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Production-Process Simulation and Life-Cycle Assessment of Metakaolin as Supplementary Cementitious Material

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Abstract: An environmental assessment of metakaolin as a supplementary cementitious material (SCM) through an integrated production-process-simulation and Life-Cycle-Assessment (LCA) approach is presented in this work. Initially, process simulation models were developed to reproduce the basic stages of the metakaolin production process. The effect of various operational parameters and scenarios, such as calcination temperature, moisture of raw material and associated drying, exhaust gas recirculation and the use of alternative-fuel combustion to provide kiln heat requirements, was evaluated. The resulting process heat-demand and CO_2-emission computations were used as inputs in the LCA along with upstream literature data using a cradle-to-gate approach. LCA results focused on the most relevant environmental impact category of cement production, the Global Warming Potential (GWP (100)). The major findings showed a strong influence of process temperature and kaolin humidity on the lifecycle GWP, since both parameters affected not only the core-process heat demand but also the upstream impact related to fossil-fuel extraction, processing, transportation and distribution. Recirculating the exhaust provided a GWP reduction potential of up to 19%. In all examined production scenarios, metakaolin depicted a lower Global Warming Potential compared to clinker due to the avoidance of emissions related to limestone calcination. As regards the impact contribution of fuels, coal was responsible for higher onsite emissions and natural gas indicated higher upstream emissions. The GWP (100) could be further reduced when alternative waste fuels such as plastic waste, MSW (municipal solid waste) and tires were used. The LCA results have been cross-checked with previous literature reports, and the corresponding deviations are accordingly explained. In any case, the LCA results of different studies are rarely directly comparable due to the numerous assumptions required, which cannot be identically replicated.

Keywords: metakaolin; supplementary cementitious materials; process modeling; life-cycle assessment; environmental impact

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1. Introduction

In 2019, the European Green Deal set the goal of zero net emissions of greenhouse gases by 2050 [1]. Supporting Europe in achieving its strategic objectives, the European Cement Association (CEMBUREAU) published a roadmap for reaching climate neutrality along the cement and concrete value chain [2]. The cement sector is the third-largest industrial energy consumer, comprising 7% of the global industrial energy use (10.7 exajoules [EJ]) [3]. Furthermore, cement production is associated with the use of large amounts of resources and is responsible for 5–7% of the global CO_2 emissions [4]. The production of 1 tonne of Portland cement results in the emission of 0.83 tonnes of CO_2 [5]. Despite its high carbon footprint, cement is expected to remain an essential material in building and infrastructure construction [6]. Measures towards reducing the environmental impact of cement industries are necessary and include: (a) the use of alternative fuels [6,7] and (b) the use of metakaolin (MK) and other cementitious materials (Supplementary Cementitious Materials—SCM) to partially substitute cement [8].

The substitution of cement by 5–10% of MK can significantly improve the mechanical properties and durability of concrete due to its enhanced pozzolanic properties (pozzolanic activity is defined as the ability of a material to react with calcium hydroxide ($Ca(OH)_2$) in the presence of water and produce materials with cementitious properties.) [9–12]. MK (Al_2O_3:$2SiO_2$) is a natural pozzolan produced by the thermal treatment of kaolin ($Al_2Si_2O_5(OH)_4$) at temperatures within 600–850 °C [8,13]. During calcination, the kaolin structure collapses with the release of bound water (dehydroxylization) and results in the formation of an amorphous phase that corresponds to MK [14]. In an experimental study by Ilić et al. [12], it was shown that a near-complete level of dehydroxylization (~97%) can be achieved at a minimum temperature of 650 °C. This dehydroxylization rate was reached after 90 min of heating time, while no additional transformation occurred at longer heating times. Higher temperatures required less heating time in order to reach the same dehydroxylization degree (e.g., 97% achieved at 700 °C after 30 min of heating). However, Ilić et al. [12] concluded that the optimal conditions of the treatment are a calcination temperature of 650 °C and a heating time of 90 min. The process temperature highly influences the composition of the product, since above 900 °C, recrystallization occurs and silicon-spinel and subsequently mullite are produced, both of which depict low pozzolanic activity [8,12]. No specific information regarding the effect of calcination time and moisture content on the product composition was found in the open literature.

It has been shown that materials with more than 40% kaolinite content are abundant on Earth [15] and their proper calcination can lead to the production of MK [11,12]. Kaolin is mostly calcined in rotary kilns (a method frequently implemented in the USA, Brazil and India) or using fluidized bed processes, which allow the reduction in calcining time from hours to minutes [8]. Information on industrial MK production units is limited in the literature. A relevant paper presented a wet-process clinker rotary kiln, which was accordingly modified to process low-grade kaolinitic clay extracted from a deposit located in Pontezuela, Cuba [16].

Apart from the improved strength and higher durability associated with its pozzolanic properties, the major driving force behind incorporating MK in the cement industry is the potential for lower carbon footprints [17]. In principle, this is expected since direct CO_2 emissions emerging from $CaCO_3$ calcination in the typical cement production route can be avoided [18]. Various studies have elaborated on the environmental impact of geopolymers, in particular MK. Habert et al. [19] examined cement substitution with geopolymers and concluded that although the reduction in Global Warming Potential (GWP) when using MK is evident, the relevant decrease is less than a factor of four when compared to 1990 emissions. Heath et al. [20] showed that substituting Portland cement (PC) binders with alternative binders made of geopolymers reduces GWP by up to 40% (although other impact categories may increase). McLellan et al. [21] demonstrated the potential of geopolymers (including MK) to reduce the climate change impact, highlighting at the same time the effect of feedstock sources on the potential impacts. In the same work, it was pointed out that MK was the most difficult material to find information or data for. Life-cycle inventories for sodium silicates production were compiled by Fawler et al. [22] using data obtained from twelve west European silicate producers comprising 93% of the total alkaline silicate production in the area. Other studies have addressed related subjects, such as the LCA of geopolymers [23] or the environmental assessment of "green" concretes [24], but have not specifically focused on MK.

The objective of this work is to present an integrated process modeling–LCA approach for the energetic and environmental evaluation of MK production. This study focuses on highlighting the impact of specific MK production-process operational parameters and scenarios on emissions emerging throughout MK's life cycle. Therefore, the developed computational process models presented here aim to provide reliable predictions of heat demand (through fuel consumption) and CO_2 emissions to be subsequently used as inputs in the LCA studies. Since there is a scarcity of reliable industrial data in the open literature and, in general, most LCA studies use fixed generic data from available databases, this integrated approach provides insight into the problem assessed as well as flexibility in the results acquired. A more comprehensive, accurate and customized LCA is thus achieved, as demonstrated in previous relevant works [25,26].

2. Materials and Methods

2.1. Process Modeling of MK Production

Although process modeling has been extensively used for the evaluation and optimization of industrial processes, including cement manufacturing [27–31], respective models addressing MK production cannot be found in the literature. To this end, the developed models aim to reproduce the basic thermal treatment stages of an MK production unit, considering that the calcination of kaolinite takes place in a rotary kiln at temperatures between 650 and 850 °C via the following reaction [8]:

$$Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O \rightarrow 2SiO_2{\cdot}Al_2O_3 + 2H_2O \quad (1)$$

Parametric studies took place to investigate the effect of: (a) calcination temperature, (b) raw material moisture, (c) exhaust gas recirculation (EGR) and (d) different fuel utilization (natural gas, solid fuels, alternative fuels) on the predicted process heat demand (fuel consumption) and CO_2 emissions.

Two basic process-model configurations were developed using: (a) natural gas (NG) combustion and (b) solid fuels (coal, petcoke and alternative fuels) combustion to provide heat to the kiln. All presented models were developed in Aspen Plus® (AspenTech, Bedford, MA, USA), a chemical process simulation software that solves energy and mass balances, kinetics and thermodynamics of chemical reactions by implementing mathematical modules associated with a wide range of industrial applications and components.

2.1.1. MK Production Process Model with NG Combustion (MK-NG Configuration)

The process models presented in this section use a stoichiometric NG–air mixture to provide the required calcination heat (MG-NG configuration). NG is represented by CH_4. Alternative versions (baseline and EGR models) were developed to examine different operational scenarios.

Baseline Model

This model reproduces a standard MK production process layout where the thermal treatment of kaolinite is carried out in a wet-process rotary kiln [16]. This model corresponds to the simplest configuration of the MK production chain and does not include the drying and exhaust gas recirculation (EGR) stages. The exhaust gas stream produced by the NG combustion flows counter-currently to the raw material feed.

The following assumptions are considered (they also apply to all process models depicted in this work):

- Ambient atmospheric pressure conditions at each stage;
- Ambient temperature (25 °C) for the inlet streams of raw kaolinite and CH_4;
- MK is treated as a mixture of Al_2O_3 and SiO_2;
- The raw material that reacts to form MK consists only of kaolinite (also defined as pure kaolin) ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$). Other substances that kaolin rock may contain are considered negligible;
- The raw-meal particle distribution has not been considered (MIXCISLD stream classes);
- A uniform calcination temperature is considered in the kiln.

The baseline-model flowsheet is presented in Figure 1. An RGIBBS reactor (block COMBUSTION) has been implemented to account for the combustion of the premixed stoichiometric NG(CH_4)–air mixture, assuming that all products reach equilibrium. The combustion product mixture (exhaust gas stream) is led to another RGIBBS reactor (block KILN) that corresponds to the rotary kiln where calcination takes place. Chemical equilibrium calculations in the RGIBBS reactors are based on the minimization of the overall Gibbs free energy of a reactive mixture. Downstream of the kiln, a stream containing the produced MK and exhaust gases is cooled down to 200 °C. Subsequently, the MK is separated from the exhaust gas mixture (EGR stream) with the use of a SEPARATOR block. A Design Spec function is set to calculate the fuel (NG-CH_4) consumption required to achieve calcination temperatures inside the kiln within a temperature range between 650 and 850 °C. Further cooling of the MK stream is anticipated downstream, but this was not considered in the model.

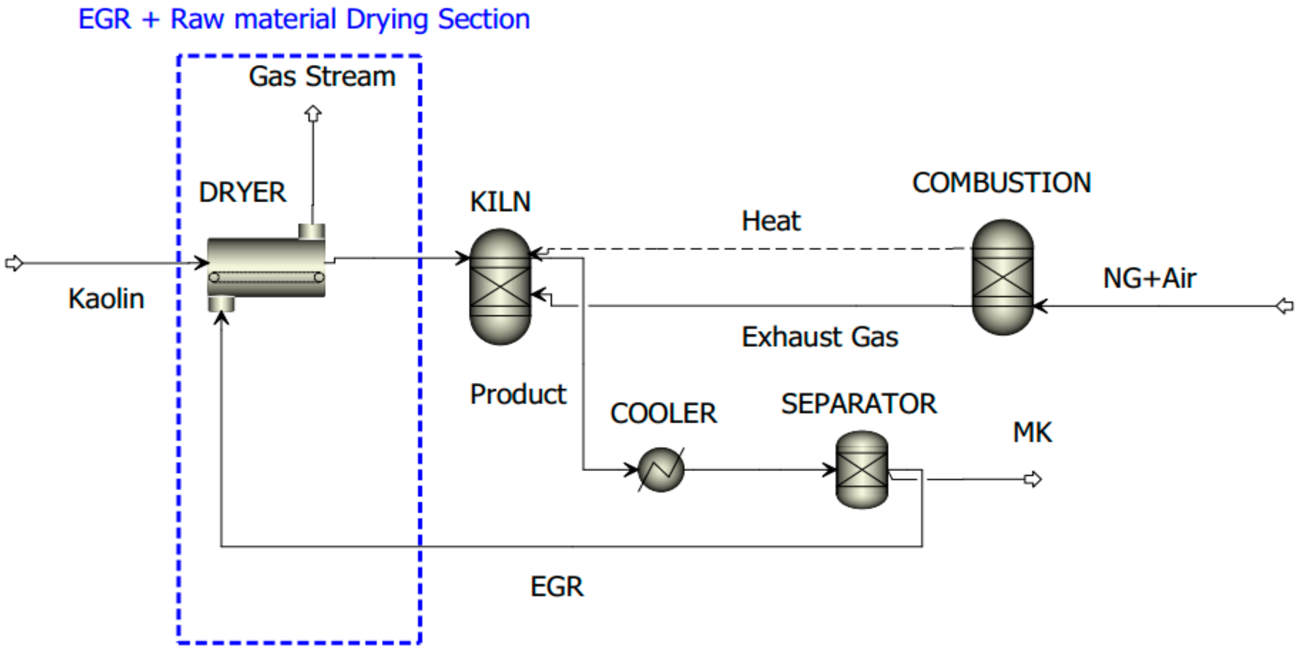

Figure 1. Process-model flowsheet for MK production. Baseline and MK-NG configuration (additional components in blue dashed frame).

EGR+ Raw-Material Drying Model (EGR Model)

The baseline process model has been extended to also consider: (a) a drying stage to remove the raw meal moisture before entering the kiln and (b) an exhaust gas recirculation (EGR) stream aiming to provide the heat required for the drying stage. These modifications have been implemented to formulate a process that reproduces the MK production process described in [13]. It should be noted that EGR (or FGR—Flue Gas Recirculation) is a common practice in the cement industry [32,33] aimed at increasing energy efficiency and mitigating CO_2 emissions.

The drying stage and EGR extensions are highlighted in Figure 1. The following set of blocks and streams have been added to the baseline model and are included in the blue dashed frame: (a) A DRYER block operating at a temperature equal to 175 °C, representative of the drying process [13]. Given that no actual experimental data are available, a shortcut dryer type has been selected. Apart from the drying temperature definition, it is assumed that the raw material is completely dried and enters the kiln with zero moisture content. (b) Downstream of the kiln, the exhaust gas stream, after being separated from the produced MK (MK stream), recirculates (at 200 °C) to be used as the inlet gas stream, providing heat to the dryer. The rest of the model consists of the same blocks, streams and operation characteristics already elaborated in the baseline model.

When the EGR model is implemented, two discrete scenarios can be formulated: (a) The heat required for the drying stage is completely covered by EGR (either from the "EGR" stream or from other waste heat resources of a prospective plant (C-EGR scenario)). In this case, no additional heat requirement is reported at the drying stage, and heat demand and CO_2 emissions are attributed solely to the kiln operation. (b) The heat required for the drying stage is partially covered by EGR (P-EGR scenario), and thus the dryer's net heat duty (as calculated by the process model) must be provided by an additional energy source. Both C-EGR and P-EGR scenarios are further elaborated in the next sections. Similarly (to the baseline model), a Design Spec function is also set to calculate the fuel (NG-CH_4) consumption to achieve calcination temperatures inside the kiln within a temperature range between 650 and 850 °C.

2.1.2. MK Production with Solid-Fuel Combustion (MK-SF Configuration)

The process models presented in this section use solid fuels to provide the required calcination heat. The solid fuels examined in this work are coal (lignite and high-rank bituminous—HRB), petcoke and three alternative fuels (tires, municipal solid waste (MSW) and plastic waste). Their proximate and ultimate analyses and heating values on a dry basis are depicted in Table 1. The heating values of selected alternative fuels (tires, MSW, plastic waste) were retrieved from [31]. The respective heating values of coal (lignite, HRB) and petcoke were calculated from their elemental analyses with the use of the following Dulong-type formula [34]:

$$HV(MJ/kg) = 0.336C + 1.418H - 0.145O + 0.0941S \quad (2)$$

Table 1. Proximate and elemental analyses of solid fuels [31,35,36].

Fuel	Coal (HRB)	Coal (Lignite)	Petcoke	Tires	MSW	Plastic Waste
Proximate analysis (wt. % dry basis)						
Moisture	0	0	0	0.62	31.2	0.6
Ash	7.40	6.09	1.25	4.81	35.17	0.4
Volatile Matter	27.60	47.01	12.63	67.06	64.83	94.77
Fixed Carbon	65.00	46.90	86.12	28.13	0	4.83
Elemental analysis (wt. % dry basis)						
C	82.26	66.68	87.05	84.39	34.88	77.02
H	4.77	4.88	3.89	7.13	4.65	12.14
N	1.01	2.82	2.03	0.24	1.02	0
S	0.83	0.38	4.05	0.01	0.15	1.09
Cl	0	0	0	1.24	1.02	0
O	3.73	19.16	2.43	2.18	23.11	4.92
Heating Value (MJ/kg)	33.9	26.6	34.8	37.8	15.4	41.5

The MK-SF configuration is presented in Figure 2. Different versions were developed to provide flexibility in the combined use of the basic solid fuel (coal or petcoke) with alternative fuels. The addition of an alternative-fuel section to partially substitute the basic solid fuel and provide a portion of the kiln heat demand is highlighted in the model flowsheet via a blue dashed line frame. All solid fuels were modeled as non-conventional solids. HCOALGEN and DCOALIGT property models were selected to calculate their enthalpies and densities, with input provided by each fuel's individual elemental analysis. The proposed MK-SF configuration depicts sections that are similar to those in the MK-NG configuration, such as those related to MK production in the kiln and the downstream cooling and separation stages. It also adopts the EGR and raw-material-drying operational scenarios. However, the following differences must be noted: (a) The NG + air stream of the MK-NG configuration is replaced by two streams (basic-fuel inlet stream and alternative-fuel inlet stream, respectively), each of which feeds an RYIELD reactor, allowing non-conventional fuels to decompose into conventional components. One calculator block is linked to each RYIELD reactor. In this block, the proximate and elemental analyses of each solid fuel are used to convert the unconventional solid-fuel composition to C, H_2, H_2O, O_2, N_2, S and Cl_2, which are subsequently mixed with air and burned in the COMBUSTION RGIBBS reactor. (b) The air stream used for combustion is separately directed to the

COMBUSTION block (RGIBBS reactor). To establish a common basis for calculations, the air flow rate predicted by the MK-NG (EGR model) simulations is also used as input in the MK-SF models. Thus, a different air flow rate for each examined kiln temperature (within the 650–850 °C range) is implemented, and a Design Spec function is used to determine the solid fuel required to achieve the set calcination temperatures. The Design Spec function predicts the fuel consumption corresponding to stoichiometric solid fuel–air combustion for the same air mass flow rate calculated for the NG combustion cases.

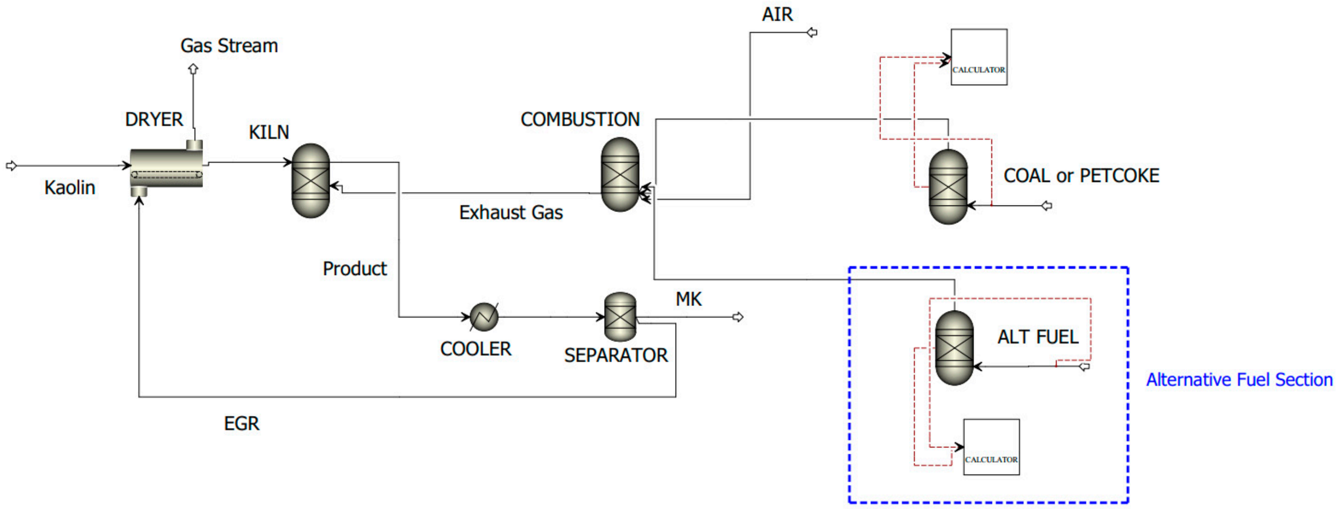

Figure 2. Process-model flowsheet for MK production (MK-SF configuration).

It should be noted that the proposed models do not reproduce a real MK production chain in detail since industrial data and information were not available. Furthermore, utilities, heat exchangers, grinding mills for size reduction and other equipment potentially used within the process were not considered. The focus was placed on predicting thermal energy requirements and CO_2 emissions associated with the drying and calcination of raw materials. Appropriate assumptions to consider additional auxiliary thermal energy and electricity requirements are elaborated in the LCA section.

2.2. LCA Modeling

The environmental impact of each production process is evaluated by implementing the Life-Cycle-Assessment methodology and using the SimaPro software (version 9.3, Amersfoort, The Netherlands). The SimaPro software package is used to compile life-cycle inventories and perform impact assessment studies. This software was chosen over alternative options due to its user-friendliness, the embedded LCA database "Ecoinvent", the well-documented datasets offered and the long-term successful application by the authors [37]. Nevertheless, its usage comes at a considerable cost. A relevant review [38] provides a thorough comparison of the features of all available LCA software.

- The main database that was used for the simulations is the Ecoinvent library, version 3.8 (released in November 2021);
- The impact assessment method used to provide the evaluation results is the IPCC 2021 method (v.1.00). It is the successor to the IPCC 2013 method, which was developed by the Intergovernmental Panel on Climate Change. It contains the Global Warming Potential (GWP) climate change factors of the IPCC, with a timeframe of 100 years.

The goal of the developed LCA approach is to assess environmental impact indicators of the production process of MK and perform comparisons to the reference case of clinker. To this end, the different scenarios of MK production simulated in Aspen Plus are analyzed using the Life-Cycle-Assessment (LCA) method in the SimaPro software. The acquired results reflect the corresponding Global Warming Potential GWP (100) impact (kg of CO_2

equivalent). This indicator refers to the functional unit of this study, which is the production of 1 kg of MK. The GWP was selected from the impact categories generally available since it corresponds to the most prominent environmental issue of cement manufacturing: carbon emissions.

Electricity generation mix and natural gas import data refer to the Greek geographical boundaries after 2020. For this purpose, new inventories have been compiled and used along with existing Ecoinvent inventories/processes. Table 2 describes the origin of the data used in the simulations, which is either from Ecoinvent inventories (E), results from process modeling (PM) or data from other sources (O).

Table 2. Origin of data used in LCA calculations (PM—process model results; E—existing Ecoinvent inventories; and O—custom-made inventories from other literature sources).

MK (All Cases)	Clinker
Fuel consumption (PM, O)	Fuel consumption (E, O)
On-site emissions (PM))	On-site emissions (E)
Electricity consumption (O)	Electricity consumption (O)
Upstream processes/emissions (E)	Upstream processes/emissions (E)

The software libraries do not contain MK. Thus, a corresponding dataset was compiled by adapting an existing Ecoinvent dataset related to clinker. It is assumed that the same clinker-producing plant is used for MK production. The raw material inputs of clinker are deleted and replaced by kaolinite. For 1 kg of MK, 1.162 kg of pure kaolin (kaolinite) is required. This value is calculated with Aspen Plus and is also verified from the mass balance in the calcination reaction.

The following assumptions and adaptations are made for all MK production cases:

- It is assumed that the same rotary kiln is utilized and that all other electricity consumptions remain constant. The refractory, the cement plant and the industrial machines are assumed to be the same as in the case of clinker.
- For MK production with NG combustion, fuel consumption is assigned to natural gas, even though pure methane has been used for the process simulations.

A limitation of using the Ecoinvent library is that it focuses on cases of obsolete data (e.g., the Greek electricity production mix before 2015) or generic European data. In this study, it is assumed that the products are produced in Greece. As a result, it is necessary to update the processes to reflect the modern Greek energy market. The natural gas (NG) import mixture of Greece is accordingly updated. The required data are obtained from the official website of DEPA (Public Gas Company, Athens, Greece), which is the main natural gas importer in Greece [39]. According to that source, during the summer of 2022, the NG import sources in Greece were the following:

– 0.4 TWh (6%) through Sidirokastro (on the Greece–Bulgaria border), from which Russian natural gas enters;
– 0.3 TWh (5%) from Kipoi in Evros (on the Greece–Turkey border), from where quantities from the Turkish gas market mix arrive;
– 1.7 TWh (28%) through Nea Mesimvria, the interconnection point of ESFA with the TAP pipeline that transports Azeri natural gas;
– 3.7 TWh (61%) via Agia Triada (opposite Revythoussa Island), importing LNG (liquefied natural gas).

Due to a lack of information regarding the origin of the natural gas imported from Turkey and Azerbaijan, the following two assumptions are made:

1. Emissions during the mining of natural gas are the same (in analogy) as in the case of Russia.
2. Emissions during the transportation of natural gas are the same (in analogy) as in the case of Russia.

As a result of the aforementioned assumptions, natural gas imported into Greece is assumed to consist of 49% natural gas originating from Russia and 51% natural gas originating mostly from the USA and imported as LNG.

Regarding the electricity supply, the Ecoinvent database contains data regarding the electricity production mix in Greece. However, this information originates from data gathered before 2015 and is outdated, mainly due to new environmental restrictions that have reduced the contribution of lignite generation. Updated data regarding the Greek electricity mix are acquired from DAPEEP [40] (Administrator of Renewable Energy Sources and Guarantees of Origin; official data are only available in Greek).

According to DAPEEP, the Greek electricity production mix for the year 2021 was produced from:

- 40.5% NG combustion;
- 11.4% lignite combustion;
- 19.2% wind power;
- 11.5% hydroelectric power;
- 7.0% oil combustion;
- 9.3% solar power;
- 1.1% biomass combustion.

Apart from domestic production, a small percentage of the electricity consumed was imported from neighboring countries (Italy, Bulgaria and North Macedonia). The available data consider the respective contributions.

This study follows the cradle-to-gate modeling approach, which refers to system boundaries starting from the extraction of raw materials and ending at the finished product exiting the manufacturing facility. The corresponding system boundaries, along with the input and output flows considered, are presented in Figure 3.

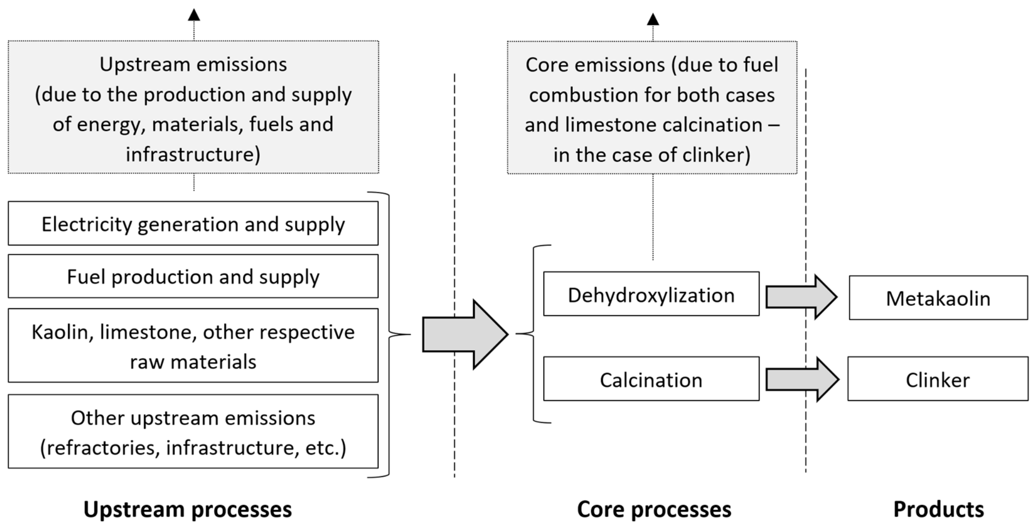

Figure 3. System boundaries and input/output flows considered.

3. Results

3.1. Process-Modeling Results

The results obtained from simulations implementing the proposed models are presented in this section. The heat demand is determined by the process operational parameters (kiln temperature, raw material moisture content) and scenarios (Baseline/EGR) and does not depend on the fuel used for combustion. Therefore, only the MK-NG configuration process models are utilized to predict the heat required in the calcination kiln and provided by NG combustion. Subsequently, simulations with all the developed process models (from both MK-NG and MG-SF configurations) were performed, resulting in the calculation of process CO_2 emissions. A comparative assessment of the CO_2 emissions emerging from the combustion of all examined fuels (NG, solid and alternative fuels) follows.

3.1.1. Heat-Demand Predictions. Parametric Studies

The effect of calcination temperature on the process heat demand emerging from NG combustion per tonne of produced MK has been examined and is presented in Figure 4. The calculations were performed for a kiln temperature range between 650 and 850 °C, which is typical of the MK production process. Two discrete models referring to respective operational scenarios were considered: (a) baseline model and (b) EGR model (with drying). In all cases, an average moisture content equal to 15 wt% [13] was attributed to the raw material (kaolinite). As expected, heat demand increased with kiln temperature. When the baseline model was implemented, heat-demand predictions varied with increasing temperature from 0.89 MWh/tonne$_{MK}$ (at 650 °C) to 1.25 MWh/tonne$_{MK}$ (at 850 °C). When the second scenario (EGR model) was implemented, the complete drying of the raw material (at 175 °C) before entering the kiln was assumed. However, calculations showed that the implemented EGR stream mass flow rate (at 200 °C) was not sufficient for the complete drying of the raw material at 175 °C, and an additional heat demand of 0.05 MWh/tonne$_{MK}$ (for all implemented kiln temperatures) would be required (as extracted from the calculated net heat duty value of the dryer block in the EGR model). As expected, fuel consumption decreased with EGR. Therefore, a reduction in the predicted process heat demand was shown, with results ranging between 0.58 MWh/tonne$_{MK}$ (at 650 °C) and 0.84 MWh/tonne$_{MK}$ (at 850 °C). An average decrease of 34% in heat demand was thus achieved.

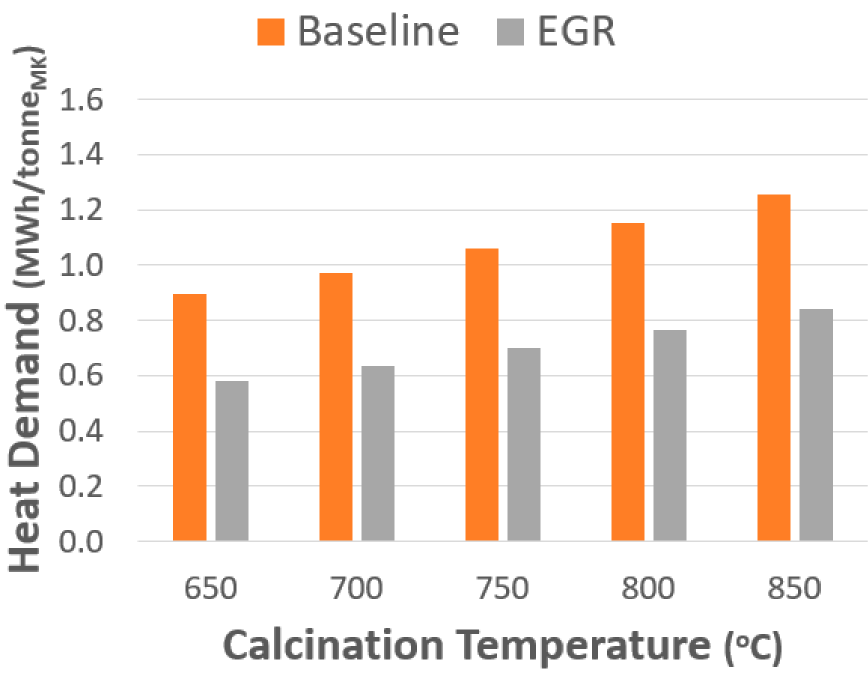

Figure 4. Calculated MK production process heat demand (MWh/tonne$_{MK}$). Impact of calcination temperature. (Fuel: NG; reference moisture content of kaolinite: 15% wt).

The effect of raw material moisture content on the MK production process heat demand is examined in this section. Upon extraction, clays can have a moisture content greater than 30% (by weight). In such cases, they are initially exposed to air and sun to achieve a first level of natural drying, resulting in a reduction in raw material moisture to within 10–20% wt. [41]. If natural drying is not adequate or feasible, various alternative types of mineral processing industry dryers can be used (such as rotary, fluidized bed, screw, etc.) to reduce the water carried in the raw material, as reviewed by Wu et al. [42]. However, most of these dryers consume fossil fuels, leading to additional process energy consumption and emissions. Therefore, as proposed by Wu et al. [42], heat recovery must be primarily evaluated if high-temperature exhaust gases are available.

Typical values of kaolinite moisture in raw material ready to be processed for MK production have been reported to be between 7 and 20% [13]. Figure 5 presents the predicted heat-demand values for both the baseline and EGR operational scenarios, considering kaolinite moisture content ranging between 5 and 30% wt., with the latter serving as a worst-case scenario. The calculations were performed at a reference kiln temperature equal to 750 °C. As anticipated, heat demand increased with kaolinite moisture content, particularly in the baseline case. In this case, the predicted heat demand varied between 0.82 (5% wt. moisture) and 1.54 MWh/kg_{MK} (30% wt. moisture). The respective heat-demand values with EGR were evidently lower and varied between 0.67 (5% wt. moisture) and 0.75 MWh/kg_{MK} (30% wt. moisture). Given that, in the EGR model, a dried kaolinite flow stream is assumed to enter the kiln, the additional heat required in higher moisture content cases is directed to the drying stage. An average decrease of 34% in heat demand is achieved when exhaust gas recirculation is applied, proportionally increasing from 18% (5% wt. moisture) to 51% (30% wt. moisture). The lower relative increase in heat demand in the EGR scenario is due to the lower temperatures (up to 175 °C) required for the dryer operation.

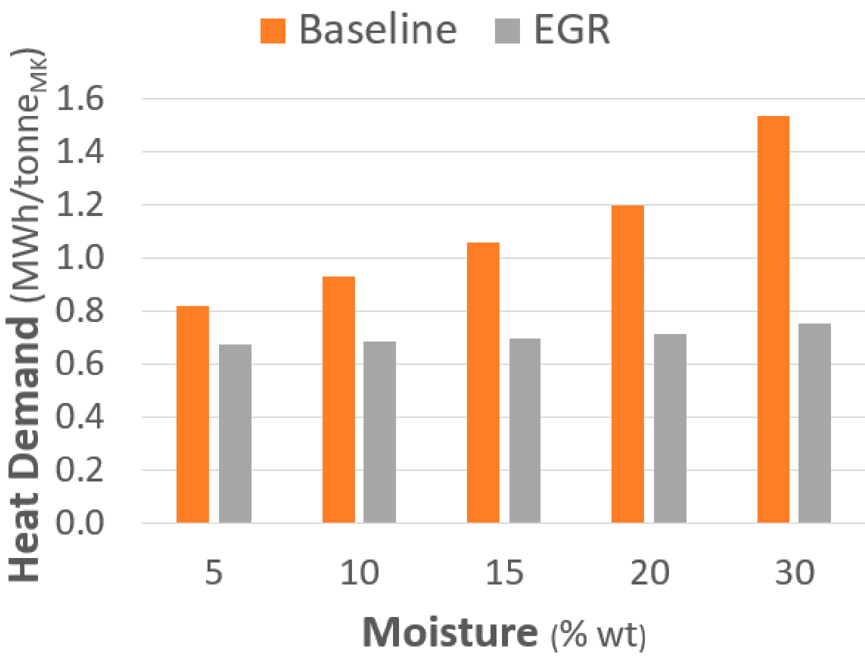

Figure 5. Calculated MK production process heat demand (MWh/$tonne_{MK}$). Impact of raw material moisture content. (Fuel: NG; reference kiln temperature: 750 °C).

Since detailed MK production industrial data were not available, the validation of the developed process models was fulfilled by comparing the heat-demand computational results with reference values obtained from the literature. It has been suggested that the energy demand for MK production is approximately equal to 2 GJ/$tonne_{MK}$ (0.56 MWh/$tonne_{MK}$) [21]. This estimation was calculated based on heating kaolin to 700 °C and assuming the evaporation of all water formed by dehydrolysis with a heat transfer and fuel utilization efficiency of 65%. An MK-production prefeasibility study [43] assumed a demand of 2.5 GJ/$tonne_{MK}$ (0.69 MWh/$tonne_{MK}$) for calcination and 3.3 GJ/$tonne_{MK}$ (0.92 MWh/$tonne_{MK}$) in total. A typical value of 2.72 GJ/$tonne_{MK}$ (0.75 MWh/$tonne_{MK}$) for MK production, including flue gas recirculation, was provided by MK producers via private communication [44]. All the reference values are close to or within the reported range of computational results (between 0.58 and 1.54 MWh/tonne$_{MK}$).

3.1.2. CO_2 Emissions. Parametric Studies

The effect of calcination temperature on the process CO_2 emissions emerging from NG combustion per tonne of MK produced is presented in Figure 6. The calculations were performed for kiln temperatures between 650 and 850 °C for the baseline and both EGR scenarios. As anticipated, the predicted CO_2 emissions followed the same trends as the respective heat-demand calculations. For the baseline model, the predicted CO_2 emissions varied between 177 kg/tonne$_{MK}$ (650 °C) and 248 kg/tonne$_{MK}$ (850 °C). As already elaborated in Section 2.1.1, a heat-demand requirement was predicted by the EGR model for the drying stage. Individual C-EGR and P-EGR scenarios were suggested, leading to different emissions. In the C-EGR case, the additional heat demand was assumed to be covered internally by exploiting other potential waste heat resources of a prospective plant and did not contribute to a further increase in CO_2 emissions. In the P-EGR, the additional heat was covered by an assisting heat source (the combustion of NG as represented by CH_4 was considered), and therefore, CO_2 emissions were higher. Specifically, CO_2 emissions obtained for the C-EGR and P-EGR cases varied between 105 and 158 kg/tonne$_{MK}$ and 115 and 167 kg/tonne$_{MK}$, respectively, in the examined kiln temperature range. Derived from the absolute difference of the emissions of the two cases, a value of 9.5 kg/tonne$_{MK}$ CO_2 was associated with the additional drying from NG combustion (P-EGR). An average reduction in CO_2 emissions of 34% was achieved when implementing P-EGR and of 38.5% with C-EGR.

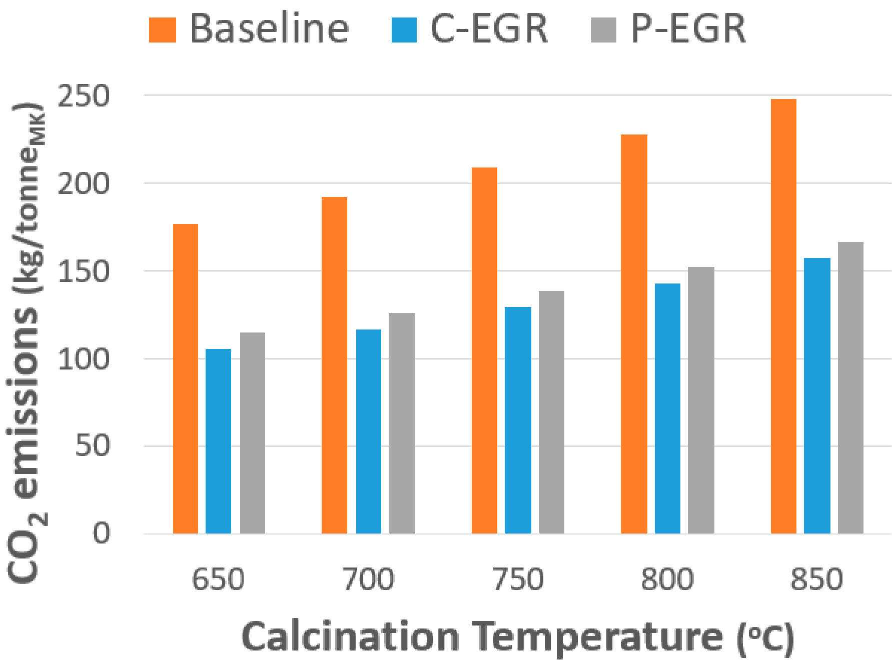

Figure 6. Calculated MK production process CO_2 emissions (kg/tonne$_{MK}$). Impact of calcination temperature. (Fuel: NG; reference moisture content of kaolinite: 15% wt).

Similarly, the effect of kaolinite moisture content (5–30% wt.) on the CO_2 emissions emerging from NG combustion per tonne of MK produced is presented in Figure 7. As expected, CO_2 emissions increased with kaolinite moisture content, particularly in the baseline case (162–305 kg/tonne$_{MK}$). The CO_2 emissions obtained for the P-EGR case ranged between 133 and 149 kg/tonne$_{MK,}$ within the examined raw material moisture content range. Given that the dry kaolinite flow stream enters the kiln and the additional heat required (particularly in the higher moisture content cases) is restricted to the drying stage and provided by other prospective plant waste heat resources, the C-EGR scenario resulted in constant CO_2 emissions of approximately 129 kg/tonne$_{MK}$.

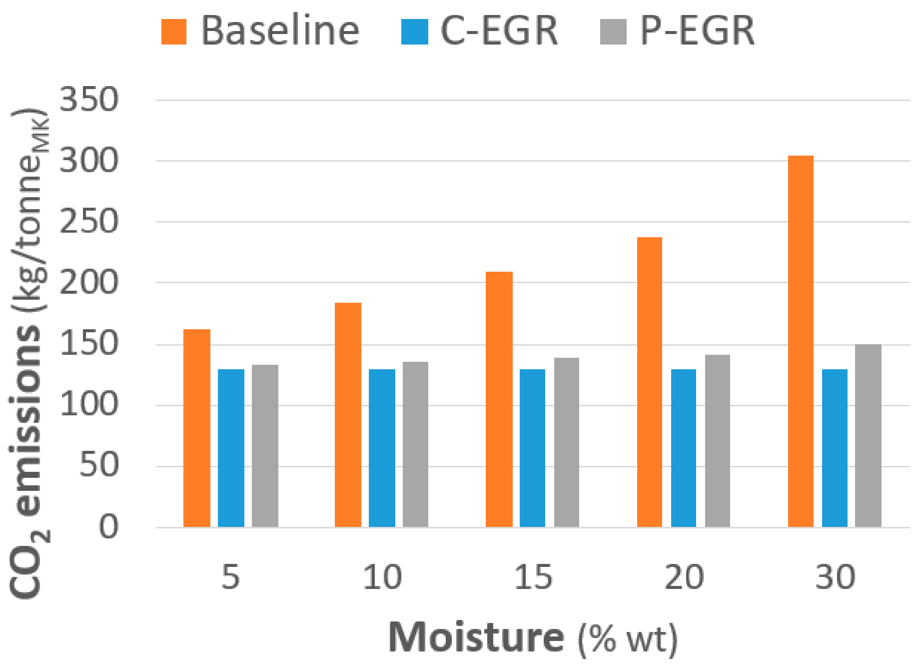

Figure 7. Calculated MK production process CO_2 emissions (MWh/tonne$_{MK}$). Impact of raw material moisture content. (Fuel: NG; reference kiln temperature: 750 °C).

Figure 8 presents a comparative assessment of CO_2 emissions associated with the combustion of various fuels frequently used in the cement industry to cover kiln heat requirements. The calculations refer to the EGR process model (C-EGR scenario) and consider kiln temperatures between 650 °C and 850 °C with 15% wt. initial raw material moisture. As expected, NG depicted the lowest CO_2 emissions, ranging between 105 and 158 kg/tonne$_{MK}$. Coal (lignite) is characterized by a lower heating value and carbon content than HRB coal. Despite increased fuel consumption, its combustion results in slightly lower emissions. Specifically, CO_2 emissions produced by lignite and HRB coal combustion ranged between 168 and 250 kg/tonne$_{MK}$ and 174 and 260 kg/tonne$_{MK}$, respectively. The emission range for petcoke was slightly higher. It was calculated in the range of 178–265 kg/tonne$_{MK}$. The overall effect of solid-fuel combustion on the calculated CO_2 emissions heavily depends on the fuels' proximate and ultimate analyses.

Figure 9 depicts the total CO_2 emissions calculated when coal (lignite) is substituted by alternative fuels commonly used in the cement industry, such as plastic waste, MSW and tires. The examined alternative fuels provided 10–40% of the thermal energy requirements as predicted from the C-EGR scenario, considering a reference kiln temperature equal to 750 °C and 15% wt. raw material moisture. Evidently, in all examined cases, CO_2 emissions tended to decrease with alternative-fuel substitution. The use of plastic waste demonstrated the highest impact, corresponding to an 8% decrease in CO_2 emissions, from 205 kg/tonne$_{MK}$ when only coal-lignite was utilized to 189 kg/tonne$_{MK}$ with 40% (of the thermal energy requirement) substitution. A maximum reduction of 5% was predicted for the respective MSW substitution. The impact of tires on CO_2 emissions was less pronounced, reaching a peak value of 1.5% for 40% substitution. Again, the overall effect of alternative-fuel substitution on the calculated CO_2 emissions heavily depends on the fuels' proximate and ultimate analyses and the carbon content. Table 1 shows that both plastic waste and tires have higher heating values than lignite, and therefore, a smaller amount of fuel is required to provide the necessary heat. It is concluded that even though both alternative fuels are characterized by a higher carbon content than lignite, their impact on the calculated CO_2 emissions remains positive. MSW presents a significantly lower heating value and carbon content than lignite. Since an increased amount of fuel is required, the overall impact of MSW proves to be less significant than that of plastic waste. In all examined cases, the combustion of dry alternative fuels was considered.

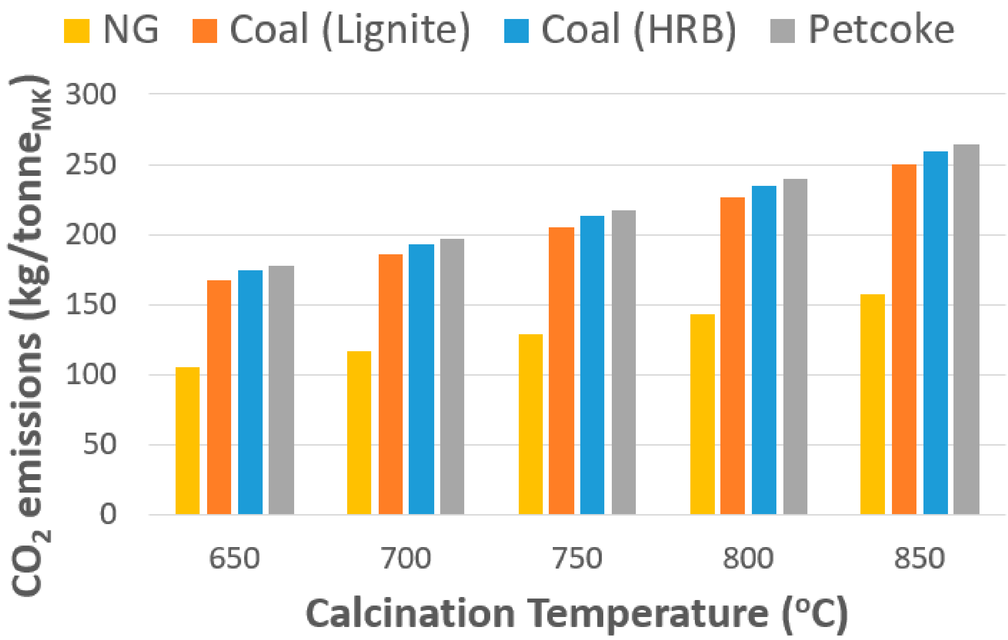

Figure 8. Calculated CO_2 emissions (kg/tonne$_{MK}$) for MK production process. (C-EGR scenario/Kiln Temperature: 650–850 °C/Reference moisture content: 15% wt).

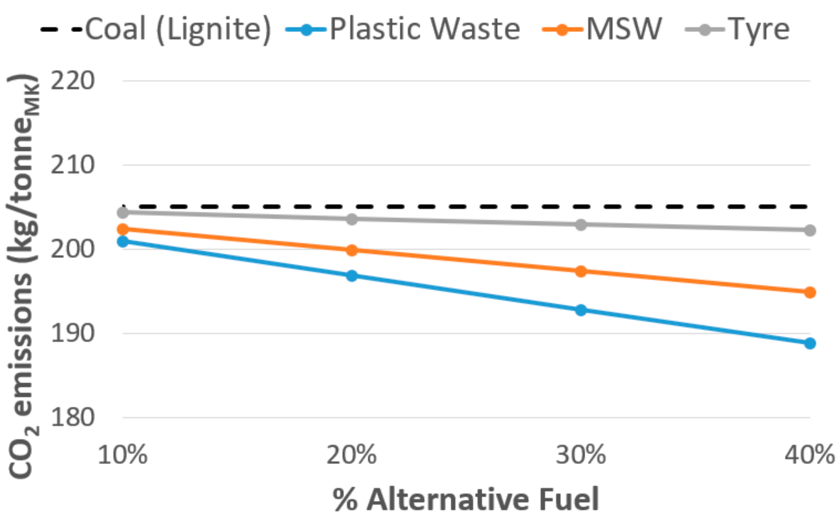

Figure 9. Calculated CO_2 emissions (kg/tonne$_{MK}$) by substituting coal (lignite) with alternative fuels. (C-EGR scenario/Reference Kiln Temperature: 750 °C/Reference moisture content: 15% wt).

3.2. LCA Results and Discussion

The results of the LCA are herewith summarized and discussed. For the typical moisture content of 15% in kaolinite and the baseline process configuration, the influence of process temperature was examined. Figure 10 shows the impact of calcination temperature on GWP. A definite increase in the GWP with rising temperatures was observed. This finding was also demonstrated in Figure 5, where the relevant process simulation results showed that a higher temperature resulted in higher core-process (combustion-related) CO_2 emissions. A strong contribution from the production of pure kaolin was also identified, providing a share at the same level as the core process emissions. There was also a slight increase in upstream CO_2 linked to NG due to more intensive fuel extraction, treatment and transportation. The other upstream sources had a constant contribution since they were assumed to remain constant independently of the MK production parameters.

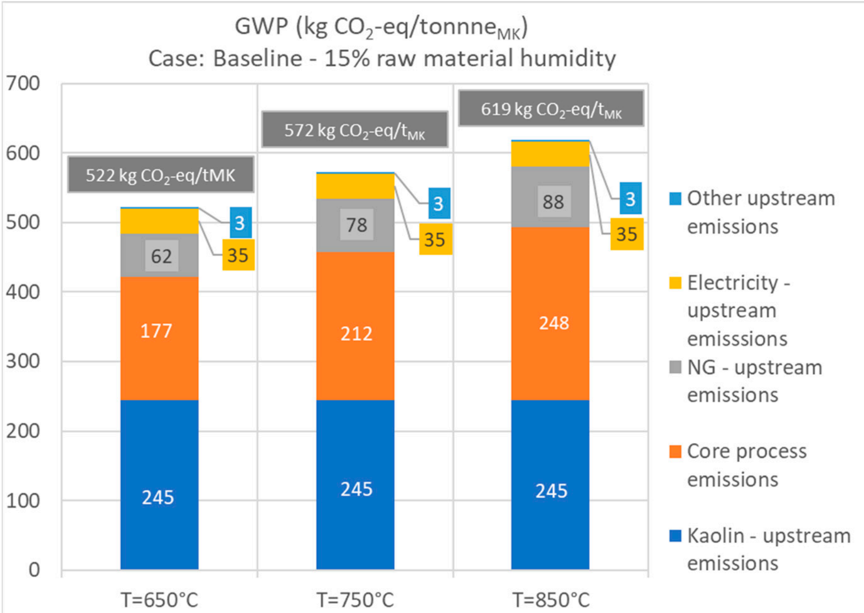

Figure 10. Influence of process temperature on the lifecycle GWP.

For the process temperature of 750 °C and the implementation of the baseline scenario with NG as fuel, the influence of moisture was examined. Figure 11 shows the impact of moisture on GWP. As expected, GWP increased with moisture content, as elaborated in the process-modeling results. An increase of 10% in raw material humidity raised the lifecycle GWP by roughly 14% due to the additional fuel demand. In parallel to Figure 10, a rising fuel demand means more intense extraction, processing, transportation and distribution activities of natural gas, thus leading to an increased corresponding contribution.

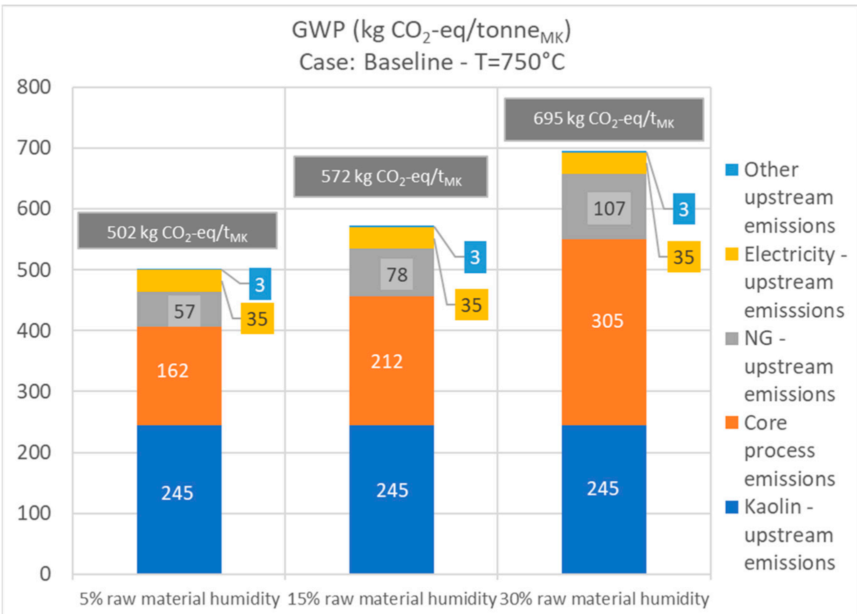

Figure 11. Influence of kaolin humidity on the lifecycle GWP.

For the typical moisture content of 15% in kaolinite and a 750 °C calcination temperature, the influence of recirculation was examined. Figure 12 shows that GWP decreased by 19% when the most convenient C-EGR case was applied. Once again, this was expected since process simulations have shown that onsite CO_2 emissions are lower when recirculation is applied.

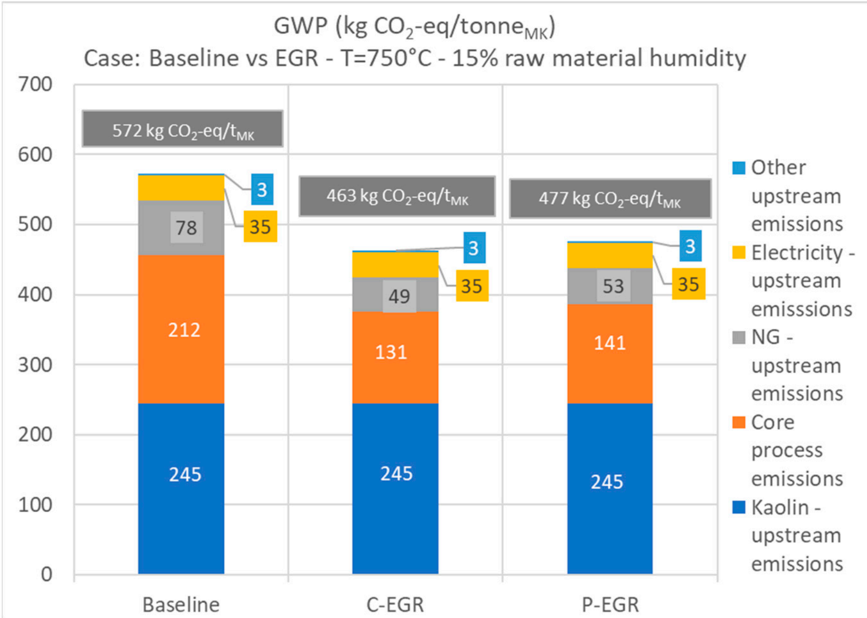

Figure 12. Influence of exhaust gas recirculation on the lifecycle GWP.

In parallel to Figure 8, the influence of adopting alternative fossil fuels is demonstrated in Figure 13. Using NG as the process fuel provided a clear reduction in terms of GWP impact, even when considering the various upstream impacts. The level of reduction ranged between 16% and 21%, depending on the fuel selected for comparison.

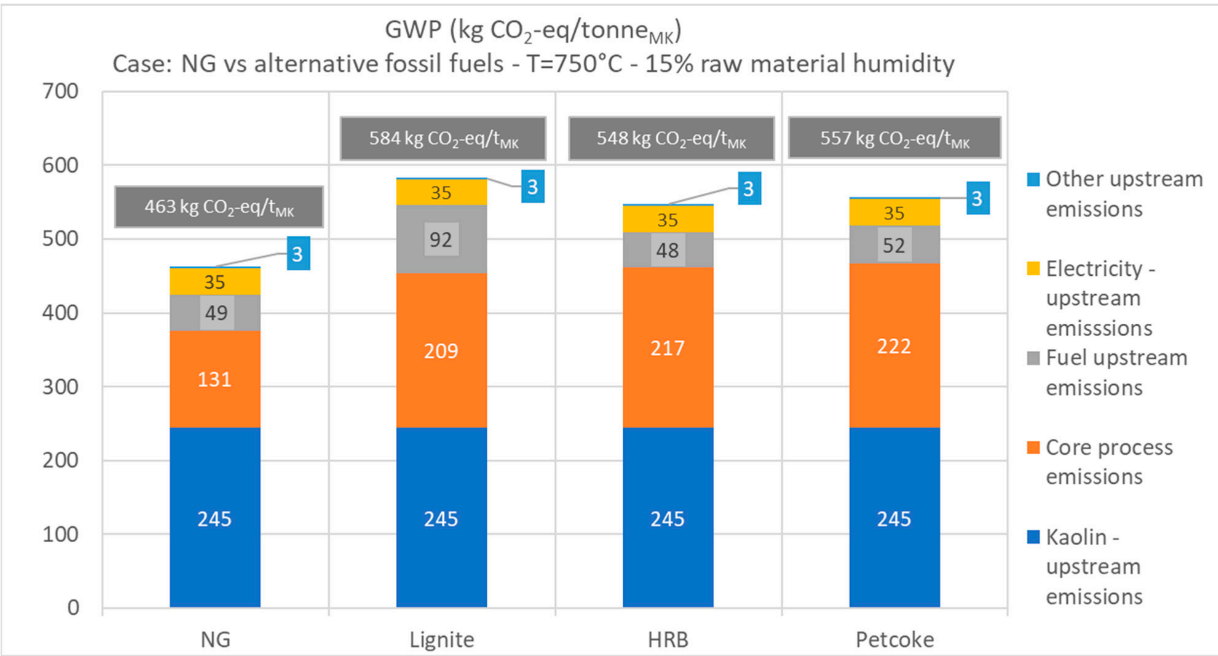

Figure 13. Influence of adopting alternative fossil fuels on the lifecycle GWP.

As regards the comparison of MK to clinker in terms of GWP impact, there is a significant carbon-emission mitigation potential identified. If we consider that the clinker cradle-to-gate GWP is estimated at 923 kg CO_2-eq/tonne$_{Clinker}$ (according to the data from the Ecoinvent database), all examined MK production cases show a reduction between 25% and 50%. The value of 923 kg CO_2-eq/tonne$_{Clinker}$ (derived from calculations using Ecoinvent data) was adopted for the comparison instead of the literature data in order to include all upstream emissions, thus ensuring comparability to the GWP (100) calculated or the MK production cases. This lower GWP impact of MK compared to conventional clinker production is largely attributed to the avoidance of CO_2 emissions from the calcination of limestone. Similar conclusions are found in the relevant literature [19–21], while the calculated level of impact reduction (25–50% depending on the assumptions of the MK production process) is in line with the corresponding value (40%) provided by Heath et al. [20].

Further GWP reduction compared to clinker can be achieved by incorporating waste fuels, as demonstrated in Figure 9. In the best case of replacing 40% of the coal with plastic waste, a reduction of 15 kg CO_2/tonne$_{MK}$ is shown. If we consider that waste fuels have zero upstream emissions, additional reductions are expected from lower fossil-fuel extraction, treatment and transportation. Therefore, the incorporation of waste fuels is shown to provide a further 4% reduction in terms of lifecycle GWP.

As regards the overall absolute GWP values calculated, they fall into the range between 463 and 695 kg CO_2-eq/tonne$_{MK}$, depending on the various parameters examined. This range corresponds to an overestimation compared to the value of 423 kg CO_2-eq/tonne$_{MK}$ by Heath et al. [20]. This difference is attributed to the omission of upstream emissions of natural gas and electricity in the work of Heath et al. [20]. These upstream contributions sum up to between 84 and 142 kg CO_2-eq/tonne$_{MK}$. Therefore, if this is added to the literature value of 423 kg CO_2-eq/tonne$_{MK}$, an overall agreement of results is identified between the two papers.

4. Conclusions

The environmental assessment of metakaolin (MK) as a supplementary cementitious material (SCM) through an integrated production-process simulation and Life-Cycle Assessment (LCA) approach is presented in this work.

Initially, process simulation models are developed, focusing on reproducing the basic stages of an MK production unit, considering that the calcination of kaolinite takes place in a rotary kiln. The effect of various operational parameters and scenarios, such as calcination temperature, moisture and drying of raw material, exhaust gas recirculation and the use of alternative-fuel combustion (to provide kiln heat requirements), is evaluated. Simulation results show that the process heat demand ranges between 0.58 and 1.54 MWh/tonne$_{MK}$ for kiln temperatures within 650–850 °C and raw material moisture content from 5 to 30% wt. Exhaust gas recirculation (EGR) can lead to average energy savings of up to 38% (the respective range in the examined operating conditions is 0.58–0.84 MWh/tonne$_{MK}$).

A comparative assessment of CO_2 emissions emerging from the combustion of various fuels (frequently used in the cement industry) to cover the MK-production kiln heat requirements has also taken place (focusing on the EGR scenarios). As expected, NG depicts the lowest CO_2 emissions, ranging between 105 and 158 kg/tonne$_{MK}$, compared to 168–250 kg/tonne$_{MK}$ for coal (lignite) and 174–260 kg/tonne$_{MK}$ for coal (HRB). The respective emission range for petcoke is slightly higher and is calculated to be between 178 and 265 kg/tonne$_{MK}$.

CO_2 emissions are also calculated when coal (lignite) is substituted by alternative fuels commonly used in the cement industry, such as plastic waste, MSW and tires. The examined alternative fuels provide 10–40% of the thermal energy requirements. In all examined cases, CO_2 emissions tend to decrease with alternative-fuel substitution. The use of plastic waste shows the highest impact. It corresponds to a maximum 8% decrease in CO_2 emissions. The overall effect of solid-fuel combustion and alternative-fuel substitution on the calculated CO_2 emissions heavily depends on the fuels' proximate and ultimate analyses, carbon content and associated heating values.

The calculated process heat demand and CO_2 emissions are used as inputs for the LCA, along with upstream data from the literature, using a cradle-to-gate approach. The major findings show a strong influence of process temperature and kaolin humidity on the lifecycle GWP, since both parameters affect not only the core-process heat demand but also the upstream impact related to fossil-fuel extraction, processing, transportation and distribution. Recirculating the exhaust provides a GWP reduction potential of up to 19%. In all examined production scenarios, metakaolin depicts a lower Global Warming Potential compared to clinker, due to the avoidance of the emissions related to limestone calcination.

As regards the impact contribution of fuels, coal is responsible for higher onsite emissions, and natural gas presents higher upstream emissions. The GWP (100) may be further reduced when alternative waste fuels such as plastic waste, MSW (municipal solid waste) and tires are used. The LCA results have been cross-checked with the previous literature, and the corresponding deviations have been explained accordingly. In any case, the LCA results of different studies are rarely directly comparable due to the numerous assumptions required, which cannot be identically replicated.

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References

1. European Commission. The European Green Deal. *Brussels*, 11 December 2019. Available online: https://ec.europa.eu/info/strategy/priorities-2019--2024/european-green-deal_en (accessed on 21 December 2022).
2. The European Cement Association CEMBUREAU. Cementing the European Green Deal. Reaching Climate Neutrality along the Cement and Concrete Value Chain by 2050. Available online: https://cembureau.eu/media/kuxd32gi/cembureau-2050-roadmap_final-version_web.pdf (accessed on 21 December 2022).
3. International Energy Agency (IEA). *Technology Roadmap—Low-Carbon Transition in the Cement Industry*; IEA: Paris, France, 2018; Available online: https://www.iea.org/reports/technology-roadmap-low-carbon-transition-in-the-cement-industry (accessed on 21 December 2022).
4. Georgiopoulou, M.; Lyberatos, G. Life Cycle Assessment of the Use of Alternative Fuels in Cement Kilns: A Case Study. *J. Environ. Manag.* **2018**, *216*, 224–234. [CrossRef] [PubMed]
5. Teklay, A.; Yin, C.; Rosendahl, L. Flash Calcination of Kaolinite Rich Clay and Impact of Process Conditions on the Quality of the Calcines: A Way to Reduce CO_2 Footprint from Cement Industry. *Appl. Energy* **2016**, *162*, 1218–1224. [CrossRef]
6. Schneider, M.; Romer, M.; Tschudin, M.; Bolio, H. Sustainable Cement Production-Present and Future. *Cem. Concr. Res.* **2011**, *41*, 642–650. [CrossRef]
7. Mokrzycki, E.; Uliasz-Bochenczyk, A. Alternative Fuels for the Cement Industry. *Appl. Energy* **2003**, *74*, 95–100. [CrossRef]
8. Rashad, A.M. Metakaolin as Cementitious Material: History, Scours, Production and Composition—A Comprehensive Overview. *Constr. Build. Mater.* **2013**, *41*, 303–318. [CrossRef]
9. Singh, M.; Garg, M. Reactive Pozzolana from Indian Clays-Their Use in Cement Mortars. *Cem. Concr. Res.* **2006**, *36*, 1903–1907. [CrossRef]
10. Fernandez, R.; Martirena, F.; Scrivener, K.L. The Origin of the Pozzolanic Activity of Calcined Clay Minerals: A Comparison between Kaolinite, Illite and Montmorillonite. *Cem. Concr. Res.* **2011**, *41*, 113–122. [CrossRef]
11. Sabir, B.B.; Wild, S.; Bai, J. Metakaolin and Calcined Clays as Pozzolans for Concrete: A Review. *Cem. Concr. Compos.* **2001**, *23*, 441–454. [CrossRef]
12. Ilić, B.R.; Mitrović, A.A.; Miličić, L.R. Thermal Treatment of Kaolin Clay to Obtain Metakaolin. *Hem. Ind.* **2010**, *64*, 351–356. [CrossRef]

13. Phinnie, R.; Graham, K.; Graham, K.; Aycock, B. Method of Producing Metakaolin. U.S. Patent 7,628,850 B2, 8 December 2009.
14. Bakera, A.T.; Alexander, M.G. Use of Metakaolin as a Supplementary Cementitious Material in Concrete, with a Focus on Durability Properties. *RILEM Tech. Lett.* **2019**, *4*, 89–102. [CrossRef]
15. Pruett, R.J. Kaolin Deposits and Their Uses: Northern Brazil and Georgia, USA. *Appl. Clay Sci.* **2016**, *131*, 3–13. [CrossRef]
16. Almenares, R.S.; Vizcaíno, L.M.; Damas, S.; Mathieu, A.; Alujas, A.; Martirena, F. Industrial Calcination of Kaolinitic Clays to Make Reactive Pozzolans. *Case Stud. Constr. Mater.* **2017**, *6*, 225–232. [CrossRef]
17. Dumani, Z.; Mapiravana, J. Metakaolin as an Alternative Ordinary Portland Cement Extender. In Proceedings of the OUT-OF-THE-BOX Human Settlements Conference, CSIR, Pretoria, South Africa, 24–25 October 2018.
18. Davidovits, J. Environmental Implications and Life Cycle Assessment LCA of Geopolymers. In Proceedings of the Geopolymer Camp 2015, CSIR, Saint Quentin, France, 6–8 July 2015; Available online: https://geopolymer.org/fichiers/gpcamp-2015/Davidovits%20-%20Environmental%20implications%20and_Life%20Cycle%20Assessment%20LCA%20of%20geopolymers.pdf (accessed on 15 December 2022).
19. Habert, G.; D'Espinose De Lacaillerie, J.B.; Roussel, N. An Environmental Evaluation of Geopolymer Based Concrete Production: Reviewing Current Research Trends. *J. Clean. Prod.* **2011**, *19*, 1229–1238. [CrossRef]
20. Heath, A.; Paine, K.; McManus, M. Minimising the Global Warming Potential of Clay Based Geopolymers. *J. Clean. Prod.* **2014**, *78*, 75–83. [CrossRef]
21. McLellan, B.C.; Williams, R.P.; Lay, J.; van Riessen, A.; Corder, G.D. Costs and Carbon Emissions for Geopolymer Pastes in Comparison to Ordinary Portland Cement. *J. Clean. Prod.* **2011**, *19*, 1080–1090. [CrossRef]
22. Fawer, M.; Concannon, M.; Rieber, W. LCI for the Production of Sodium Silicate Life Cycle Inventories for the Production of Sodium Silicates. *Int. J. LCA* **1999**, *4*, 207–212. [CrossRef]
23. Salas, D.A.; Ramirez, A.D.; Ulloa, N.; Baykara, H.; Boero, A.J. Life Cycle Assessment of Geopolymer Concrete. *Constr. Build. Mater.* **2018**, *190*, 170–177. [CrossRef]
24. Marinković, S.; Dragaš, J.; Ignjatović, I.; Tošić, N. Environmental Assessment of Green Concretes for Structural Use. *J. Clean. Prod.* **2017**, *154*, 633–649. [CrossRef]
25. Voultsos, I.; Katsourinis, D.; Giannopoulos, D.; Founti, M. Integrating LCA with Process Modeling for the Energetic and Environmental Assessment of a CHP Biomass Gasification Plant: A Case Study in Thessa-ly, Greece. *Eng. Adv. Eng.* **2020**, *1*, 2–30. [CrossRef]
26. Alifieris, O.; Katsourinis, D.; Giannopoulos, D.; Founti, M. Process Simulation and Life Cycle Assessment of Ceramic Pigment Production: A Case Study of Green Cr_2O_3. *Processes* **2021**, *9*, 1731. [CrossRef]
27. Kaante, U.; Zevenhoven, R.; Backman, R.; Hupa, M. Cement manufacturing using alternative fuels and the advantages of process modelling. *Fuel Process. Technol.* **2004**, *85*, 293–301. [CrossRef]
28. Zhang, Y.; Cao, S.X.; Shao, S.; Chen, Y.; Liu, S.L.; Zhang, S.S. Aspen Plus-Based Simulation of a Cement Calciner and Optimization Analysis of Air Pollutants Emission. *Clean Technol. Environ. Policy* **2011**, *13*, 459–468. [CrossRef]
29. Kaddatz, K.T.; Rasul, M.G.; Rahman, A. Alternative Fuels for Use in Cement Kilns: Process Impact Model-ling. In *Proceedings of the Procedia Engineering*; Elsevier Ltd.: Amsterdam, The Netherlands, 2013; Volume 56, pp. 413–420.
30. Rahman, A.; Rasul, M.G.; Khan, M.M.K.; Sharma, S. Aspen plus Based Simulation for Energy Recovery from Waste to Utilize in Cement Plant Preheater Tower. In *Proceedings of the Energy Procedia*; Elsevier Ltd.: Amsterdam, The Netherlands, 2014; Volume 61, pp. 922–927.
31. Rahman, A.; Rasul, M.G.; Khan, M.M.K.; Sharma, S.C. Assessment of Energy Performance and Emission Control Using Alternative Fuels in Cement Industry through a Process Model. *Energies* **2017**, *10*, 1996. [CrossRef]
32. Hasanbeigi, A.; Price, L.; Lin, E. Emerging Energy-Efficiency and CO_2 Emission-Reduction Technologies for Cement and Concrete Production: A Technical Review. *Renew. Sustain. Energy Rev.* **2012**, *16*, 6220–6238. [CrossRef]
33. Granados, D.A.; Chejne, F.; Mejía, J.M.; Gómez, C.A.; Berrío, A.; Jurado, W.J. Effect of Flue Gas Recirculation during Oxy-Fuel Combustion in a Rotary Cement Kiln. *Energy* **2014**, *64*, 615–625. [CrossRef]
34. Buckley, T.J. Calculation of Higher Heating Values of Biomass Materials and Waste Components from Elemental Analyses. *Resour. Conserv. Recycl.* **1991**, *5*, 329–341. [CrossRef]
35. Yi, L.; Feng, J.; Qin, Y.H.; Li, W.Y. Prediction of Elemental Composition of Coal Using Proximate Analysis. *Fuel* **2017**, *193*, 315–321. [CrossRef]
36. Commandre, J.-M.; Salvador, S.; Sylvain, S.; Commandré, J.-M.; Salvador, S. Lack of Correlation between the Properties of a Petroleum Coke and Its Behaviour during Combustion. *Fuel Process. Technol.* **2005**, *86*, 795–808. [CrossRef]
37. Giannopoulos, D.; Founti, M. Parametric comparative analysis of lifetime energy demand and CO_2-eq savings of a SOFC m-CHP unit. In Proceedings of the European Fuel Cell Forum 2011, Lucerne, The Switzerland, 28 June–1 July 2011; Chapter 16. pp. 47–67.
38. Silva, D.A.L.; Nunes, A.O.; Moris, V.A.d.S.; Piekarski, C.M.; Rodrigues, T.O. How important is the LCA software tool you choose Comparative results from GaBi, openLCA, SimaPro and Umberto. In Proceedings of the VII Conferencia Internacional de Análisis de Ciclo de Vida en Latinoamérica (CILCA) 2017, Medellín, Colombia, 12–15 June 2017; pp. 1–6. Available online: https://www.researchgate.net/publication/318217178_ (accessed on 1 February 2023).
39. DEPA-Commercial. Available online: Https://Www.Depa.Gr/ (accessed on 15 December 2022).
40. DAPEEP—Administrator of Renewable Energy Sources and Guarantees of Origin. Available online: Https://Www.Dapeep.Gr/ (accessed on 15 December 2022).
41. Hanein, T.; Thienel, K.C.; Zunino, F.; Marsh, A.T.M.; Maier, M.; Wang, B.; Canut, M.; Juenger, M.C.G.; ben Haha, M.; Avet, F.; et al. Clay Calcination Technology: State-of-the-Art Review by the RILEM TC 282-CCL. *Mater. Struct. Mater. Et Constr.* **2022**, *55*, 3. [CrossRef]

42. Wu, Z.H.; Hu, Y.J.; Lee, D.J.; Mujumdar, A.S.; Li, Z.Y. Dewatering and Drying in Mineral Processing Industry: Potential for Innovation. *Dry. Technol.* **2010**, *28*, 834–842. [CrossRef]
43. NLK. *Ecosmart Concrete Project: Metakaolin Pre-Feasibility Study*; NLK Consultants Inc.: Vancouver, BC, Canada, 2002.
44. Martínez, J.C.; (Cemex Research Group AG, Brügg, Switzerland). Personal communication, 2020.