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Process Simulation and Life Cycle Assessment of Ceramic Pigment Production: A Case Study of Green Cr_2O_3

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Abstract: This study presents a combined process modeling—Life Cycle Assessment (LCA) approach for the evaluation of green Cr_2O_3 ceramic pigments production. Pigment production is associated with high calcination temperatures, achieved through the combustion of fossil fuels. Therefore, it is necessary to evaluate its environmental impact with regards to energy requirements and CO_2 emissions. Initially, a process model is developed to simulate the final calcination stage of the traditional pigments production process. It is validated against titanium dioxide (TiO_2) white production industrial data and adjusted for Cr_2O_3 production. Three alternative processes are examined: two for pigment grade (PIGM1, PIGM2) and one for metallurgical (MET) Cr_2O_3. Heat demand and CO_2 emissions computed by the developed process models are used as input in the LCA along with upstream data from the literature using a cradle-to-gate approach. The implementation of the LCA has resulted in calculated Global Warming Potential (GWP100) ranging from 7.9 to 12.8 CO_2-eq and fossil Primary Energy Demand (PED) between 91.4–159.6 MJ-eq (all referring to 1 kg of pigment production). It is depicted that the biggest part of the emissions originates from the upstream production and transportation of raw materials (contributing up to 96% of total CO_2 emissions) and other sources (electricity, production plant, etc.), rather than the examined calcination stage (contributing from 1.3 to 3.5% of GWP).

Keywords: ceramic pigments; life cycle assessment; environmental impact

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1. Introduction

Pigments are small particles which are practically insoluble in an applied medium. They are used for their coloring, protective or magnetic properties [1,2]. Ceramic pigments in particular are pigments used in the ceramic industry and are practically metal transition oxides depicting the following essential characteristics: (a) thermal stability by maintaining their identity at high temperatures, (b) chemical stability by maintaining their identity when fired with glazes or ceramic matrices and (c) high tinting strength when dispersed and fired with glazes or ceramic matrices [3,4].

One well-known ceramic pigment with widespread use is titanium oxide (TiO_2). It has been commercially available as a whitening agent since the early 20th century and is implemented in various domestic and industrial applications [5]. TiO_2 pigments are inert, thermodynamically stable and have a high refractive index, thus providing bright hiding and bright opacity for most applications [6,7]. They appear in anatase, rutile and brookite form. Notably, rutile white pigment is of significant economic importance [8]. TiO_2 pigments are produced from a variety of ores with two different processes: the sulfate process (representing a total of approximately 40% of the total TiO_2 production) using concentrated sulfuric acid and the chloride process (comprising a respective 60% of the total TiO_2 production) which uses chlorine gas. Both processes differ in their chemistry and raw material requirements [9].

Cr-doped materials have been extensively used as ceramic pigments with a wide range of colors and tonality [10]. For example, Cr_2O_3-Al_2O_3 oxides' color ranges from green to red depending on the chromium content. The green color is associated with higher Cr_2O_3 content [11]. Pigment quality chromium (III) oxide is a light to dark green powder [12] characterized by chemical and thermal stability [13]. It can be used in both pigment and metallurgical applications [14] with the basic difference being the purity of the oxide and the size of the produced crystal grains. Chromic oxide green pigments find wide applications in paints and coatings, in construction as additives in cement and other building materials, in printing and other color related applications where performance in green color is combined with a necessity for wear, corrosion and chemical resistance [15,16].

The traditional industrial process for the production of ceramic pigments usually consists of the following steps [4]: (a) grinding, (b) calcination, (c) washing, (d) micronization and (e) tinting strength and quality control of the color tone. During calcination, the material is heated to high temperatures (usually ranging between 800–1200 °C, depending on the pigment), causing changes to its crystal structure and grain size [5]. These temperatures are achieved through the combustion of fossil fuels [5,17] such as natural gas [5,8] and oil [18]. Variations of the traditional ceramic production route have either been implemented or proposed by various patents for Green Cr_2O_3 pigment production [13–16,19–21]. Furthermore, a green process has also been developed at laboratory and small scale demo pilot plant level, depicting higher efficiency (the total Cr yield is increased) and improved environmental impact (toxic waste such as Cr^{6+} is significantly reduced) [14,15]. It should be noted that waste management studies are also reported in the literature, where industrial residues rich in chromium have been appropriately processed and subsequently recycled to be used as raw material for the production of green ceramic pigments [10,22].

Life Cycle Assessment (LCA) is a widely used approach for the assessment of environmental aspects and potential impacts of a process by using an inventory of system inputs and outputs and by interpreting the results of the inventory analysis according to the objectives of the study [23,24]. Therefore, it can be used as an essential decision-making tool for all industrial sectors [25]. LCA studies reported in the literature for ceramic pigments are scarce and focus mainly on the evaluation of TiO_2 production methods. Reck and Richards [18] provided an overview of various environmental aspects associated with the production of TiO_2 pigment (using both sulfate and chloride methods) highlighting the positive contribution of the LCA methodology towards more sustainable developments. Middlemass et al. [5] performed LCA simulations for the evaluation of a novel TiO_2 production process featuring alkaline roasting of titania slag (ARTS) and depicted the environmental benefits of the ARTS process compared to traditional sulfate and chloride methods. Liao et al. [26] implemented LCA simulations to calculate thermodynamic resource indicators and evaluate both sulfate and chloride methods used for the production of titania (TiO_2 pigment) in Panzhihua city, Southwest China. Grubb and Bakshi [27] calculated the life cycle impact of emissions, energy requirements and exergetic losses for a novel process of TiO_2 nanoparticles production emerging from an ilmenite feedstock.

The objective of this work is to introduce a comprehensive and integrated process modeling—LCA approach for the evaluation of Green Cr_2O_3 ceramic pigments production, focusing on energy requirements and CO_2 emissions. In order to perform life cycle simulations, it is essential to have appropriate input for the pigment production process. In general, most LCA studies use fixed data from previous simulations. However, in order to overcome uncertainties associated with the lack of industrial data in the literature, computational process models have been developed and are depicted. These models aim to reproduce alternative Cr_2O_3 pigment production process scenarios based on variations of the traditional process. Emphasis is given on the calcination stage, which is crucial to the characterization of the process energetic performance and environmental impact, since combustion of fossil fuels is required to provide heat in order to achieve high calcination temperatures (800–1200 °C). Heat demand and CO_2 emissions computed by the developed models are used as input in the LCA. This integrated process modeling—LCA approach has been proved to provide insight and flexibility to the production process, thus leading to a more detailed, accurate and customized LCA approach [28,29].

2. Materials and Methods

2.1. Process Modeling of Ceramic Pigment Production

Process modeling is a very useful tool supporting the optimization and environmental assessment of industrial processes and can be implemented for the simulation of ceramic pigment production processes. Although it has been thoroughly used for the simulation of production chains in the cement industry, including calcination stages in rotary kilns [30–33], respective models addressing the production of ceramic pigments are not available. The models have been developed in Aspen Plus© a chemical process simulation software that solves energy and mass balances, kinetics and thermodynamics of chemical reactions, etc.

Initially a model has been developed in Aspen Plus© to account for the production of rutile TiO_2 using the sulfate method, which comprises similar stages to the traditional ceramic pigment route (including calcination). The rutile TiO_2 model is validated against actual fuel consumption and energy demand measurements. It is also used as the basis for further developments and modifications leading to the development of the respective Cr_2O_3 pigment production models. Given the lack of actual industrial data for the Green Cr_2O_3 pigment production chain, the respective TiO_2 model is practically used as validation reference for all developed models presented in this work.

2.1.1. Development of a Process Model for Rutile TiO_2 Production Using the Sulfate Method

The sulfate method includes a calcination stage [8,9,34] where a "filter cake" is calcined in a rotary kiln at approximately 1000 °C. The kiln heat requirements are provided by combustion of natural gas in a separate chamber [8]. This process can be considered relevant to the respective Green Cr_2O_3 pigment production process which similarly implements a calcination stage with kiln temperatures ranging between 800–1200 °C (and is presented in the following section of the paper). Therefore, it can be used as reference for the validation of the developed process models despite utilizing different raw materials.

In the sulfate method [8], the "filter cake" enters the kiln with the following composition: $0.936TiO(OH)_2 \cdot 0.064(TiOSO_4 \cdot H_2O) \cdot 4.295H_2O$ (or $TiO_2 \cdot 0.064SO_3 \cdot 5.295H_2O$).

The "filter cake" is produced according to the following process: raw materials such as ilmenite ($FeTiO_3$) and/or titanium slag are digested with sulfuric acid, resulting in a solution containing $FeSO_4$ and $TiOSO_4$. The solution is subsequently cooled at 10 °C to crystallize and remove iron. The remaining $TiOSO_4$ is precipitated by hydrolysis with steam, mainly as solid titanium oxide hydrate $TiO(OH)_2$ and (to a lesser extent) solid titanyl sulfate hydrate $TiOSO_4 \cdot H_2O$. The hydrolysate is dewatered with the use of rotary drum filers until water content reaches approximately 55% wt.

Reactions occurring inside the kiln are presented in Table 1 [34]. Reaction R1 corresponds to the evaporation of moisture. During this stage the temperature of the cake does not exceed 100 °C. Dehydration of adsorbed water (Reactions R2 and R3) is completed at approximately 500 °C, while the removal of the sulfate groups (Reaction R4) takes place between 600 and 700 °C. Finally, transition of anatase TiO_2 to rutile TiO_2 (Reaction R5) occurs within a temperature range of 700 to 1000 °C [18,34]. The final product is a ceramic pigment that is white in color.

Table 1. Chemical reactions and enthalpies at 25 °C inside the kiln during calcination for the production of rutile TiO_2 [34].

Reaction Number	Reaction	$\Delta h_{Reaction}$ (kJ/Mol) (25 °C)
R1	$H_2O_{(l)} \rightarrow H_2O_{(g)}$	44.0 ± 0.06
R2	$TiO(OH)_2 \rightarrow TiO_{2(a)} + H_2O_{(g)}$	89.7 ± 8.0
R3	$TiOSO_4 \cdot H_2O \rightarrow TiOSO_4 + H_2O_{(g)}$	89.7 ± 8.0
R4	$TiOSO_4 \rightarrow TiO_{2(a)} + SO_{2(g)} + 0.5O_2$	396.9 ± 172.6
R5	$TiO_{2(a)} \rightarrow TiO_{2(r)}$	-5.6 ± 0.8

An actual plant producing white rutile TiO_2 pigment is simulated in this work [8]. The "cake" is fed to the rotary kiln. The calcined material exits from the bottom of the kiln with a temperature of approximately 925 °C and is cooled with the use of air. The heat necessary for the kiln temperature is produced by the combustion of natural gas with: (a) recycled flue gas and (b) an air stream (primary air) heated by the calcined material exiting the kiln). Unwanted air from the environment also enters the combustion chamber (false air). The produced flue gas flows countercurrent to the material and exits from the top side of the rotary kiln. After passing through an electrostatic filter, part of the flue gas is recycled back to the combustion chamber while the rest is used for other purposes or is released into the atmosphere. The actual input and output process data for fuel consumption, TiO_2 production and temperature for all essential streams participating in the production process are depicted in Table 2.

Table 2. Ginsberg and Modigell unit [8] input and output values.

Measured Input Parameters	Parameter Value
Primary air temperature	169 °C
Primary air flow rate	8750 m^3 STP/h
Recycled gas temperature	303 °C
Recycled gas flow rate	5810 m^3 STP/h
Natural Gas flow rate	740 m^3 STP
Natural Gas Lower Heating Value (LHV)	10.2 kWh/m^3 STP
Filter cake throughput	8250 kg/h
False air flow rate	3850 m^3 STP/h
Clinker throughput	3650 kg/h
Ambient temperature	14 °C
Measured output parameters	**Parameter value**
Clinker temperature	924 °C
Off gas temperature	375 °C

A model has been developed in Aspen Plus to account for the aforementioned rutile TiO_2 production process. It is presented in Figure 1. The basic stages of the process as well as the essential inlet stream flow rates and temperatures (as enlisted in Table 2) are reproduced. The "cake" enters the rotary kiln with a total mass flow of 8250 kg/h. It is modeled as a mixture of H_2O, $TiO(OH)_2$ and $TiOSO_4 \cdot H_2O$ with inlet mass fractions obtained from typical filter cake composition ($TiO_2 \cdot 0.064SO_3 \cdot 5.295H_2O$). Most of the chemical components that participate in the production of rutile TiO_2 already exist in the database of Aspen Plus. However $TiO(OH)_2$, $TiOSO_4 \cdot H_2O$ and $TiOSO_4$ do not, so they have to be user defined. Density and specific heat capacity values available in the literature [35] are incorporated into the present model for the components participating at Reactions R1–R5.

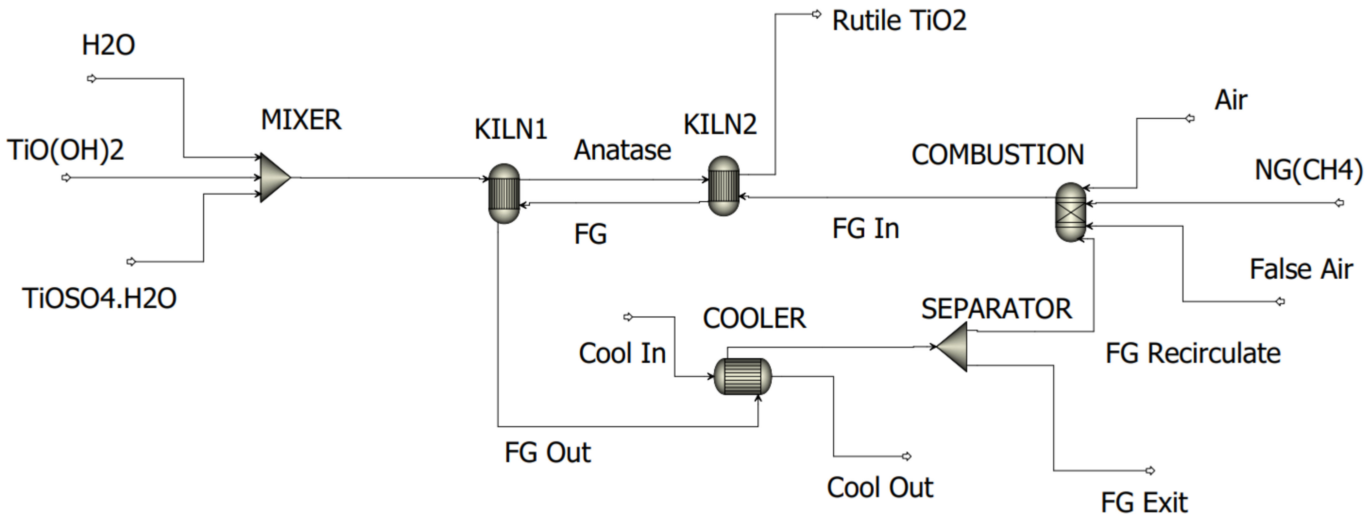

Figure 1. Process model for the production of rutile TiO_2 using the sulfate method.

Two RGIBBS reactors have been implemented for the simulation of the kiln [27], hence assuming that all components involved in the reactions reach equilibrium. In the first reactor (block KILN1) Reactions R1–R4 take place producing anatase TiO_2 which is subsequently fed to the second reactor (block KILN2) and transformed to rutile (Reaction R5). An RGIBBS reactor (block COMBUSTION) is also utilized for the combustion of natural gas (as represented by CH_4) providing heat to the kiln. The produced exhaust gases are mixed with both false air and recirculated flue gas (stream FG Recirculate). The resulting mixture (stream FG In) is led inside the kiln. In order to take into account flue gas recirculation, exhaust gas exiting KILN1 is cooled (block COOLER) until it reaches a set temperature of 303 °C as indicated by the industrial data. It is subsequently split into two parts, one of which is led back to the burner (stream FG Recirculate). Mass flow streams of air, false air and recirculating flue gas entering the burner have been used as input in the present calculations. They are calculated by converting the STP (standard temperature and pressure conditions -0 °C and 1 bar) volumetric flow streams (shown in Table 2) to mass flow streams using both air ($\rho_{air, STP}$ = 1.292 kg/m^3 [28]) and flue gas densities ($\rho_{RcG, STP}$ = 1.789 kg/m^3—calculated by the process model). The required fuel consumption to achieve an exit temperature of 924 °C (clinker output temperature according to the data)is calculated with the use of a Design Spec function.

2.1.2. Green—Cr_2O_3 Pigment Production

According to the traditional process [14–16] Cr_2O_3 is produced by a mixture of chromite ore ($FeO{\cdot}Cr_2O_3$), sodium carbonate (Na_2CO_3), limestone and dolomite oxidized at approximately 1100 °C. The produced sodium chromate (Na_2CrO_4) is washed, cooled and then mixed with H_2SO_4 to produce sodium dichromate ($Na_2Cr_2O_7$). Cr_2O_3 of pigment or metallurgical grade Cr_2O_3 emerges from the thermal reduction of $Na_2Cr_2O_7$ through either Reaction (1) or Reactions (2) and (3):

$$Na_2Cr_2O_7 + (NH_4)_2SO_4 \rightarrow Cr_2O_3 + Na_2SO_4 + N_2 + 4H_2O \quad (1)$$

$$Na_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2CrO_3 + 2NaHSO_4 + H_2O \quad (2)$$

$$2CrO_3 \rightarrow Cr_2O_3 + 3/2O_2 \quad (3)$$

In this work process modeling studies focus on the simulation of pigment grade Cr_2O_3 production by reducing $Na_2Cr_2O_7$ and calcining the product mixture. The predicted energy demand and CO_2 emissions values are used as input in the LCA approach.

Based on alternative mixture preparation pathways, the following models have been developed:

(a) Cr_2O_3-PIGM1: an indicative route for green Cr_2O_3 pigment production through mixture preparation and subsequent calcination based on Reaction (1) is considered [13];
(b) Cr_2O_3-PIGM2: the model takes into account the production of pigment grade Cr_2O_3 from the calcination of non-pigment grade Cr_2O_3 [21];
(c) Cr_2O_3-MET: a similar production process for the production of metallurgical grade Cr_2O_3 has been considered as a measure for comparison. The model implements inlet streams and temperatures indicated by [19].

The Cr_2O_3-PIGM1 Model

Based on the patent of Mansmann et al. [13], a process model has been developed considering that $Na_2Cr_2O_7$ and $(NH_4)_2SO_4$ are mixed in a molar 1:1 analogy and calcined in 950 °C. The addition of water to the mixture results in the formation of a paste entering the kiln and is considered advantageous for the formation of pigments. Based on the same, patent water content can reach 45% by weight of the total mixture but preferably in the range of 20–30%. Three alternative scenarios have been taken into account with respect to the presence of water in the kiln corresponding to water concentration in the mixture equal to 10, 20 and 30%, respectively. Furthermore, a parametric study has been performed evaluating the effect of kiln temperature to the calculated process heat demand and CO_2 emissions. Studies focus on a kiln temperature range between 950–1100 °C which can be considered as representative for pigment production [13].

Figure 2 presents the flowsheet of the model developed in Aspen Plus to simulate the Cr_2O_3-PIGM1 process. $Na_2Cr_2O_7$, $(NH_4)_2SO_4$ and water are fed to an RGIBBS reactor (block KILN) where calcination occurs at 950 °C and Cr_2O_3 is formed. An RGIBBS reactor (block COMBUSTION) has also been implemented to provide the heat for calcination, through the combustion of a stoichiometric natural gas (as represented by CH_4)—air mixture (stream NG+AIR Premixed). Flue gas is separated from the products with the use of a Flash2 separator (block GAS SOLID SEPARATOR).

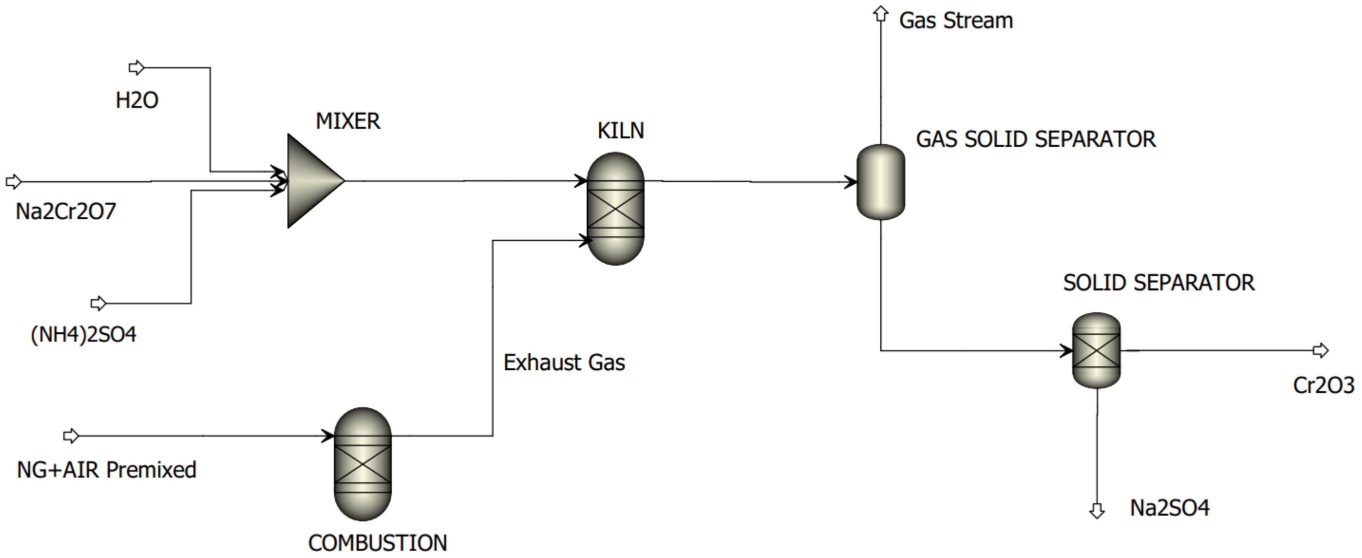

Figure 2. The Cr_2O_3-PIGM1 process model flowsheet.

The Cr_2O_3-PIGM2 Model

This model reproduces a method proposed by [21] for the production of pigment grade Cr_2O_3 from non-pigment Cr_2O_3. According to the example, 1100 g of non-pigment Cr_2O_3 are mixed with 5 g Na_2SO_4. The resulting mixture is then calcined at 982 °C. Subsequently, the product is washed and filtered to remove any existing soluble salts. This example is examined by the developed model. Given that pigment formation is anticipated in a temperature range within 925–1200 °C, a parametric study has also taken place considering additional calcination temperatures. It should be noted that the non-pigment grade Cr_2O_3 can be in the form of dry powder, thus water addition for the formation of a wet filter cake is not necessary and was not taken into account.

Figure 3 presents the flowsheet of the model developed in Aspen Plus to simulate the Cr_2O_3-PIGM2 process. It is a simple process where a mixture of non-pigment grade Cr_2O_3 and Na_2SO_4 is calcined at approximately 1000 °C without taking into account any reactions involved. Therefore, a simple heater block (KILN) has been incorporated for the calcination of Cr_2O_3 inside the kiln. This is a simple, conceptual approach calculating the theoretical—baseline duty required to heat the specified Cr_2O_3 mass flow to the respective kiln temperature (1000 °C). An RGIBBS reactor (block COMBUSTION) has been implemented to provide the heat for calcination, through the combustion of a premixed, stoichiometric natural gas (as represented by CH_4)—air mixture (stream NG+AIR Premixed). Flue gas is separated from the products with the use of a Flash2 separator (block GAS SOLID SEPARATOR).

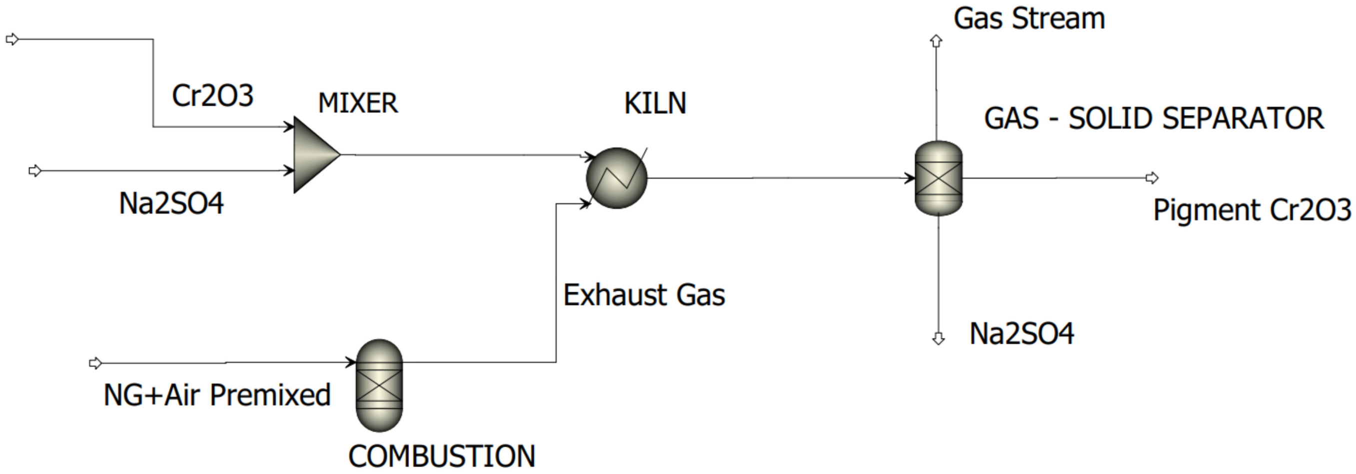

Figure 3. The Cr_2O_3-PIGM2 process model flowsheet.

The Cr_2O_3-MET Process

According to Swales et al. [19], 113 kg of sodium dichromate ($Na_2Cr_2O_7$) are mixed with 30 kg of water and 60 kg of ammonium sulfate [$(NH_4)_2SO_4$]. The resulting mixture is heated to 600 °C, where Reaction (1) occurs. The products of the reaction are washed to remove soluble salts, dried and then calcined at 1150 °C. The calcined product is washed with water and dried, resulting in the production of metallurgical grade Cr_2O_3 product. It should be noted that metallurgical grade Cr_2O_3 must depict lower impurity levels than the pigment grade Cr_2O_3 and this requirement leads to the implementation of the two different calcination stages considered.

Figure 4 presents the flowsheet of the process model developed in order to simulate the Cr_2O_3-MET process. An aquatic solution of reactants $Na_2Cr_2O_7$, $(NH_4)_2SO_4$ is fed to an RGIBBS reactor (block KILN1) where Reaction (1) occurs. The Reactor temperature must be equal to 600 °C. Produced Cr_2O_3 is separated from the rest of the products through a Flash 2 separator (block SOLID SEPARATOR). The outlet temperature of this block is set to 100 °C to emulate the temperature of solids after the washing and drying process which is necessary to separate the soluble salts from Cr_2O_3. Cr_2O_3 is subsequently fed to a heater (block KILN2) and heated to 1150 °C. This stage represents the calcination of Cr_2O_3 to produce metallurgical grade chromium oxide. The selection of a simple heater block to account for the Cr_2O_3 thermal treatment inside the kiln is associated with the absence of chemical reactions during calcination. Two RGIBBS reactors (COMBUSTION1-2 blocks) have been implemented to provide the required heat for calcination, through the combustion of a premixed, stoichiometric natural gas (as represented by CH_4)—air mixture (stream NG+AIR Premixed). Flue gas is separated from the products of the kiln with the use of a Flash2 separator (block GAS SOLID SEPARATOR). The drying process has not been modeled in the current simulation, however it is assumed that heat required for drying can be extracted from potential recirculation of hot flue gas exiting the considered separators and thus no further energy demand must be calculated.

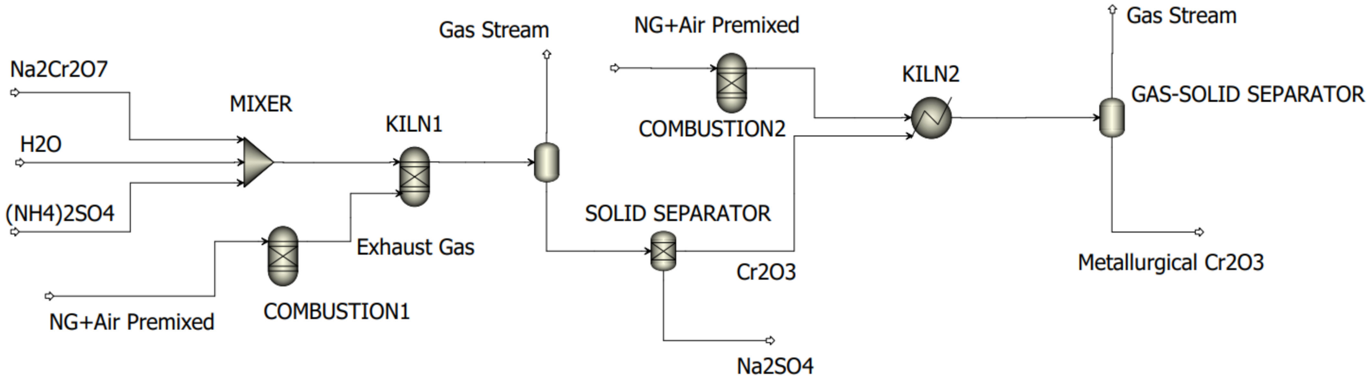

Figure 4. Flow sheet of pigment quality Cr_2O_3 production process. (Cr_2O_3-MET).

2.2. LCA Modeling

The environmental impact of each production process is evaluated by implementing Life Cycle Assessment methodology and using the SimaPro software (version 8.3), following a cradle-to-gate approach. The software package SimaPro is used for compiling life cycle inventories and performing impact assessment studies. A cradle-to-gate assessment refers to the emissions and requirements, starting from the extraction of the raw materials to the finished product at the factory exit.

- The main database that was used for the simulations is the Ecoinvent library, version 3.7 (released in September 2020);
- The impact assessment methods which provided the evaluation results were the EPD (2018), version 1.01 and the Cumulative Energy Demand (CED), version 1.11.

The goal of the developed LCA approach is to conduct an environmental assessment of the production process of each pigment. This is achieved by calculating the Global Warming Potential GWP (100) impact (kg of CO_2 equivalent) and fossil Primary Energy Demand (Fossil PED in MJ equivalent). Both indicators refer to the functional unit of the study, and the respective production of 1 kg of pigment (referenced as kg Cr_2O_3 or kg_{prod}). The pigment production corresponds to the Greek geographical boundaries (regarding electricity generation mix and natural gas imports) and all data inputs refer to the decade 2010–20. For this purpose, new inventories have been compiled and used, alongside with existing Ecoinvent inventories/processes. Table 3 describes where the data used in the simulations originates from [Ecoinvent inventories (E), results from process modeling (PM) and data from other sources (O)].

Table 3. Origin of data used in Life Cycle Assessment (LCA) calculations (PM: Process Model results; E: Existing Ecoinvent inventories and O: Custom made inventories from other literature sources).

Cr_2O_3-PIGM1	Cr_2O_3-PIGM2	Cr_2O_3-MET
Fuel consumption (PM) On-site emissions (PM)) Electricity consumption (O) Upstream processes/emissions (E)	Fuel consumption (PM)) On-site emissions (PM)) Electricity consumption (O) Upstream processes/emissions (E)	Fuel consumption (PM)) On-site emissions (PM)) Electricity consumption (O) Upstream processes/emissions (E)

The corresponding system boundaries, alongside with input and output flows considered are presented in Figure 5.

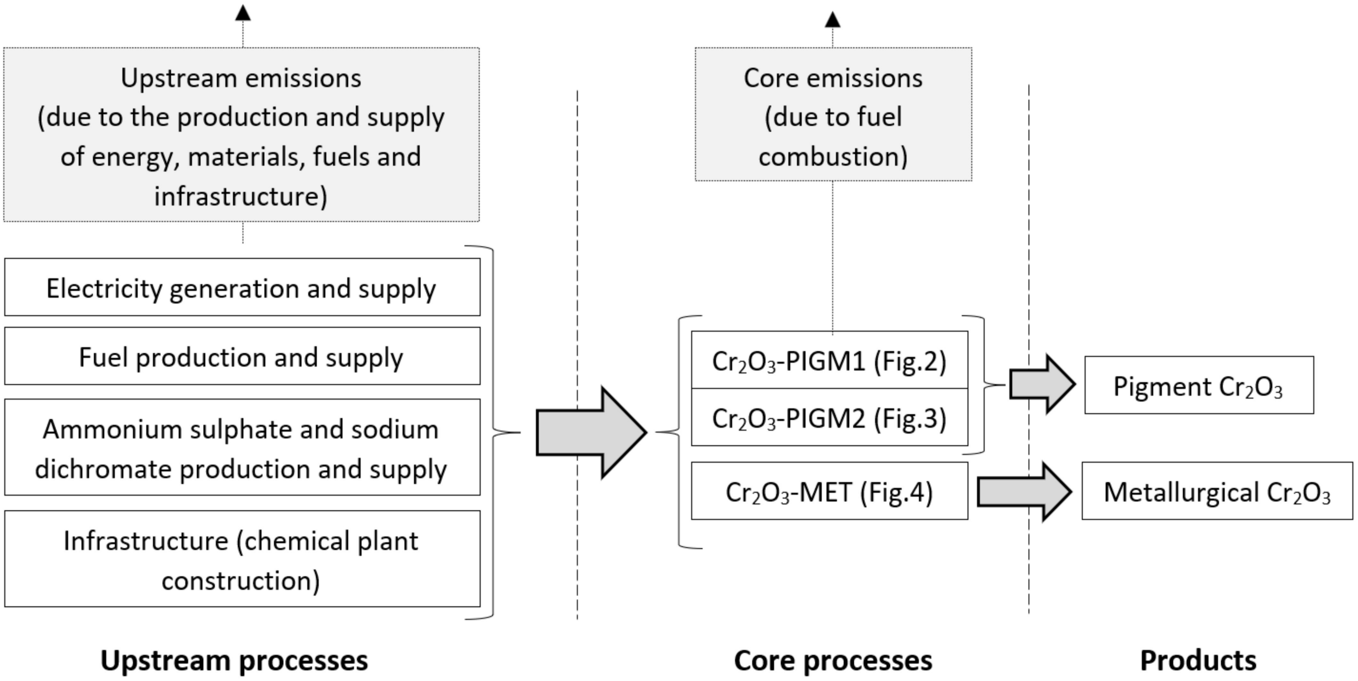

Figure 5. System boundaries and input/output flows considered.

Processes in the Ecoinvent library (version 3.7) of SimaPro version 9.01 are either based on older data (e.g., a Greek electricity production mix from 2010) or are based on data from other countries. In this study, it is assumed that the production of pigments occurs in Greece. As a result, it is necessary to update the processes which will be used to reflect the modern Greek energy market.

2.2.1. Natural Gas Import Mix

Initially, the natural gas import mixture of Greece is accordingly updated. The required data is obtained from the official website of DEPA (Public Gas Company), which is the main natural gas importer in Greece [36].

According to DEPA, natural gas imported into Greece consists of:

- 67% natural gas originating from Russia with pipeline transport;
- 16% natural gas originating from Algeria and imported as Liquefied Natural Gas (LNG);
- 17% natural gas imported from Turkey with pipeline transport;

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

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

As a result of the aforementioned assumptions, natural gas imported into Greece is assumed to consist of 84% natural gas originating from Russia and 16% natural gas originating from Algeria and imported as LNG.

2.2.2. Electricity Production Mix

The Ecoinvent database contains data regarding the electricity production mix of Greece. However, this information originates from data gathered in 2010 and is outdated when compared to more recent data, mainly due to new environmental restrictions, which reduced the contribution of lignite generation. Updated data regarding Greek electricity mix are acquired from DAPEEP [37] (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 of 2018 was produced from:

- 29.95% natural gas combustion;
- 29.28% lignite combustion;
- 12.38% wind power;
- 11.29% hydroelectric power;
- 9.01% oil combustion;
- 7.46% solar power;
- 0.59% biomass combustion;
- 0.05% other fossil fuels combustion.

Apart from domestic production, a small percentage of the electricity consumed was imported from neighboring countries (Italy, Bulgaria and North Macedonia). However, to simplify the simulation and due to lack of recent data, it is assumed that all of the electricity required is produced in Greece. This assumption is expected to have a negligible effect on the results.

2.2.3. Other Assumptions

Apart from heat consumption in the rotary kiln, further data on heat and electricity consumptions are required to perform a cradle-to-gate analysis of the pigment production process. Due to lack of relevant data, it is assumed that heat and electricity requirements of processes which are not available in the Ecoinvent libraries are equal to those of a conventional cement production plant. The reason for using data from cement production as "proxy" are the similarities regarding the two production lines, since the core heat driven process occurs in a rotary kiln, followed by an air cooler [30].

According to Atmaca and Yumrutas [38] who used actual industrial data from a cement plant, total electrical energy consumption for cement production is 110 kWh/t of cement or 0.11 kWh/kg of cement. A big part of this electrical consumption is used in the rotary kiln, which requires approximately 0.065 kWh per kg of material produced. This electrical consumption is assumed to be equal to the electrical consumption of each rotary kiln used in the production of ceramic pigments.

Atmaca and Yumrutas [38] also state that the rotary kiln system is the most energy-intensive stage in cement production, accounting for approximately 90% of the total thermal energy demand. As a result, the total required heat consumption (HC) during the production process of a pigment will be calculated (where it is necessary) as:

$$\mathrm{HC} = \mathrm{ED}/0.9 \tag{4}$$

where ED is the energy demand for the production of the pigment in kWh/kg of material produced, as received from the process models described in Section 2.1.2.

The final step before performing the LCA study is to specify the emissions originating from the construction of infrastructure (buildings and facilities used in the production process). The infrastructure emissions are reduced to the functional unit of the study, therefore after following the assumptions already provided by the LCA software regarding typical plant capacity and total years of operation, the value of 4×10^{-10} "pieces" of a chemical factory, used for organic chemicals production (buildings and facilities included), is required. This value of plant "pieces" is the reciprocal number of the lifetime production in kg, or in other words, "how many plants does it take to produce 1 kg of product"? It is assumed that the lifetime production of the pigment facility can be calculated from the corresponding annual production capacity and lifetime of the typical organic chemical plant included in the Ecoinvent library.

Using the aforementioned assumptions and modifications to existing SimaPro processes, all the processes that will be used in the LCA of each pigment are modified to take into account the new data.

2.3. LCA of Green Cr_2O_3 Pigment Production Process

As already stated, three alternative mixture preparation pathways have been considered for Cr_2O_3 production. The first two pathways correspond to Cr_2O_3 pigment quality production (Cr_2O_3-PIGM1 and Cr_2O_3-PIGM2) and the third one to metallurgical quality (Cr_2O_3-MET). All production processes will be evaluated with a cradle-to-gate approach, in order to determine their environmental impact.

The first process that was evaluated was the production of pigment grade Cr_2O_3, (Cr_2O_3-PIGM1) through mixture preparation and subsequent calcination based on Reaction (1). Thermal consumption was received from the process modeling results while electricity consumption is considered to be equal to 0.065 kWh/kg of pigment (electricity required for the operation of 1 rotary kiln). Table 4 enlists the LCA input information for the assessment of Cr_2O_3-PIGM1 production route.

Table 4. LCA input for the pigment grade Cr_2O_3 production route (Cr_2O_3-PIGM1).

Process/Resource/Material Name	**Quantity Produced/Required/Emitted**
Products	
Pigment Cr_2O_3 from PIGM1 process	1 kg
Materials/fuels	
Industrial water, deionized/kg	0.458 kg
Chemical plant, organics, U (modified to fit modern Greek energy system)	4×10^{-10}
Natural gas, high pressure, at consumer, U (modified to fit modern Greek energy system; assuming 90% combustion efficiency)	2.069 kWh
Sodium dichromate, at plant, U (modified to fit modern Greek energy system)	1.724 kg
Ammonium sulfate, as N, at regional storehouse, U (modified to fit modern Greek energy system)	0.915 kg
Electricity/heat	
Electricity, medium voltage, production GR, at grid, U (modified to fit modern Greek energy system)	0.065 kWh
Emissions to air	
Oxygen	0.0077 kg
Nitrogen	2.37 kg
Water	2.44 kg
Carbon dioxide, fossil	0.39 kg
Carbon monoxide, fossil	0.001 kg
Nitrogen dioxide	8.1×10^{-7} kg
Nitric oxide	0.003 kg
Hydrogen	0.0003 kg

Production of pigment quality Cr_2O_3 from non-pigment Cr_2O_3 (Cr_2O_3-PIGM2) incorporates fuel consumption and emissions from the respective process models and electricity consumption (for the operation of 1 rotary kiln), It is assumed that the production of pigment quality Cr_2O_3 occurs in a similar production plant as the other production routes considered.

Table 5 enlists the LCA input information for the assessment of the Cr_2O_3-PIGM2 production route. There is a significant uncertainty regarding the production process of "non-pigment" Cr_2O_3 since the corresponding patent [21] does not provide the necessary data for the quantification of the relevant upstream emissions. A possible assumption is to consider this input stream as a waste low-grade product of an existing production chain, thus assigning zero impact to the process input. However, a more conservative approach is followed, assuming primary CrO_3 production, followed by thermal decomposition in order to produce Cr_2O_3. Ecoinvent provided the upstream emissions of CrO_3 production, while the thermochemical balance of Reaction (3) provided the theoretical minimum heat needed for this transformation.

Table 5. LCA input for the pigment grade Cr_2O_3 production route from non-pigment Cr_2O_3 (Cr_2O_3-PIGM2).

Process/Resource/Material Name	Quantity Produced/Required/Emitted
Products	
Green Cr_2O_3 pigment	1 kg
Materials/fuels	
Natural gas, high pressure, at consumer, U (modified to fit modern Greek energy system; assuming 90% combustion efficiency)	0.502 kWh
Natural gas for producing the necessary heat for the thermal decomposition of CrO_3 to Cr_2O_3 (thermochemical balance of Equation (3))	0.1 kWh
CrO_3 production and supply	0.952 kg
Sodium sulfate production and supply	0.048 kg
Electricity/heat	
Electricity, medium voltage, production GR, at grid, U (modified to fit modern Greek energy system)	0.065 kWh
Emissions to air	
Oxygen	0.0019kg
Nitrogen	0.58 kg
Water	0.59 kg
Carbon dioxide, fossil	0.095 kg
Carbon monoxide, fossil	0.0028 kg
Nitrogen dioxide	1.97×10^{-7} kg
Nitric oxide	0.0007 kg
Hydrogen	8.3×10^{-5} kg

The production of metallurgical grade Cr_2O_3, as described in Section 2.2. All relevant assumptions have been described in Section 2.2.1. Table 6 enlists the LCA input information for the assessment of Cr_2O_3-MET production route.

Table 6. LCA input for the metallurgical Cr_2O_3 (Cr_2O_3-MET) production.

Process/Resource/Material Name	Quantity Produced/Required/Emitted
Products	
Cr_2O_3 metallurgical	1 kg
Materials/fuels	
Industrial water, deionized/kg	0.46 kg
Chemical plant, organics, U (modified to fit modern Greek energy system)	4×10^{-10} p
Natural gas, high pressure, at consumer, U (modified to fit modern Greek energy system; assuming 90% combustion efficiency)	1.158 kWh
Sodium dichromate, at plant, U (modified to fit modern Greek energy system)	1.72 kg
Ammonium sulfate, as N, at regional storehouse, U (modified to fit modern Greek energy system)	0.92 kg
Electricity/heat	
Electricity, medium voltage, production GR, at grid, U (modified to fit modern Greek energy system)	0.065 kWh
Emissions to air	
Oxygen	0.0044 kg
Nitrogen	1.33 kg
Water	1.37 kg
Carbon dioxide, fossil	0.219 kg
Carbon monoxide, fossil	0.0065 kg
Nitrogen dioxide	0.000000453 kg
Nitric oxide	0.0017 kg
Hydrogen	0.00019 kg

3. Results

3.1. Results of Process Models Simulations

3.1.1. Results of Rutile TiO_2 Production Simulation. Validation of Model

The model developed in Aspen Plus has been implemented for the simulation of the rutile TiO_2 production unit. In order to validate the developed model, computational results are compared to the aforementioned industrial data [8].

The outcome of this assessment is presented in Table 7. It is shown that in order to reach a temperature of 924 °C at the outlet of the kiln (as suggested by the industrial data), fuel consumption equal to 535 kg/h CH_4 is predicted. However, this value is not directly comparable to the available STP volumetric flow of natural gas. Therefore, fuel consumption is converted to heat consumption.

Table 7. Validation of the developed process model. Comparison of simulation results against industrial data [8].

Variable	Calculated Value	Industrial Data	Deviation [%]
Fuel Consumption	535 kg/h (CH_4)	740 m^3 STP/h (NG)	N/A
Energy Consumption (kWh/kgTiO_2)	2.03	2.07	−1.7
Produced rutile TiO_2 mass flow (kg/h)	3655	3650	0.16
Outlet Temperature (°C)	924	924	[-]

It should be noted that in all presented simulations the required heat is provided by natural gas (as represented by methane) combustion and assuming a LHV of 50 MJ/(kg for methane [24]. Energy demand (ED) for the pigment production is calculated in kWh/(kg of produced pigment) as shown below:

$$ED = LHV \times m_f/(3600 \times m_{pigment}) \quad (5)$$

where:

- ED: heat required for the production of the pigment in [kWh/(kg of pigment)];
- LHV: lower heating value of the fuel in [MJ/(kg of fuel)];
- m_f: fuel mass flow, received through the process simulation in [(kg of fuel)/h];
- 1/3600: conversion coefficient from kJ to kWh [h/s];
- $m_{pigment}$: mass flow of the pigment produced, received through the process simulation in [(kg of pigment)/h].

The actual energy consumption of the plant is calculated with the use of the STP volume flow of natural gas, its lower heating value and the mass flow of the calcined product (all values are available in Table 2) as depicted below:

$$\text{Real plant consumption} = V_{NaG} \times H_{u,NaG}/m_{Cl} = 740 \times 10.2/3650 \approx 2.07\ kWh/kg_{TiO2} \quad (6)$$

On the other hand, Equation (2) is used for the calculation of the energy consumption predicted by the model. The value 2.03 kWh/kg_{TiO2} is computed depicting a 1.7% deviation from the respective industrial value and thus providing a satisfactory agreement between computational results and industrial data. Furthermore, the predicted mass flow of the calcined product depicts a small deviation of approximately 0.16% when compared to the respective industrial value.

Evidently, the process model developed for the simulation of rutile TiO_2 production with the sulfate method can be used to produce results with small deviations when compared to actual industrial data. Therefore, it can be considered as a reliable tool for the development of models reproducing typical Cr_2O_3 pigment production processes depicting similar process stages (e.g., calcination).

3.1.2. Results of Green Cr_2O_3 Production Simulation

Figure 6 presents predicted heat demand and CO_2 emissions per kg of calcined product for the Cr_2O_3-PIGM1 process. The calcination temperature is equal to 950 °C. Three alternative scenarios of water concentration to the mixture entering the kiln (10–20–30% per weight, respectively) are considered. Natural gas combustion (as represented by CH_4) provides the calculated heat requirements and leads to the predicted CO_2 emissions. As can be seen, water content in the kiln mix significantly increases the process heat demand. Predicted heat demand ranges from 1.1 kWh/kg_{prod} (for water content equal to 10%) to 3.2 kWh/kg_{prod} (30% water content). A similar behavior is depicted for the calculated CO_2 emissions which vary between 0.22–0.64 kg/kg_{prod}. Furthermore, four alternative scenarios corresponding to standard pigment formation calcination temperatures (950–1100 °C) are shown in Figure 7. For this set of simulations water content in the kiln is considered to be equal to 20%. Evidently, predicted heat demand increases with temperature and ranges from 1.86 kWh/kg_{prod} (T = 950 °C) to 2.64 kWh/kg_{prod} (T = 1100 °C). Calculated CO_2 emissions depict a similar trend and vary between 0.37–0.52 kg/kg_{prod} (950–1100 °C).

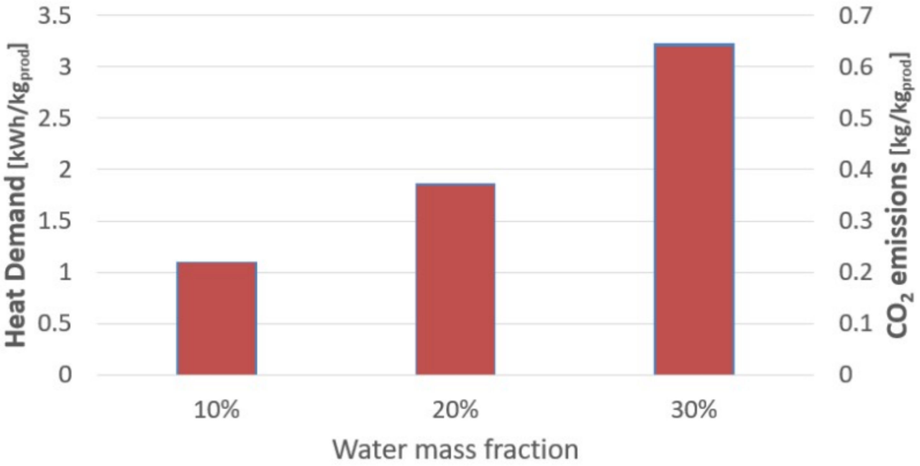

Figure 6. Calculated heat demand and CO_2 emissions for Cr_2O_3-PIGM1 process for various water concentrations in the kiln mix (reference calcination temperature: 950 °C).

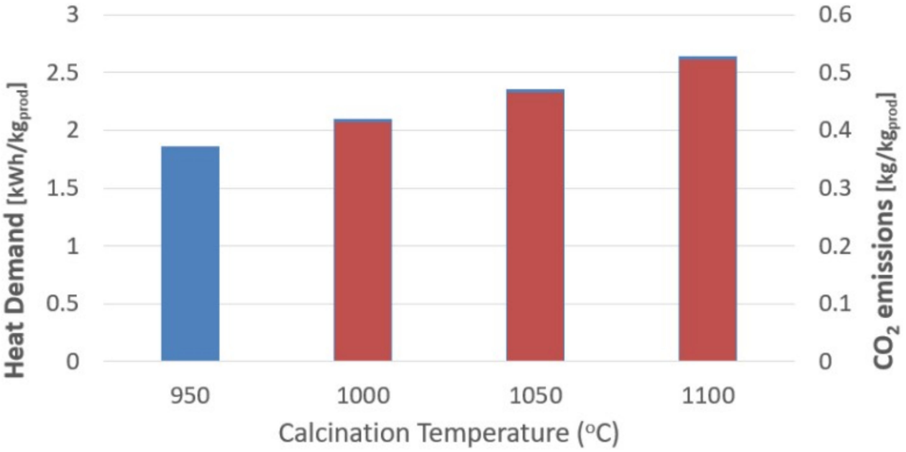

Figure 7. Calculated heat demand and CO_2 emissions for Cr_2O_3-PIGM1 process for various calcination temperatures (water content in the kiln mix: 20%).

Figure 8 presents a parametric study depicting the effect of kiln temperature in the predicted heat demand and CO_2 emissions for the Cr_2O_3-PIGM2 process. Six alternative scenarios of kiln temperature (950–1200 °C) are considered in order to represent standard pigment formation conditions. A temperature equal to 982 °C corresponds to the reference scenario obtained from the patent description [21]. As can be seen, predicted process heat demand and CO_2 emissions are significantly lower than those emerging from the Cr_2O_3-PIGM1 process. This is justified by the absence of water in the kiln since non-pigment Cr_2O_3 and Na_2SO_4 are dry mixed. Heat demand values range between 0.42–0.72 kWh/kg_{prod} with increasing temperature. CO_2 emissions obtain values within 0.08–0.13 kg/kg_{prod}. Upstream heat consumption and CO_2 emissions for the production of non-pigment Cr_2O_3 are taken into account in the LCA approach.

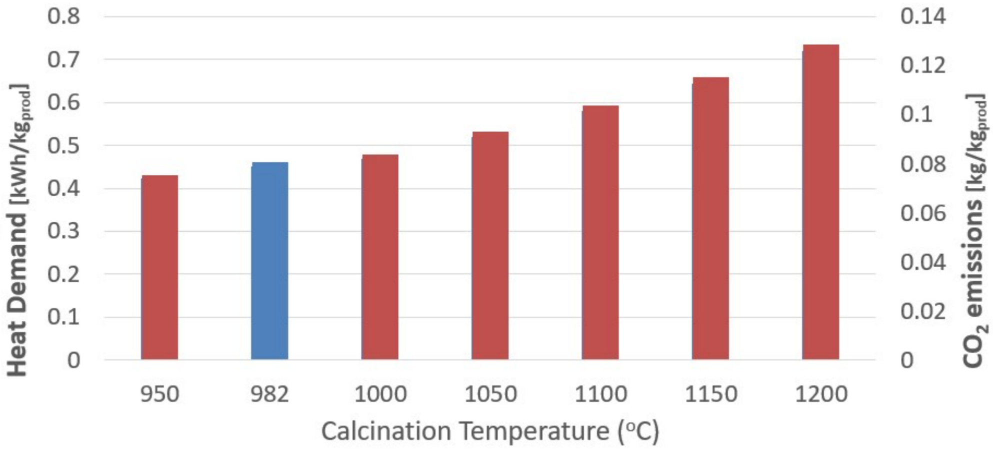

Figure 8. Calculated heat demand and CO_2 emissions for Cr_2O_3-PIGM2 process for various calcination temperatures (reference temperature: 982 °C).

A comparative assessment of the predicted heat demand and CO_2 emissions for the three implemented process scenarios (Cr_2O_3-PIGM1/Cr_2O_3-PIGM2/Cr_2O_3-MET) is presented in Figure 9. Results are shown for reference kiln temperatures T = 950 °C (Cr_2O_3-PIGM1), 982 °C (Cr_2O_3-PIGM2) and 600/1150 °C (Cr_2O_3-MET). Cr_2O_3-PIGM1 is the most energy-intensive process due to the presence of increased concentrations of water in the kiln. Although Cr_2O_3-MET implements two kilns in order to ensure the production of a metallurgical grade Cr_2O_3 with very low impurities, the emerging total heat demand is equal to 1.04 kWh/kg_{prod}, significantly lower than the respective Cr_2O_3-PIGM1 demand. It should be noted that a 15% (per weight) water concentration is accounted for in the first kiln mix of the Cr_2O_3-MET process. Respective heat demand is lower because: (a) water concentration is lower than the 20% concentration considered in the reference Cr_2O_3-PIGM1 scenario and (b) the first kiln temperature remains at a lower temperature (T = 600 °C), whereas the second resembles the kiln operation of the PIGM2 pathway (associated with lower heat requirements and CO_2 emissions). Calculated CO_2 emissions are equal to 0.2 kg/ kg_{prod}. It should be noted that in all examined scenarios, potential drying or evaporation of sodium dichromate and/or ammonium sulfate solutions prior to the kiln has not been taken into account. It is assumed that heat required for drying/evaporation can be extracted from recirculation of hot flue gas and thus no further energy demand is required. A possible scenario associated with the implementation of a dry mix entering the kiln is reflected in the Cr_2O_3-PIGM2 calculations.

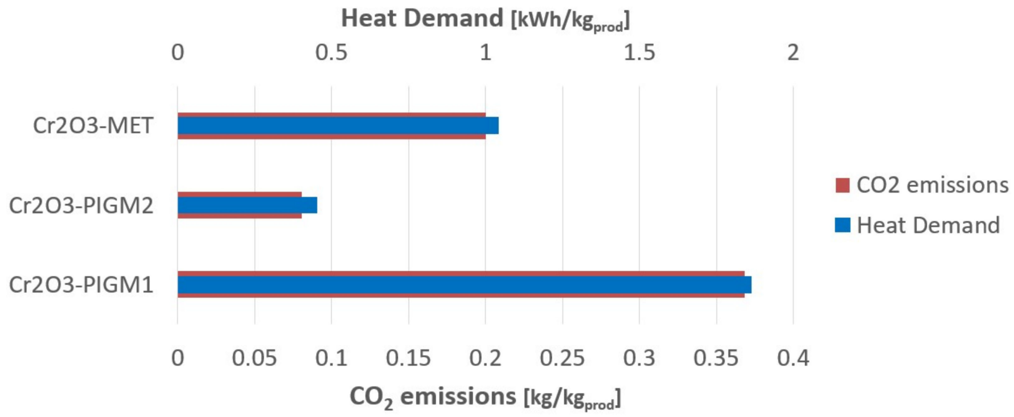

Figure 9. Calculated heat demand and CO_2 emissions for the three implemented process scenarios (Cr_2O_3-PIGM1/Cr_2O_3-PIGM2/Cr_2O_3-MET).

3.2. Results of Cr_2O_3 Production LCA Simulations

3.2.1. LCA Results of Pigment Cr_2O_3 Production, According to Case PIGM1

As mentioned previously, the process simulation provided a series of intermediate results for the PIGM1 case. An overview of the corresponding results of LCA for the production of pigment Cr_2O_3-PIGM1 is presented in Table 8.

Table 8. LCA results of Cr_2O_3-PIGM1 production process.

Parameter	Results			
	Calcination T: 950 °C; 10% water content	Calcination T: 950 °C; 20% water content	Calcination T: 1100 °C; 20% water content	Calcination T: 950 °C; 30% water content
CO_2 from fossil fuels	11.39 kg	11.60 kg	11.81 kg	11.97 kg
GWP (100)	12.15 kg CO_2-eq	12.38 kg CO_2-eq	12.62 kg CO_2-eq	12.80 kg CO_2-eq
Non-renewable energy from fossil fuels	148.5 MJ-eq	152.5 MJ-eq	156.5 MJ-eq	159.6 MJ-eq

The contribution of each (main) process that participates in the LCA for the production of pigment quality Cr_2O_3-PIGM1 (Calcination T: 950 °C; 20% water content), is presented in Figures 10 and 11. The GWP is predicted to be equal to 12.38 kgCO_2-eq per kg of Cr_2O_3 product. A total of 152.5 MJ-eq is predicted for the fossil PED. According to the results, the upstream emissions of producing ammonium sulfate and sodium dichromate are responsible for the biggest part of the emissions and energy requirements (approximately 95%).

3.2.2. LCA Results of Pigment Cr_2O_3 Production, According to Process PIGM2

An overview of the corresponding results of LCA for the production of pigment Cr_2O_3-PIGM2 is presented in Table 9.

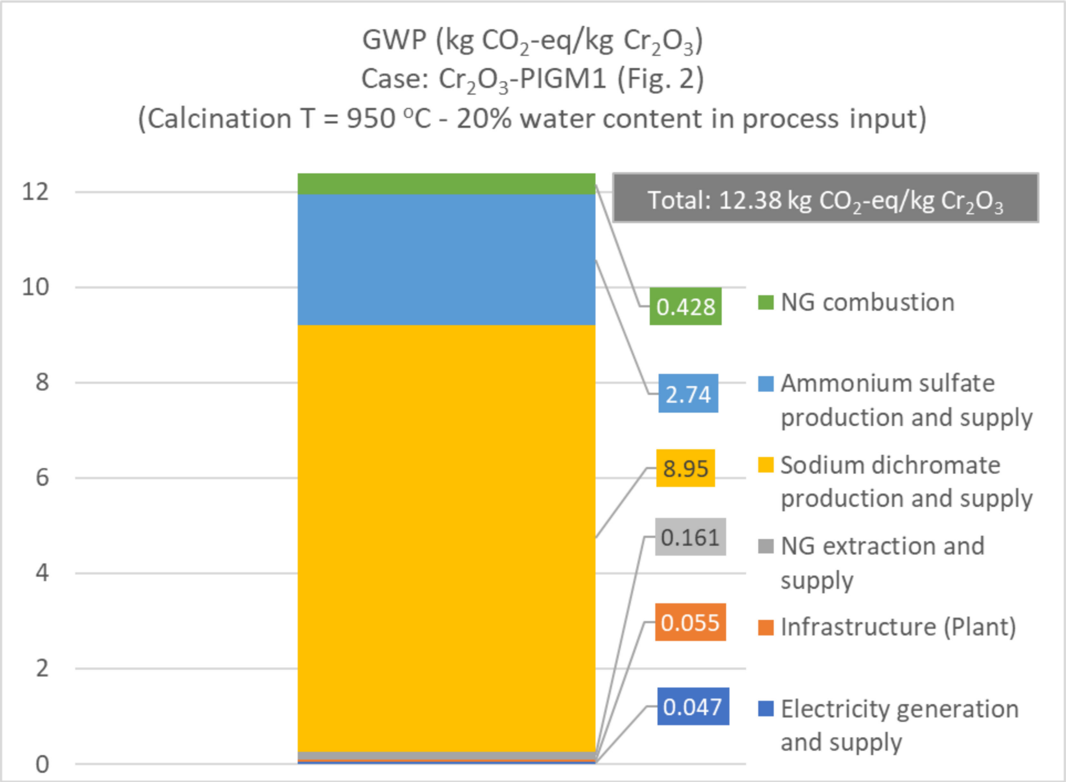

Figure 10. Global Warming Potential (GWP100) in kg of CO_2 equivalent during the production process of pigment quality Cr_2O_3-PIGM1.

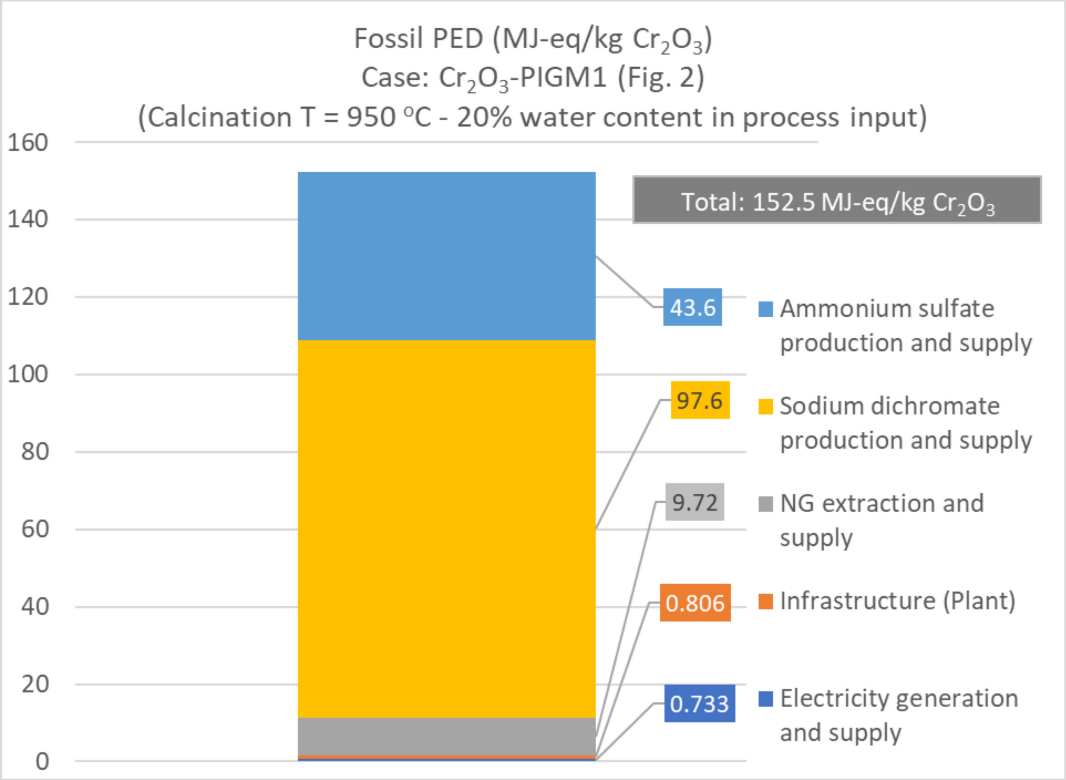

Figure 11. Fossil Primary Energy Demand (PED) in MJ equivalent for the production process of pigment quality Cr_2O_3-PIGM1.

Table 9. LCA results of pigment quality Cr_2O_3-PIGM2 production process.

Parameter	Results		
	Calcination T: 950 °C; 20% water content	Calcination T: 982 °C; 20% water content	Calcination T: 1200 °C; 20% water content
CO_2 from fossil fuels	7.46 kg	7.47 kg	7.53 kg
GWP (100)	7.91 kg CO_2-eq	7.92 kg kg CO_2-eq	7.99 kg kg CO_2-eq
Non-renewable energy from fossil fuels	91.4 MJ-eq	91.6 MJ-eq	93.0 MJ-eq

LCA results for the production of pigment quality Cr_2O_3 using the PIGM2 process are presented in Figures 12 and 13. The GWP is predicted to be equal to 7.92 kg CO_2-eq per kg of Cr_2O_3. A total of 91.6 MJ-eq is predicted for the fossil PED. By assessing the contribution of each individual stage participating in the Cr_2O_3 production chain, it is evident that the upstream emissions of producing the chromium anhydride (CrO_3) are responsible for the biggest part of the emissions and energy requirements during the production of pigment Cr_2O_3-PIGM2 (approximately 96%). The results for the PIGM2 case demonstrate an emission and primary energy reduction potential (35 and 40%, respectively compared to the PIGM1 case), for two reasons: (a) a lower process energy requirement and (b) (most importantly) less raw material requirements.

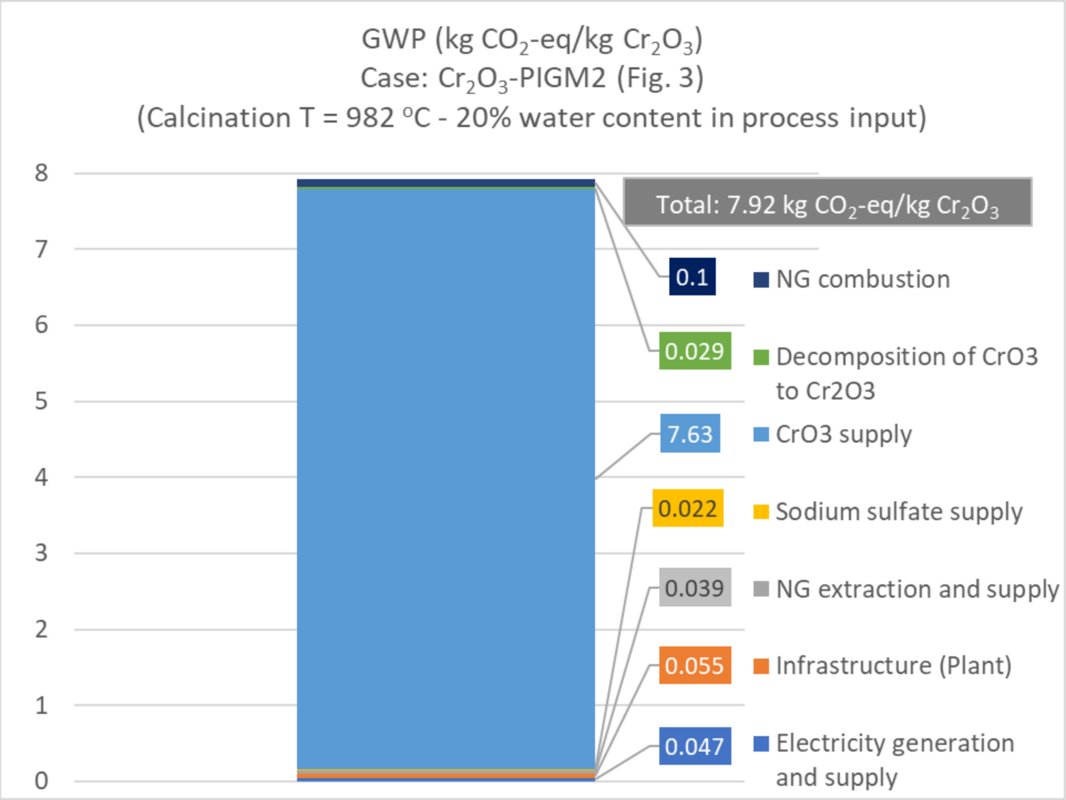

Figure 12. GWP (100) in kg of CO_2 equivalent during the production process of pigment quality Cr_2O_3-PIGM2.

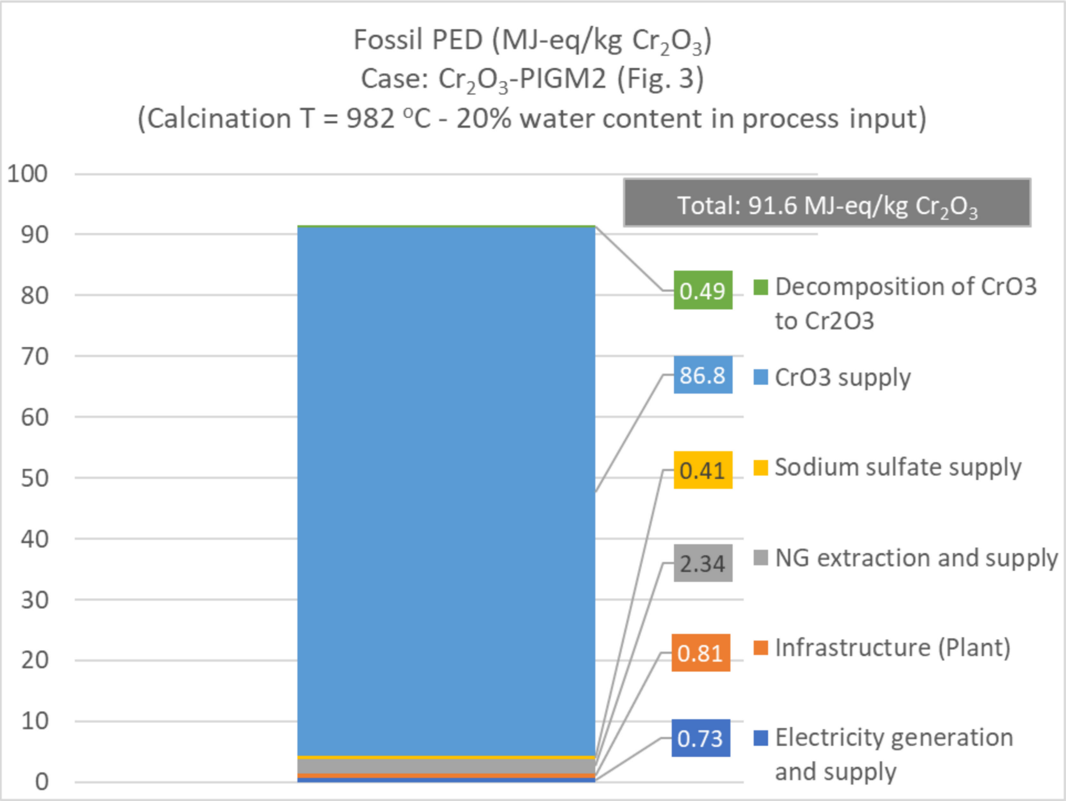

Figure 13. Fossil PED in MJ equivalent for the production process of pigment quality Cr_2O_3-PIGM2.

3.2.3. LCA Results of Metallurgical Cr_2O_3 Production

An overview of the results of LCA of metallurgical (Cr_2O_3 -MET) production process, is presented in Table 10:

Table 10. LCA results of metallurgical Cr_2O_3 production process.

Indicators	Results
CO_2 from fossil fuels	11.36 kg
GWP (100)	12.11 kg of CO_2 equivalent
Fossil PED	148 MJ equivalent

LCA results for the production of metallurgical Cr_2O_3 are presented in Figures 14 and 15. The GWP is predicted to be equal to 12.11 kg CO_2-eq per kg of Cr_2O_3. A total of 148.2 MJ-eq is predicted for the fossil PED. By assessing the contribution of each individual stage participating in the Cr_2O_3 production chain, it can be stated that the upstream production of sodium dichromate and ammonium sulfate is responsible for the biggest part of the emissions and energy requirements from non-renewable fuels (95–97%).

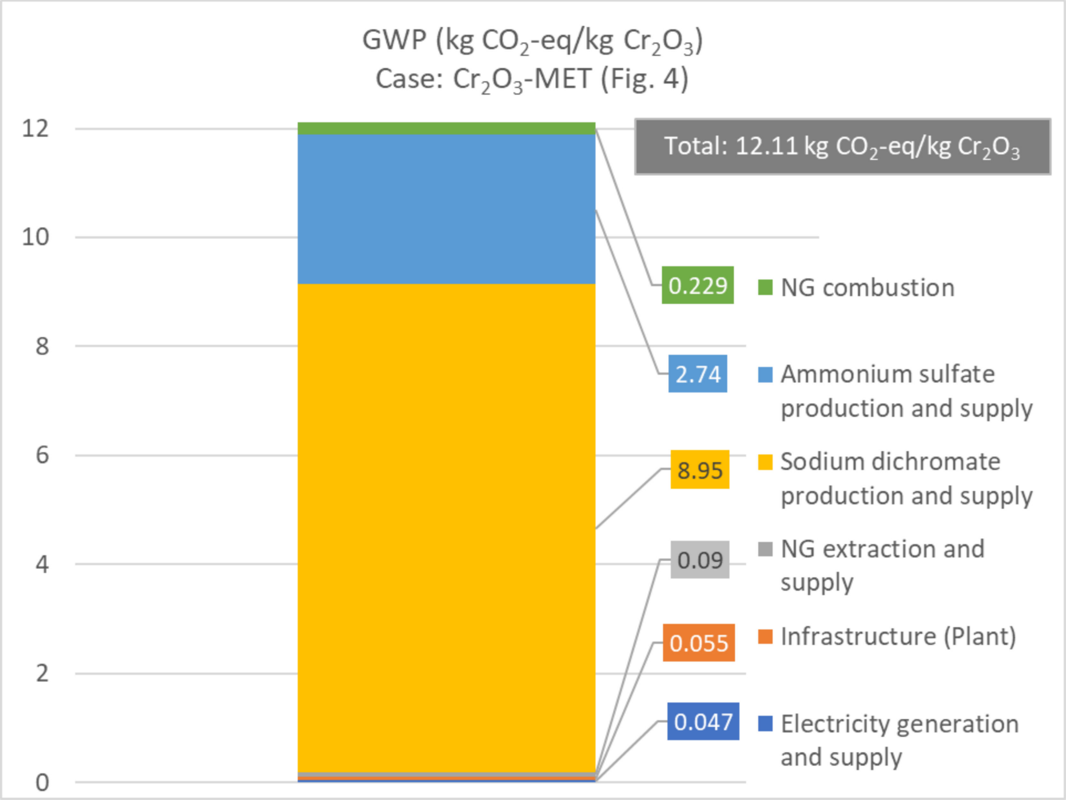

Figure 14. GWP (100) in kg of CO_2 equivalent during metallurgical Cr_2O_3 production.

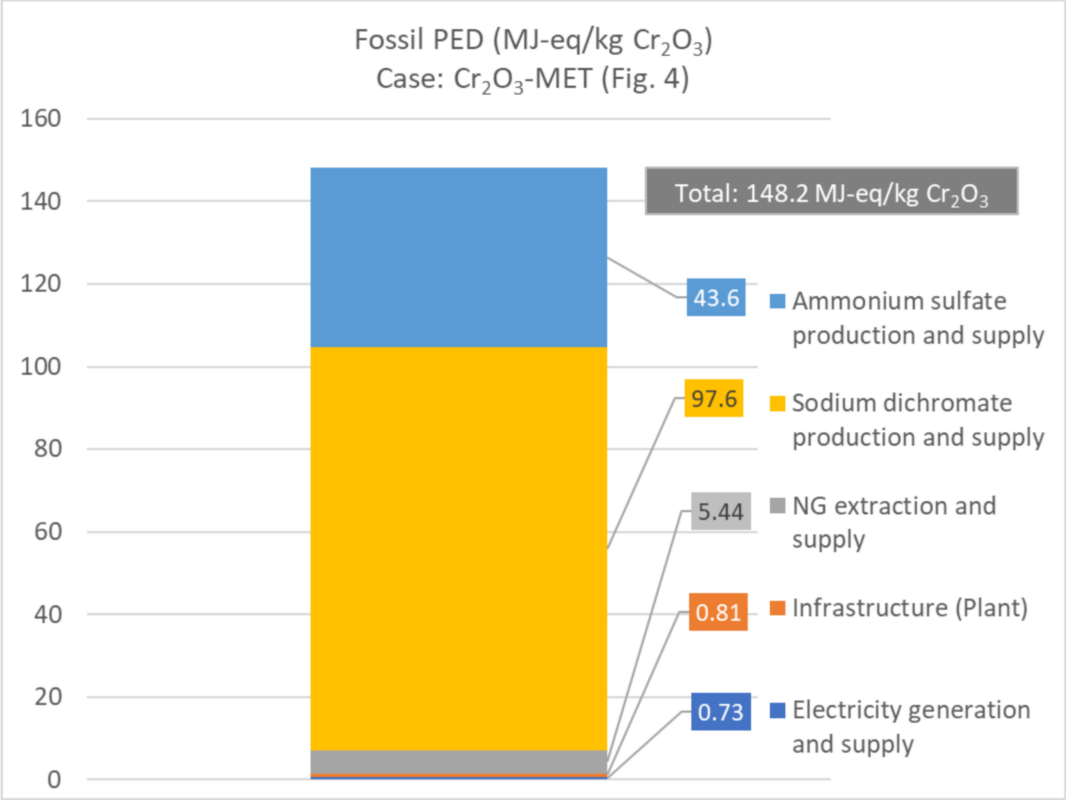

Figure 15. Fossil PED in MJ equivalent during the production of metallurgical Cr_2O_3.

4. Discussion

The performed LCA provided a useful insight into the most important environmental aspects of the Cr_2O_3 production chains considered. The performed simulations resulted in a total GWP (100) ranging from 7.9 to 12.8 CO_2-eq and fossil PED between 91.4–159.6 MJ-eq (all referring to 1 kg of pigment production).

In all examined cases the impact of producing Cr_2O_3 was predominantly assigned to upstream processes of producing the raw materials. Only minor contributions in terms of greenhouse gases were calculated to originate from the natural gas combustion during the final firing process which was simulated in the first part of this work. This means that optimizing the core heat treatment can provide benefits, however, a strategy to reduce overall emissions and primary energy requirements should primarily consider the impact brought in by raw materials. To be more specific, the Cr_2O_3-MET case shows a GWP contribution of 1.9% for on-site emissions (process NG combustion), the Cr_2O_3-PIGM1 3.5% and the Cr_2O_3-PIGM2 1.3%, respectively.

In the case of assuming an alternative fossil fuel for the energy demand of the core processes, the life cycle GWP components to be affected are the combustion emissions (green component in Figures 10 and 14, dark blue in Figure 12) and the production/supply emissions (gray component in Figures 10, 12 and 14). Due to the higher carbon content compared to natural gas, fuel oil and coal provide more GWP for producing 1 MJ of heat (+30% GWP for fuel oil and +83% for coal, as calculated according to the Ecoinvent data), However, the small GWP contribution of the core combustion emissions leads to minor corresponding increases in terms of overall GWP. For example, in the Cr_2O_3-PIGM1 case, the overall GWP increased by 1.3% if considering light fuel oil and 4.9% if assuming coal as the core process fuel.

Due to the absence of case-specific industrial data, the electric consumption of the kiln was assumed to be the same of a cement plant kiln. This choice has been justified, however it can be commented as underestimated, if considering the production capacity difference between a very large cement kiln and a small to medium pigment kiln. Nevertheless, the contribution of the respective electricity generation and supply flow (as observed in Figures 10–15) was minimal, ranging between 0.37–0.59% for GWP and 0.48–0.8% for fossil PED. Therefore, even if assuming a quite high specific electricity production by a factor of three, the overall GWP result will be affected by less than 2%, which is not considered as significant.

The impact of transporting the input materials was not considered, since providing a minimal contribution of app. 1%. This value is the result of a scenario involving the transportation of 2.6 kg of raw materials (see Table 4) with a container ship from the Netherlands (Rotterdam) to Greece (Pireaus) (distance of 2842 n.m. or 5263 km). The corresponding result was a value of 0.131 kg of CO_2-eq per kg produced, while the total GWP impact for Cr_2O_3-PIGM1 case was 12.38 kg of CO_2-eq per kg produced.

The results for the Cr_2O_3-PIGM2 case demonstrate an emission and primary energy reduction potential (35 and 40%, respectively), for two reasons: its lower process energy requirement and (most importantly) fewer raw material requirements. The Cr_2O_3-PIGM1 case shows higher core process energy requirements, due to the water content in the kiln mix, but the effect is minimal in terms of the life cycle approach. In parallel to the previous finding, minimal final result (in terms of GWP and fossil PED) sensitivity has been identified in the cases of variable water input or calcination temperature.

However, the input data used do not originate from actual industrial operation, making various assumptions necessary, such as the thermochemical balance used for the calculation of the energy required for the thermal decomposition of CrO_3. Additionally, the LCA libraries may be a reliable source of information; nevertheless, the corresponding results acquired should not be considered as valid for any other production case.

In any case, the present work contributes to a field with very little literature coverage, providing an energetic and environmental benchmark of the traditional and alternative pathways for producing an important industrial product. An additional contribution can be claimed by the introduction of a combined methodology, which approaches both simulation modeling and environmental assessment. The corresponding benefit is demonstrated in the final results, where the effect of the variation of operational parameters in the core process can be evaluated in terms of the overall production chain, integrating the upstream impacts.

5. Conclusions

Modern ceramic pigments are widely used for their coloring, as well as their protective or magnetic properties. The most widespread production process for ceramic pigments includes high temperature calcination using a rotary kiln. The current study focuses on the production process of green Cr_2O_3 pigment. Due to the high temperature requirements of this specific process, it is necessary to evaluate its environmental impact with regards to energy requirements and CO_2 emissions. Towards this direction, a combined process modeling—LCA—approach for the evaluation of green Cr_2O_3 ceramic pigments production was implemented. A process model was developed to simulate the final calcination stage of pigments production. Initially, the model was validated against titanium dioxide (TiO_2) white production data. Subsequently, it was adjusted in order to perform simulations of three alternative approaches of Cr_2O_3 production: two for pigment grade and one for metallurgical. Process simulation results show that heat requirements vary between 0.5–3.1 kWh/kg_{prod} depending on the kiln temperature and water concentration inside the kiln. Similarly, calcination process CO_2 emissions range between 0.08–0.64 kWh/kg_{prod}. These values were used as input, along with upstream data from the literature in a Life Cycle Assessment (LCA) study, using a cradle-to-gate approach. The production of each pigment was assumed to occur in Greece under current conditions. LCA results include CO_2 emissions from fossil fuels in kg, GWP (100) in kg of CO_2 equivalent and energy from non-renewable (fossil) fuels required in MJ equivalent, all referring to the respective cases of producing 1 kg of pigment. The emerging results show that GWP (100) ranges from 7.9 to 12.8 CO_2-eq and fossil PED between 91.4–159.6 MJ-eq. It was depicted that the biggest part of the emissions originated from the production and transportation of its starting materials (contributing up to 96% of total CO_2 emissions) and other facilities (electricity, production plants, etc.), rather than the examined calcination process (contributing from 1.3 to 3.5% GWP).

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