	486.20	781.10	IS
CO_2 released into the atmosphere, z_2	880.89	797.04	787.12	310.85	15.94	IS
Flue gas emissions (kg/t clinker)						
O_2 emission, m_{O2}	339.47	284.12	276.14	72.05	284.12	IS
CO_2 emission, z_2	880.89	797.04	787.12	310.85	15.94	IS
N_2 emission, m_{N2}	2068.21	1679.20	1624.57	9.13	1679.20	IS
H_2O emission, m_{H2O}	28.64	32.82	31.57	32.82	32.82	IS
Raw material consumption, m_j (kg/t clinker)						
Limestone	1310.86	1313.22	1313.72	1313.22	1313.22	IS
Clay	0.00	0.00	0.00	0.00	0.00	IS
Sand	161.61	161.25	161.33	161.25	161.25	IS
Fe source	10.88	11.23	11.22	11.23	11.23	IS
Fuel consumption, m_k and m_l (kg/t clinker)						
Coal	0.00	0.00	0.00	0.00	0.00	IS
Petroleum coke	106.06	59.85	57.57	59.85	59.85	IS
Refuse-derived fuel	0.00	0.00	0.00	0.00	0.00	IS
Sewage sludge	0.00	0.00	0.00	0.00	0.00	IS
Tyre-derived fuel	0.00	26.45	25.44	26.45	26.45	IS
Meat bone meal	0.00	0.00	0.00	0.00	0.00	IS
Clinker phase, m_o (kg/t clinker)						
C_3S (50% < m < 60%)	527.86	529.18	529.52	529.18	529.18	IS
C_2S (10% < m < 35%)	350.00	350.00	350.00	350.00	350.00	IS
C_3A (1% < m < 15%)	10.00	10.00	10.00	10.00	10.00	IS
C_4AF (1% < m < 15%)	83.87	84.94	84.93	84.94	84.94	IS
Cement kiln upgrade selection						
Improved refractories		√	√	√	√	IS
Process control						IS
Increased preheater stage (5 → 6)			√			IS
CCS technology selection						
Oxyfuel combustion				√		IS
Post combustion					√	IS

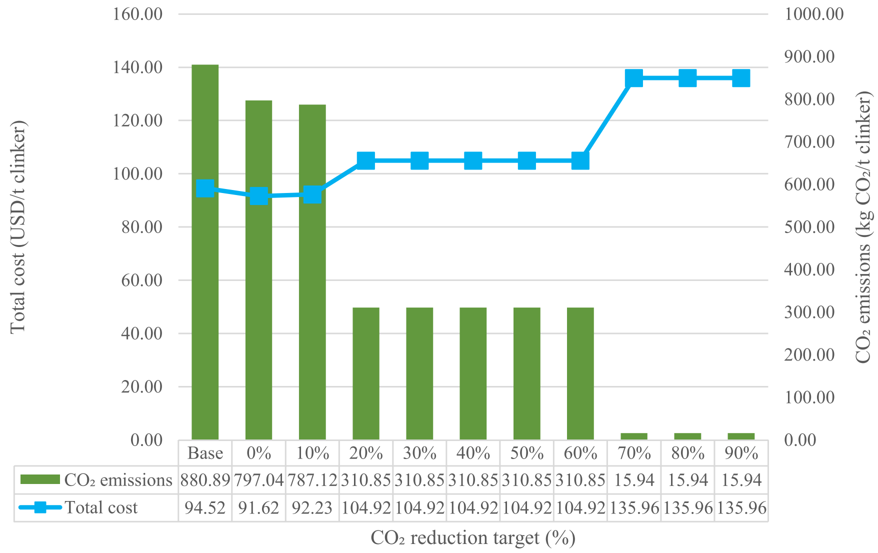

Fig. 2 – Relationship between CO_2 reduction target with the total cost and total CO_2 emissions.

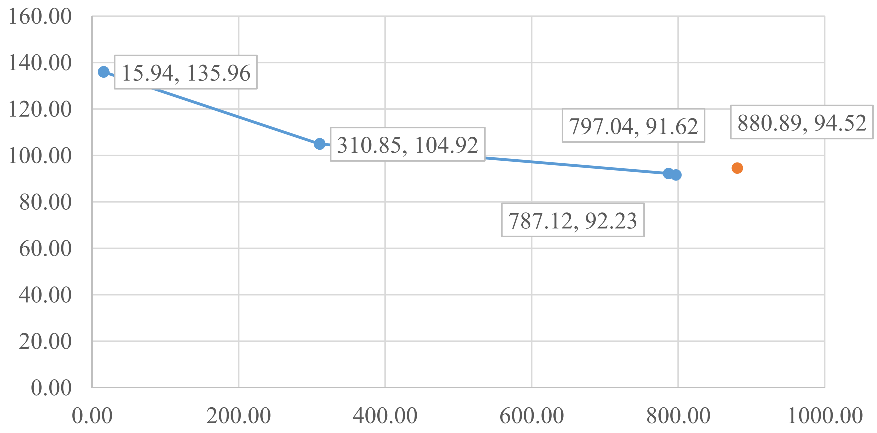

Fig. 3 – Pareto front for all solutions.

abatement measures applied were co-processing with PC as primary fuel and TDF as alternative fuel, while the cement kiln improvement measure chosen was refractories improvement. The increase of the preheater stage was additionally chosen at a 10 % reduction target. For the reduction target of 20 %, oxyfuel combustion was chosen along with co-processing (PC and TDF as fuels) and refractories improvement as the kiln improvement method. The technology selection remained until 60% reduction target. At a 70 % reduction target, post combustion was selected with co-processing of PC and TDF, and improved refractories were selected for kiln improvements. Changes in the mass of clinker phases could be generally seen whenever changes in raw materials or fuel consumption occurred. The technological pathways applied to achieve the optimal results in this study are available in Appendix E.

However, it must be noted that these results are achieved by several simplifications listed in Section 2.2, such as the assumptions of flue gas stream that only consists of inert N_2 and H_2O, CO_2, and O_2, whereas in reality, there would be acid gases, such as SO_2 and NO_x emissions. The assumption of additive kiln improvements efficiency was applied due to the lack of technological information. Although no previous studies with the same improvements have been linearly added, the assumption has been applied to energy-efficient applications in cement plants by Adebiy et al. (2015), Ogbeide (2010) and Ba-Shammakh (2008). Price et al. (2009) suggested that an average of 23 % potential primary energy savings could be achieved if cement plants operated at a best practice level. Compared to this study's 28 %, the assumption is sufficient to obtain a rough idea of the technological pathway that could be further improved as more information on the effects of specified technologies on each other is known. The assumption of clinker that consists of four major phases as per Bogue calculation is also one of the limitations as there are other minor phases available in clinker. The models with only mass balance and energy demand are also one of the limitations. In general, the extent of plant cost estimation varies on the case-by-case scenarios with no set of general assumptions that will fit all circumstances. For the carbon capture and storage system, for example, the assumptions vary for plant configuration in terms of air pollution control required, and also the cost details of transport and storage systems. For this work, the estimation of the carbon capture system comprises only CO_2 capture cost with no estimation of other costs, such as CO_2 transport and storage. Meanwhile, for the essential stage of CCS, there is still no set of standard criteria to assess the cost of CO_2 transport and storage due to its highly site-specific nature.

Fig. 2 shows the effect of CO_2 reduction target on the total cost and CO_2 emissions. An optimal cost of USD 92.23/t clinker was achieved with a 10 % CO_2 reduction, which is an increase

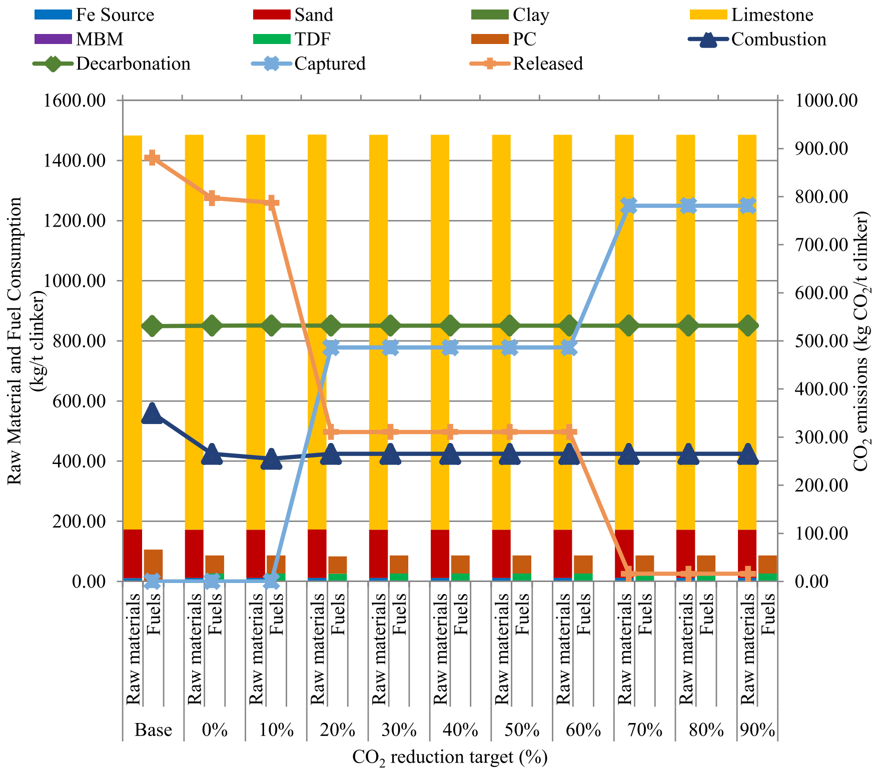

Fig. 4 – Effects of CO_2 reduction target on the consumption of raw materials and fuels, CO_2 emissions from fuel combustion and raw material decarbonation, and CO_2 captured and released.

from 0 % reduction target (USD 91.62/t clinker) due to the additional cost of two kiln improvements selected. CO_2 emitted was also lower due to the selections. The cost significantly increased at a 20 % reduction target due to the selection of the oxyfuel combustion system. The total cost increased to USD 104.92/t clinker and remained until 60% CO_2 reduction target. The ability of oxyfuel combustion to mitigate about 61 % of carbon emissions was the reason for the constant value. The constant CO_2 released into the atmosphere from 30 % to 60 % of the reduction target was also contributed by the selection of oxyfuel combustion. The cost increased considerably to USD 135.96/t clinker at a 70 % reduction target due to the selection of post combustion as the capture system. This selection further reduced the CO_2 released into the atmosphere to 15.94 kg/t clinker.

Fig. 3 shows the Pareto front for all solutions revealing the trade-off between the total cost and CO_2 emissions. The highest cost was obtained to achieve the least CO_2 emission, while the least total cost was reached when CO_2 emission was at 797.04 kg/t clinker. The highest CO_2 emission was obtained when the total cost was 94.52 USD/t clinker.

Fig. 4 presents the effect of CO_2 reduction target on the consumption of raw materials and fuels, CO_2 produced from the decomposition of raw materials, CO_2 produced from fuel combustion, CO_2 captured, and CO_2 released. The CO_2 released indicates the amount of CO_2 that is emitted into the atmosphere after the capture process. Three raw materials are consumed throughout the optimisation study with most of them being limestone. Other materials are sand and Fe source. At 0 % reduction target, the raw materials used are limestone (1313.22 kg/t clinker), sand (161.25 kg/t clinker) and Fe source (11.23 kg/t clinker). The raw material combination produced 531.82 kg/t clinker CO_2 emissions from decarbonation, an increase from the base case. With an additional mitigation method selected at a 10 % reduction target, the raw material consumption increased slightly to compensate for reduced fuel consumption (i.e., to fulfil the product specification constraint subjected by the Bogue equation). The slight increase contributed to higher decarbonation emission of 532.02 kg/t clinker. Same kiln improvements methods and co-processing fuel selections from 20 % to 90 % reduction target reflected on the same amount of raw material consumption and constant CO_2 emissions from decarbonation. Even with the selection of the oxyfuel combustion system, the raw material consumption and decarbonation emission remained the same at a 20 % reduction target when compared with 10% reduction target. This is because CO_2 is captured after exiting the cement kiln. Similarly, at a 70 % reduction target, even with the selection of the post-combustion capture system, as CO_2 capture takes place at the end of the production line, no change in raw material consumption and emission is experienced.

At 0% reduction target, the fuel consumption changed from 106.06 kg/t clinker of PC in the base case to 59.85 kg/t clinker of PC and 26.45 kg/t clinker of TDF for the partial thermal substitution and improved refractories. The use of TDF and efficient kiln technology reduced CO_2 emissions from fuel combustion from 350 kg/t clinker to 265.23 kg/t clinker. The selection of both increased preheater stage and improved refractory efficiently reduced the thermal demand by 10 %, which simultaneously reduced the CO_2 emitted from fuel combustion. Similar to raw material consumption, from 20 % to 90 % reduction target, the value of both fuel usage and CO_2 emissions from fuel combustion followed the values at 0% reduction because the selection of capture system does not affect clinker production. From the figure, it can be observed that the amount of CO_2 captured remained at 0 kg/t clinker from 0 % reduction to 10 % reduction. With the selection of the oxyfuel capture system at a 20 % reduction

Fig. 5 – Effects of CO_2 reduction target on flue gas composition.

Table 6 – Comparison of optimised results with Kookos et al. (2011).

	This study	Kookos et al. (2011)
Total cost, z_1 (USD/t clinker)	135.96	4.58
Final thermal energy demand (GJ/t clinker)	2.50	3.5
Thermal substitution rate, TSR (%)	30	32
CO_2 reduction target, FCO_2 (%)	98	1.44
CO_2 emissions (kg CO_2/t clinker)		
Total CO_2 produced, m_{CO2}	767.29	841.69
CO_2 captured, $\sum_{F \in \&DUERQ\ FDSWXUH} \vartheta_F \theta_F$	751.94	0.00
CO_2 released into the atmosphere, z_2	15.35	841.69
Raw material consumption, m_j (kg/t clinker)		
Limestone	1314.72	1284.09
Clay	0.00	0.86
Sand	161.51	0.00
Fly ash	0.00	176.435
Fe source	11.20	5.69
Fuel consumption, m_k and m_l (kg/t clinker)		
Coal	0.00	22.24
Petroleum coke	53.00	51.90
Refuse-derived fuel	0.00	15.00
Sewage sludge	0.00	15.00
Tyre-derived fuel	23.42	10.00
Meat bone meal	0.00	10.00

target, the amount of CO_2 captured was 486.20 kg/t clinker and 310.85 kg/t clinker CO_2 was released. At a 70 % reduction target, the CO_2 captured from the cement kiln was 781.10 kg/t clinker and 15.94 kg/t clinker CO_2 was released into the atmosphere. The values remained until 90 % reduction target.

Fig. 5 shows the effects of CO_2 reduction target on flue gas composition. The flue gas composition presented in the figure is the composition after going through the capture system. As the reduction target increased, the composition distribution changed according to the technology selection. A decrease in flue gas was observed with the selection of kiln refractory improvement and increased preheater stage at a 10 % reduction target compared to 0 % reduction target where only improved kiln refractory was selected. At 20–60 % reduction target, a substantial reduction of N_2 emission was experienced due to the selection of oxyfuel combustion where pure O_2 was fed instead of air with mostly N_2. The O_2 produced also decreased by 20 %. The decrease was due to a 10 % controlled volume of O_2 in exit flue gases. With lower volume exiting the kiln, lower O_2 was experienced·H_2O remained constant throughout the majority of the increased reduction target (except at 10 % reduction target where increased preheater stage was selected along with the usual improved kiln refractory) due to the same amount of fuel consumed.

4.1.1. *Comparison of optimisation results with a previous study*

As the core technology in producing cement has not evolved much based on the manufacturing process illustrated in IEA (2018), a comparison with Kookos et al. (2011) was conducted. The key differences between this study and Kookos et al. (2011) are the addition of kiln improvements and carbon capture and storage as additional mitigation measures to achieve higher mitigation, the addition of water vapour in flue gas stream, full incorporation of SO_3 in clinker product, and CO_2 formation is included in fuel and process emissions. Kookos et al. (2011) studied the possibility of co-processing in a cement plant by modelling the material balance of solid and gas phases around the cement kiln. The model was tested by changing the TSR value. The maximum TSR value achieved by Kookos et al. (2011) was 32 %.

Table 6 shows the results from Kookos et al. (2011) at 32 % (the highest CO_2 emission that can be reduced from the proposed model), with the result from this study at 98 % CO_2 reduction, which was obtained through further optimisation by increasing 1% reduction target until an infeasible solution was achieved (99 % reduction target generated an infeasible solution). A significant difference can be seen in terms of cost minimisation between this study and Kookos et al. (2011) due to

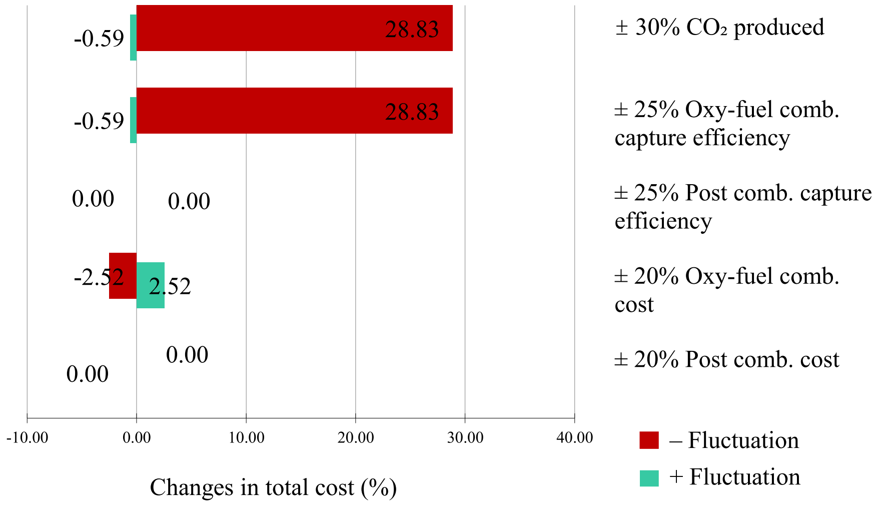

Fig. 6 – Sensitivity analysis for total cost.

the inclusion of fixed capital cost and operating cost of cement plant, selection of energy-efficient kiln, and carbon capture system. The selection of more mitigation measures enabled this study to achieve a 98% CO_2 reduction compared to Kookos et al. (2011) with a 1.44 % reduction. The selection of an energy-efficient kiln is reflected by the energy demand from this study that reduced from 3.5 GJ/t clinker to 2.50 GJ/t clinker, while the selection of carbon capture technology is reflected by the amount of CO_2 captured and released into the atmosphere. In addition, fly ash and clay were chosen by Kookos et al. (2011) instead of sand. Besides, Kookos et al. (2011) assumed that no constraints were applied in fuel mixture, which means that all types of fuels could be chosen to be co-processed instead of just two fuels to be co-processed in this study.

4.2. *Sensitivity analysis*

In this section, the base case is at the TSR of 30% and 65% CO_2 reduction target. For the base case, the technologies selected were refractories improvement, increased preheater stage, oxyfuel capture, and PC and TDF as co-processed fuels.

As shown in Fig. 6, the fluctuation in CO_2 produced from the cement kiln resulted in a significant impact on the total cost as it is related to technology selection. Instead of selecting refractories improvement and increasing preheater stage at the base for kiln improvements, only refractories improvement was selected at + 30 %, resulting in –0.59 % impact on the total cost. At –30 % CO_2 base, post combustion was selected as opposed to oxyfuel combustion, resulting in a much higher impact of + 28.83 % in the total cost. With oxyfuel capture being the primary selection for the capture process due to its lower capital and OM costs, changes in oxyfuel combustion efficiency show a significant impact on the total cost. When the oxyfuel system efficiency decreased, post combustion was selected instead, hence increasing the total cost significantly. Changes in oxyfuel combustion capital and OM costs, in general, show a greater impact on the total cost compared to post combustion (± 2.52 %). The big difference in costs between the capture systems causes oxyfuel combustion to always be chosen. Thus, a fluctuation of ± 20 % in the oxyfuel combustion capital and OM costs directly fluctuated the total costs. Meanwhile, the fluctuating CO_2 base and oxyfuel efficiency resulted in different ranges of impact (–0.59 % and +28.83 %, respectively), where the change in the cost of oxyfuel capture resulted in symmetric deviations of ± 2.52 %. The impact on total cost is related to technology selection. The asymmetric impact is caused by the selection of post-combustion capture instead of oxyfuel capture with negative deviations of CO_2 produced, and oxyfuel capture efficiency shows a greater impact on the total cost. Meanwhile, a lesser impact is shown by positive deviations of both parameters, where only refractories improvement is selected to improve thermal energy usage. In contrast to the symmetric impacts, both fluctuations in oxyfuel combustion capture costs resulted in the same technology selection compared to the base. The only difference is in the cost of the selected technologies. Thus, a symmetric deviation (± 20 %) resulted in a symmetric impact (± 2.52 %).

Fig. 7 shows the effects of the amount of CO_2 produced from the kiln, capture rate, and carbon capture capital and OM costs on CO_2 emitted into the atmosphere. Changing the efficiency of the oxyfuel combustion system by ± 25 % resulted in the highest impact on CO_2 emissions. As an oxyfuel system is typically chosen due to its lower capital and OM cost compared to post combustion, fluctuating the efficiency of the system will fluctuate the CO_2 released into the atmosphere. At –25 % capture efficiency of oxyfuel combustion system, post combustion is selected instead to fulfil the reduction target, while the oxyfuel combustion system is the selected capture system at the positive deviation. At + 25 % capture efficiency of the oxyfuel combustion system, even if the efficiency is improved, the increase in efficiency is still not as efficient as the post-combustion system. Thus, while it fulfils the reduction target, a lower impact on the CO_2 released is achieved due to lower CO_2 captured. CO_2 produced is directly related to CO_2 released into the atmosphere. Thus, changes of ± 30 % in the CO_2 produced from the cement kiln also resulted in a significant impact on the CO_2 released with a negative deviation of –94.81 %. This is contributed by the selection of post-combustion capture rather than oxyfuel capture. Thus, a higher amount of CO_2 was captured, resulting in a higher impact on CO_2 released. A lower impact of + 1.26 % was achieved for + 30 % CO_2 produced due to small changes in kiln improvements selected, where the same capture system is selected and instead of two kiln improvements selected in the base case, only one improvement is selected in this scenario. No changes can be seen in the fluctuation of the costs for the capture system.

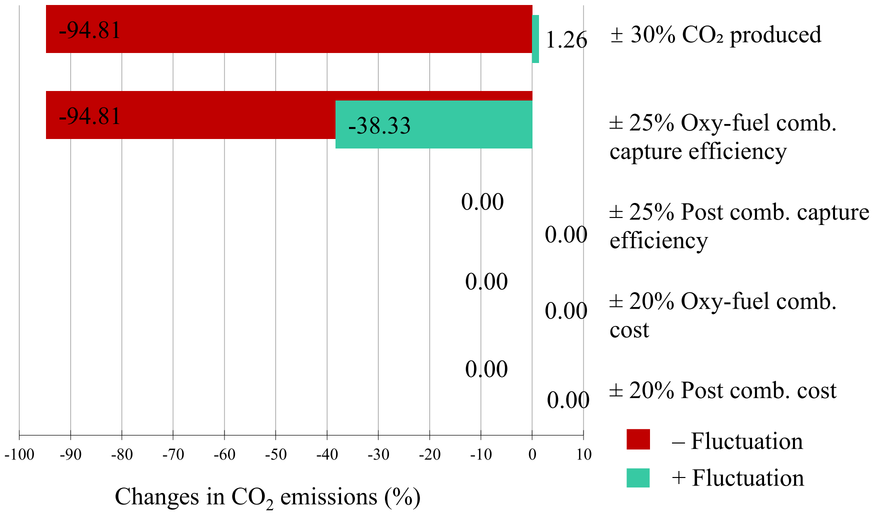

Fig. 7 – Sensitivity analysis for CO_2 released into the atmosphere.

From both figures, it can be seen that improving the oxyfuel combustion system capture rate is important to achieve an optimal cement plant due to its effects on both total cost and CO_2 emissions.

5. Conclusion

A multi-objective MILP optimisation model of cement manufacturing is developed and solved using GAMS. The model is developed to minimise both total cost and CO_2 emissions and is subjected to several constraints, including mass balance, thermal energy demand, technology selection, etc. The model is particularly useful as a decision-making tool as the model allows decision-makers to observe technological pathways and the total cost of clinker production for varying reduction targets. Academically, this model might serve as a base that provides general quantitative insights into cement production and will give a better understanding of limitations that can be met by mitigation strategies.

At most, 90–100 % CO_2 emission reduction can be achieved from the combination of co-processing, kiln improvements, and capture technology. The raw material consumptions are 1313.22 kg/t clinker of limestone, 161.25 kg/t clinker of sand, and 11.23 kg/t clinker of Fe source. Fuel usage is 59.85 kg/t clinker of PC and 26.45 kg/t clinker of TDF. The CO_2 released into the atmosphere dropped from 880.89 kg/t clinker at the base to 15.94 kg/t clinker at 90–00 % reduction target with the installation of co-process, improvement in kiln refractories, and post-combustion carbon capture. The optimal cost increased to USD 135.96/t clinker from 70 % carbon reduction target onwards, which is expected for post-combustion capture technology with the high installation cost. When post-combustion capture is selected, the CO_2 leaving the cement kiln is 797.04 kg/t clinker, with N_2, H_2O, and O_2 produced from the cement kiln of 1679.20, 32.82, and 284.12 kg/t clinker, respectively.

Estimation of other emissions, such as SO_2 and NO_x, can also be incorporated for future work. In practice, the majority of cement plant emissions is CO_2 with more than 90% of emissions share, followed by SO_2 and NO_x. Mitigation strategies for other emissions can be discussed alongside CO_2 mitigation strategies. With the potential of mitigating more than 90 % of carbon emitted from a cement plant, post-combustion capture technology is missing for lower carbon emissions. The applicability should be further explored for future work, especially in a cement plant where the presence of other emissions produced from the cement kiln, if not controlled, can be detrimental to the working of post-combustion capture technology.

Code availability

The authors declare that code supporting the findings of this study are available at DOI: 10.17632/bc5n7w8zvp.1.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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APPENDIX A

Fig. A.1 shows an example of technical pathways that can be obtained from constructed superstructure in Fig. 1. In Fig. A.1, the raw meal consists of limestone as the raw materials, as well as co-processed coal and RDF. Heat for clinker formation in the cement clinker is provided by the co-processed fuels. To reduce thermal demand, improving kiln refractories is selected. Decarbonation of limestone and coal and RDF combustion produce clinker and flue gases. The CO_2 in the flue gas stream is captured by post-combustion technology, while the separated flue gas is released into the atmosphere.

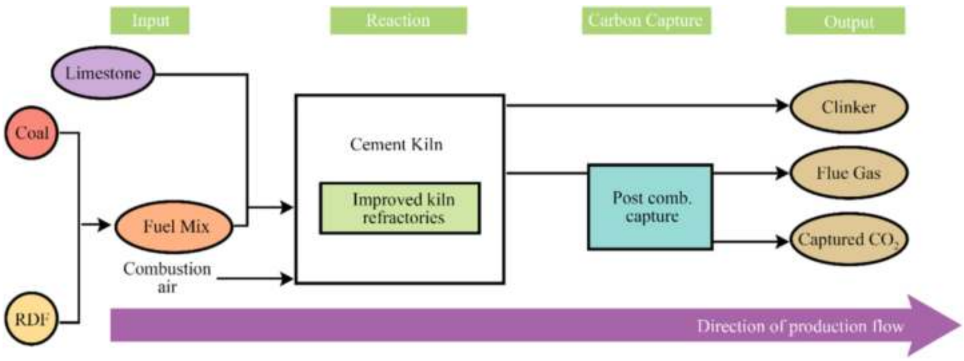

Fig. A.1 – Example of technological pathway obtained from Fig. 1.

APPENDIX B

See Fig B.1-B.5.

Input-Output model for constraints in this study include:

General input-output model:

Mass balance input-output model:

Flue gas input-output model:

Thermal energy input-output model:

CO_2 emission reduction input-output model:

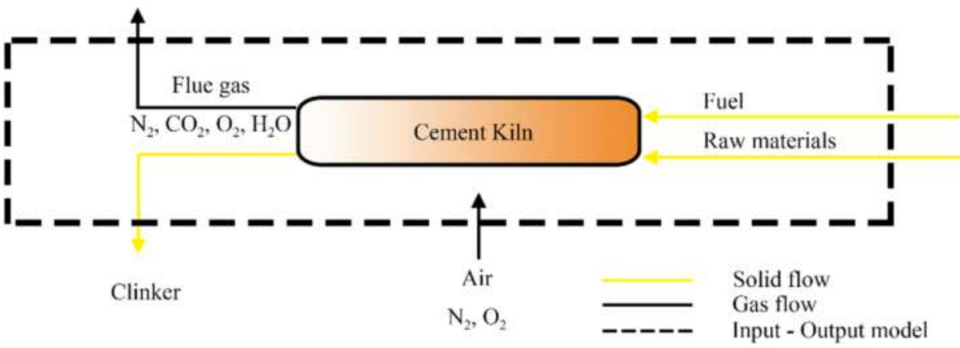

Fig. B.1 – General process flow of a cement plant.

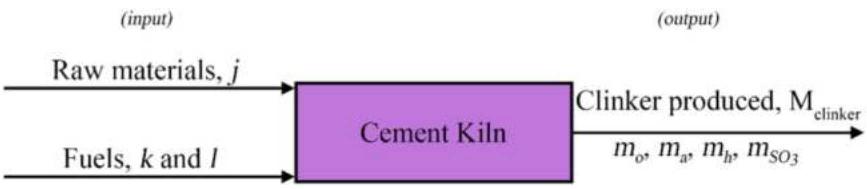

Fig. B.2 – Illustration of mass balance constraint. *j* denotes the raw materials, *k* denotes the fossil fuels, *l* denotes the non-fossil fuels, *o* denotes the oxides present in materials, *a* denotes the alkalis present in materials, *h* denotes the heavy metals present in materials, and SO_3 denotes the sulphurs present in materials.

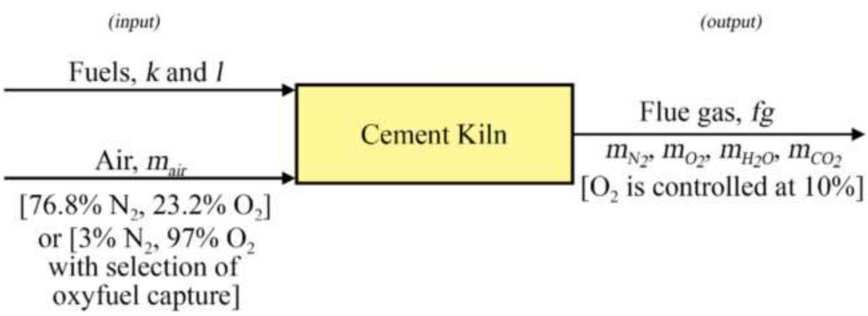

Fig. B.3 – Illustration of flue gas constraint. *fg* denotes the flue gases, *k* denotes fossil fuels, *l* denotes non-fossil fuels, N_2 denotes N_2 gas, O_2 denotes O_2 gas, H_2O denotes vapour, and CO_2 denotes CO_2 gas.

Fig. B.4 – Illustration of thermal energy constraint. *k* denotes fossil fuels, *l* denotes non-fossil fuels, *r* denotes kiln improvements, TED denotes the energy demand, TDI_r denotes the improvement by selected technologies *r*, and TSR denotes the substitution rate of non-fossil fuels *l*.

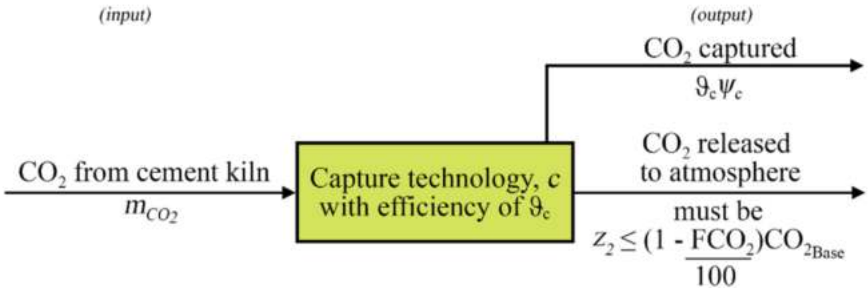

Fig. B.5 – CO_2 emission reduction constraint. *c* denotes the capture technologies, ϑ_c denotes the efficiency, ψ_c denotes the linearisation variable, m_{CO2} denotes the CO_2 from cement kiln, CO_{2Base} is the base/current CO_2 emission, and FCO denotes the reduction target.

APPENDIX C

See Fig C.1,C.2.

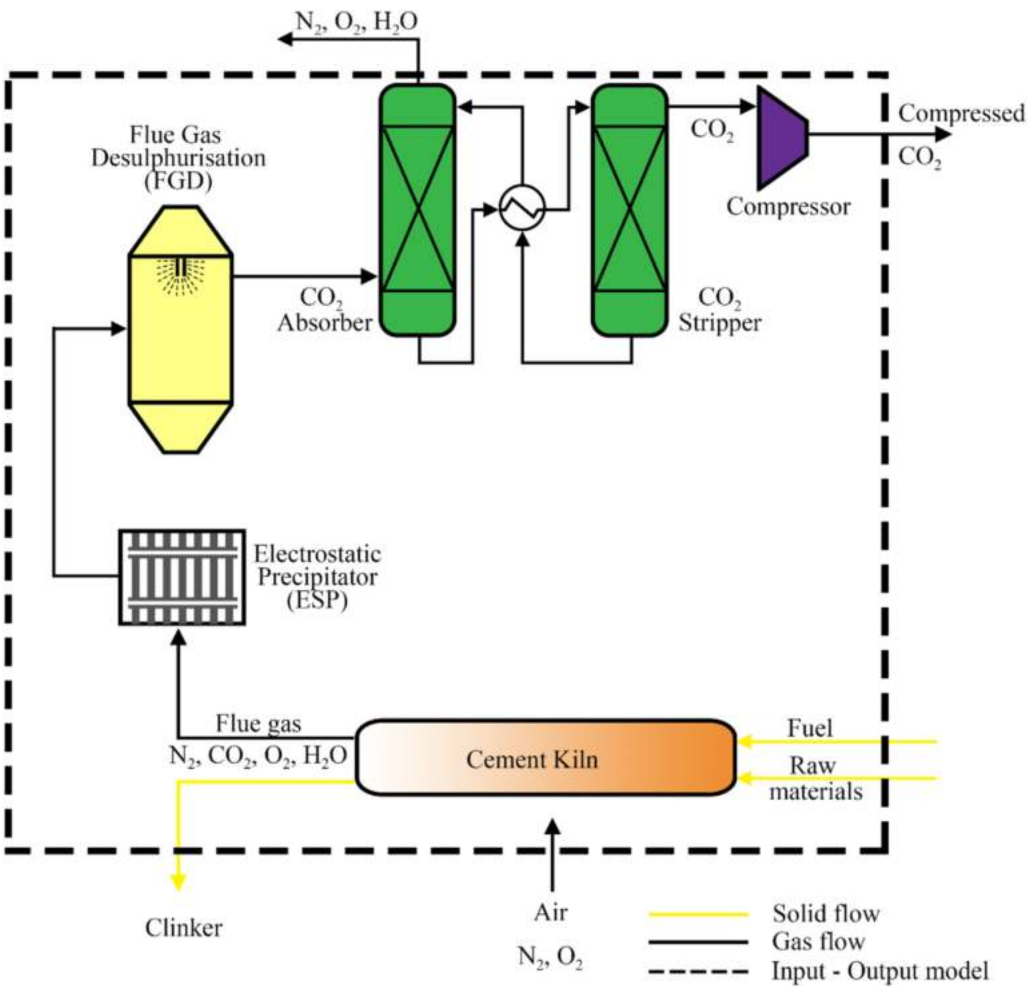

Fig. C.1 – General process flow of a cement plant with post-combustion carbon capture.

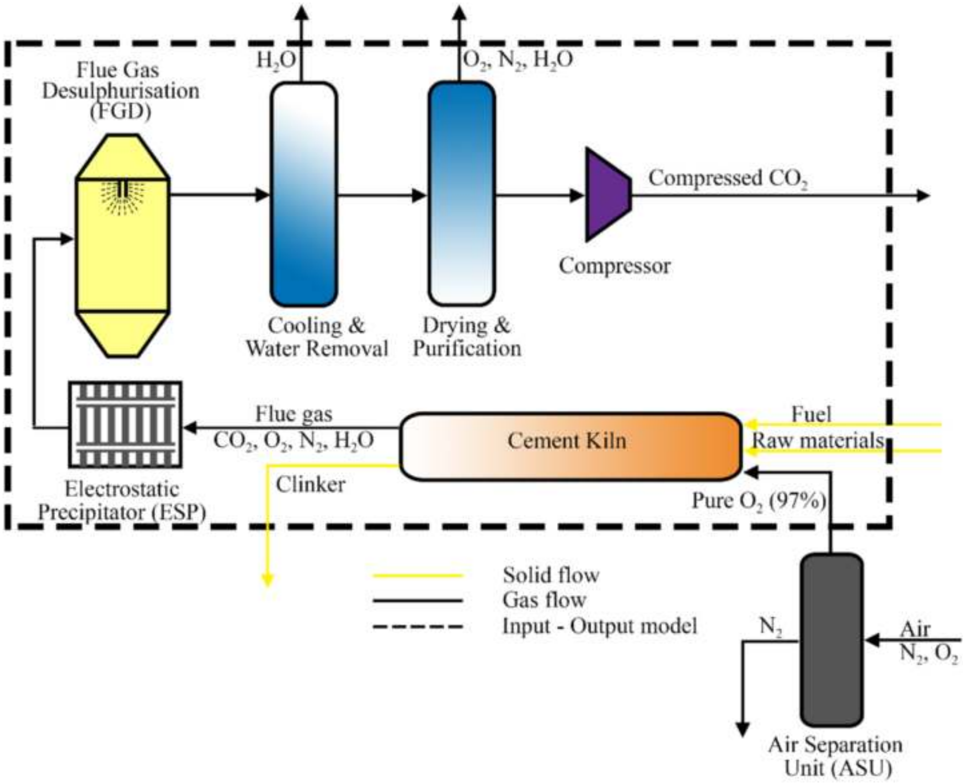

Fig. C.2 – General process flow of a cement plant with oxyfuel combustion carbon capture.

APPENDIX D

This section gather the data used for this study.

See Table D.1-D.6.

Choosing M constant value.

In principle, the value for big M constant selected should be sufficiently big but not too big to avoid complications during the solving process. Thus, for simplicity, the M values chosen in this study are about twice the corresponding variable typical values. In Eqs. 12–13, the corresponding variable is m_{air}. The air demand acquired from Nhuchhen et al. (2021) is 1591 Nm^3/t clinker, which equals to 2046.87 kg/t clinker with the assumption of 23.2 mass% O_2 and 76.8 mass% N_2 of air. The M value set for Eqs. 12–13 was then chosen as 4000 kg/t clinker. As Eqs. 17–20 correspond to the mass of fuels, the M value used was 60,000 kg/t clinker, higher than the availability of fuels. Based on 900 kg/t clinker CO_2 emission from Benhelal et al. (2013), the M value for Eqs. 31–32 was set at 2000 kg/t clinker.

How Infeasible Solution is achieved.

Infeasible solution (IS) is achieved once a 100% reduction target is set. In Eq. 30, $m_{CO_2} - \sum_{c\in Carbon\ capture} \vartheta_c \psi_c \le (1 - FCO_2/100)CO_{2Base}$, when 100 % reduction is applied, the mass of carbon emission on the left-hand side of the equation must be less or equal to 0 kg/t clinker. Assuming that co-processing, all kiln improvements, and post combustion are selected as mitigation measures, the least value that can be achieved by the process pathway is 15.35 kg/t clinker, which is greater than 0 kg/t clinker required by 100 % reduction target, resulting in an infeasible solution.

Table D.1 – Raw materials data (Kookos et al., 2011; Díaz et al., 2011, U. S. Geological Survey, 2014, Willett, 2011).

Raw materials, j		Limestone	Clay	Sand	Iron source
Cost, C (USD/kg)		0.02	0.04	0.01	0.01
Chemical Formula	Molecular weight, MW	Mass fraction dry material, ω			
SiO_2	60.08	0.1	0.5	0.8	0.01
Al_2O_3	101.961	0.01	0.1	0.05	0.005
Fe_2O_3	159.69	0.01	0.11	0.025	0.95
CaO	56.0774	0.5	0.04	0.03	0.02
MgO	40.3044	0.005	0.12	0.02	0.01
K_2O	94.196	0.003	0.0022	0.015	0.001
Na_2O	61.97894	0.001	0.014	0.005	0.001
SO_3	80.066	0.0001	0.001	0.0005	0.003
LOI	–	0.371	0.1128	0.05	0.002

Table D.2 – Fuels data (Kookos et al., 2011).

Parameters	Fossil fuels, k		Alternative fuels, l			
	Coal	PC	RDF	SS	TDF	MBM
Net Calorific Value, NCV (GJ/kg)	0.03	0.033	0.026	0.016	0.032	0.017
Oxygen required, ST (kg O_2/kg)	2.32	2.67	2.16	1.59	2.34	1.45
Emission Factor, CEF (kg CO_2/kg)	2.75	3.30	2.20	1.58	2.56	1.54
Environment effects factor, Ø	0	0	0.5	0.5	0	1
Cost, C (USD/kg)	0.11	0.10	0.05	0.04	0.03	0.02
Availability, A (t/y)	–	–	30000	30000	20000	20000
Mass fraction of dry material, ω						
C	0.75	0.9	0.6	0.43	0.7	0.42
H	0.05	0.03	0.1	0.09	0.07	0.06
O	0.08	0.01	0.25	0.272	0.1	0.153
S	0.003	0.04	0.01	0.002	0.015	0.004
N	0.0001	0.01	0.001	0.018	0.005	0.075
Ash	0.1	0.01	0.1	0.2	0.1	0.3
Mass fraction of ash						
SiO_2	0.525	0.4	0.4	0.4	0.22	0.005
Al_2O_3	0.3	0.1	0.25	0.15	0.1	–
Fe_2O_3	0.1	0.07	0.02	0.05	0.015	–
CaO	0.03	0.01	0.2	0.2	0.11	0.2
MgO	0.01	0.03	0.025	0.025	0.015	–
K_2O	0.015	0.005	0.01	0.01	0.01	0.005
Na_2O	0.005	0.005	0.01	0.01	0.01	–
SO_3	0.015	0.02	0.02	0.01	0.15	–
Cl	0.001	0.001	–	–	0.004	–
NiO	–	0.15	–	–	–	–
V_2O_5	–	0.2	–	–	–	–
ZnO	0.0002	0.00005	0.000085	0.0007	0.35	–
Cd	0.00001	0.000001	0.000001	0.000005	0.000005	–
Pb	0.0002	0.00001	0.00005	0.003	0.00005	–
Tl	0.000004	0.00008	–	–	0.0000001	–
As	0.000002	0.000005	0.000005	0.00002	0.0000001	–
Hg	–	–	0.000002	0.000015	–	–

PC, Petroleum coke
RDF, Refuse derived fuel
SS, Sewage sludge
TDF, Tyre derived fuel

Table D.3 – Clinker analysis data (Kookos et al., 2011).

	Bogue value, B_p					
Oxides, o / Phases, p	SiO_2	Al_2O_3	Fe_2O_3	CaO	Mass Limit, M_P (%)	
					Lower	Upper
C_3S	– 7.6	– 6.72	– 1.43	4.07	50	60
C_2S	8.6	5.07	1.08	– 3.07	10	35
C_3A	0	2.65	– 1.69	0	1	15
C_4AF	0	0	3.043	0	1	15

Table D.4 – Co-process data (Kookos et al., 2011).

Parameters	Alternative fuels, l			
	RDF	SS	TDF	MBM
Capital cost, FCI_l (USD/t clinker)	0.108	0.108	0.162	0.162
Operating and maintenance cost, OM_l (USD/kg fuel)	0.0054	0.0054	0.0108	0.0108

Table D.5 – Kiln improvements data (Worrell, and ECRA et al., 2008, 2009).

Measures, r	FCI_r (USD/t clinker)	Thermal Improvements, TDI_r (%)*
Improved kiln refractories	0.25	19
Improved process control in kiln	1.70	6
Increase preheater stage (5 → 6)	0.88	3

* Improvement in thermal energy obtained from sources are expressed in GJ/t clinker, thus, using 3.25 GJ/t clinker as the basis of thermal energy demand, TDI_r is calculated as $\frac{[\text{improvement in} \frac{GJ}{t} \text{clinker}]}{3.25 \frac{GJ}{t} \text{clinker}} \times 100\%$

Table D.6 – CCS data (IEAGHG, and Chen et al., 2008, 2004*).

Capture system, c	Oxyfuel combustion	Post combustion
Capital cost, FCI_c (USD M)	50.04	205.96
Operating and maintenance cost, OM_c (USD M/yr)	8.49	23.99
System removal rate, ϑ_c (%)	61	98*
Effect of post combustion capture selection, N_c	1	0

* Chen et al. (2004); range of 90 – 98 %. Highest removal is used.

APPENDIX E

See Fig E.1-E.4.

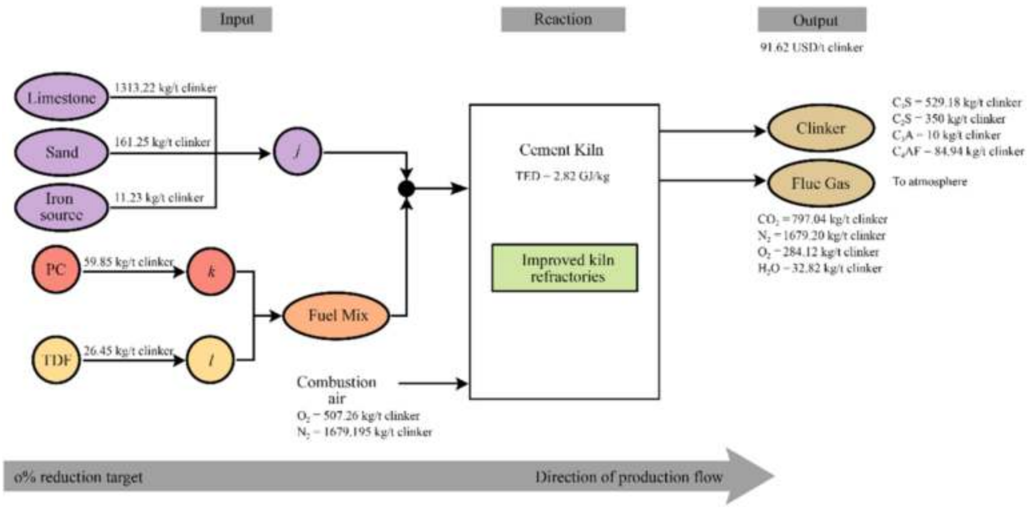

Fig. E.1 – Technological pathways for 0 % CO_2 reduction target. *j* denotes the raw materials, *k* denotes the fossil fuels, *l* denotes the nonfossil fuels.

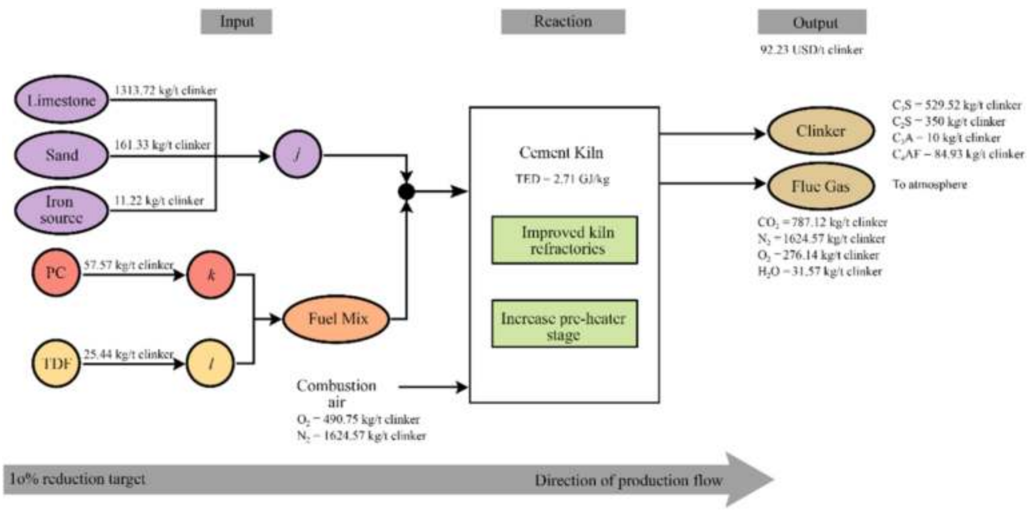

Fig. E.2 – Technological pathways for 10 % CO_2 reduction target. *j* denotes the raw materials, *k* denotes the fossil fuels, *l* denotes the nonfossil fuels.

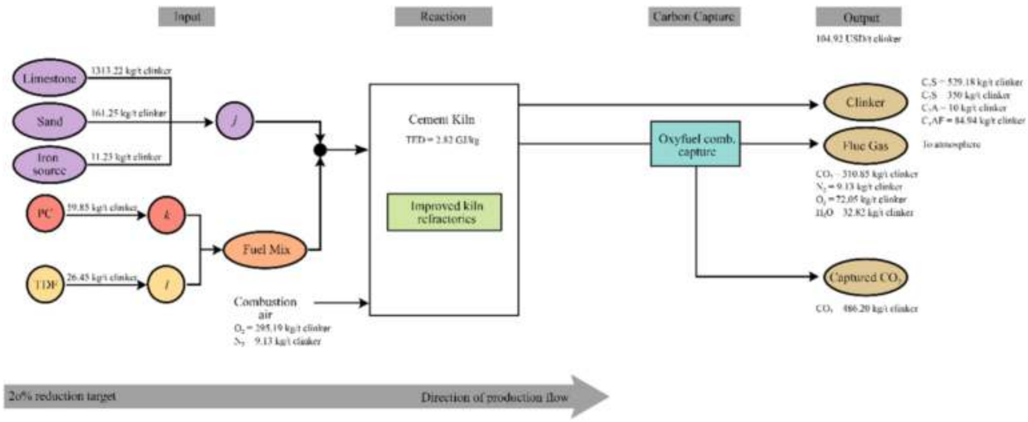

Fig. E.3 – Technological pathways for 20 % CO_2 reduction target. *j* denotes the raw materials, *k* denotes the fossil fuels, *l* denotes the nonfossil fuels.

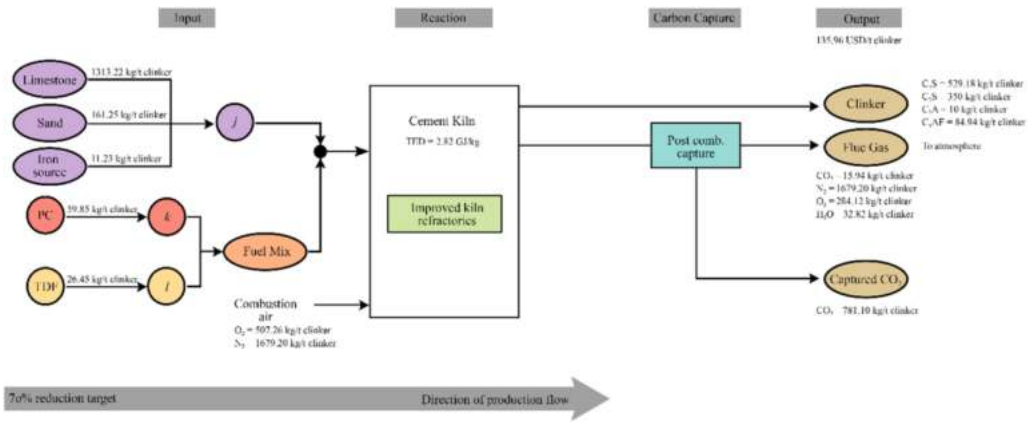

Fig. E.4 – Technological pathways for 70 % CO_2 reduction target. *j* denotes the raw materials, *k* denotes the fossil fuels, *l* denotes the nonfossil fuels.

At different reduction target, different technological pathways are achieved. Below shows the different technological pathways.

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