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Evaluation of refuse-derived and tyre-derived fuels in cement industry: a study on emission characteristics

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Abstract: This paper evaluates the impact of alternative fuels utilised in a cement facility in Central Anatolia, Turkey, on CO₂, SO₂, H₂O, and NO_x emissions. We implemented Chemkin-Pro and NASA CEA to investigate 16 fuel scenarios at temperatures between 973.15 K and 1,473.15 K. The modelling results demonstrate that high volatility and oxygen content in refuse-derived fuel contributed to an increase in NO_x formation. Conversely, the low volatility and high carbon content of petcoke led to a decrease in NO_x emissions. In scenario 13, the tyre and refuse-derived fuel combination yielded the lowest NO_x emissions.

Keywords: alternative fuel; cement production; CO₂ reduction; combustion gas emission; global warming; RDF; TDF.

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1 Introduction

Cement production is the major carbon dioxide (CO₂) emissions (Cansiz et al., 2023), accounting for 26% of total industrial emissions (Luo et al., 2024). Multifaceted efforts are underway to prevent global warming and eliminate emissions from cement production, with more than 20 countries aiming to achieve net zero emissions by 2050 as part of the United Nations sustainability goals (Rende et al., 2018). CO₂ emissions from cement factories could be reduced by processing alternative fuels, but in some cases, non-CO₂ air pollutants could increase. Based on analyses of the impact of non-CO₂ emissions, it was observed that sulphur dioxide (SO₂) emissions from the US cement industry increased when replacing coal with scrap tyres and solid waste, while a slight decrease was observed for biomass and waste oil. Collaboration with sewage sludge was found to decrease SO₂ emissions from the US cement industry. It was reported that the US cement industry could reduce NO_x emissions when using alternative fuels instead of coal and that collaboration with waste oil represented the greatest potential for the nitrogen oxide (NO_x) reduction. In descending order, sewage sludge, solid waste, scrap tyres, and biomass were reported to have the lowest potential for reducing NO_x emissions (Hasanbeigi and Bhadbhade, 2023). The adiabatic flame temperatures (AFTs) of the fuels can be determined depending on the moisture, volatility, and ash content; It is important in determining the feeding locations of fuels and emissions released as a result of combustion (Sharma, 2023). There are several studies in the literature conducted using different software programs to calculate gas emissions resulting from combustion. Sieradzka et al. (2020) performed modelling of refuse-derived fuel (RDF) of Pyrolysis gas in different temperatures by using Ansys Chemkin-Pro software (chemical kinetics simulator). Oxy-methane, oxy-hydrogen, air-methane, and air-hydrogen AFTs were

determined under stoichiometric conditions, with a reaction temperature of 298.15 K and a pressure of 1 bar by modelling the reaction mechanisms at NASA chemical equilibrium analysis (CEA) (Marzouk, 2023). Carotenuto et al. (2022) developed a numerical model using a restricted chemical equilibrium approach for the gasification of sewage sludge and implemented it in the Aspen Plus software. Sánchez et al. (2024) developed a model by open source field operation and manipulation (OpenFOAM) was implemented for modelling the combustion chamber of a Ward-Cimpa furnace to increase furnace efficiency and explore the possibility of using agricultural waste as fuel.

The novelty of this study is that it is unique in the literature because it compares NASA CEA and Chemkin-Pro simulations to evaluate emissions from alternative and fossil fuels in the cement calciner. The original values for the study to be conducted are as follows: In the existing system, measurements will be taken from the calciner of the cement plant and these data will be verified using NASA CEA and Chemkin-Pro simulations. The AFT of fuels fed from the calciner and kiln will be calculated and the combustion gas composition as vol.% will be calculated based on the ultimate and proximate analysis results. In addition to the existing system, 15 scenarios belonging to alternative models will be developed by altering the ratios of alternative fuels and fossil fuels fed from the calciner and main burner. Alternative models with the closest calorific value to the current system will be selected and emissions such as CO₂, NO_x, SO_x and H₂O (moisture) will be compared, injection points will be determined according to fuel types and verified with literature.

2 Material and methods

2.1 Boundary conditions

According to the data obtained from the control room of a cement factory with a clinker production capacity of 1,647 ton/day, a total of 78 tons of petcoke and lignite mixture is fed into the system, with 9 ton/day coming from the existing calciner and 69 ton/day from the existing main burner. Of the petcoke and lignite mixture used, 65% is petcoke and 35% is lignite. No tyre-derivative fuel (TDF) is provided to the main burner. The total feeding fuel of the existing calciner is 248 tons/day while the total feeding fuel of the existing main burner is 124 tons/day. Existing calciner is illustrated in Figure 1. Sixteen scenarios were examined for combustion gas emissions by modifying the ratios of fossil fuels and alternative fuels introduced into the calciner and main burner. In the existing model (scenario 1), when the petcoke and lignite ratios used in the entire system are taken into account, 9 tons of petcoke and lignite mixture is used in the calciner and 69 tons of petcoke and lignite mixture is used in the main burner. In Scenario 1 (fuel ratio 65% petcoke and 35% lignite), the fuel distribution in the calciner is 2.36% petcoke, 1.27% lignite, 68.55% RDF, 25.8% TDF and 2.02% waste oil, while 36.17% petcoke, 19.48% lignite, 40.32% RDF and 4.03% waste oil is used in the main burner. In alternative model 1, the petcoke and lignite mixture in the entire system is again 9 tons in the calciner and 69 tons in the main burner. In this model where 11 scenarios are examined, TDF and waste oil are not used. The RDF ratio is determined at around 96% in the calciner and about 44.4% in the main burner. In scenario 2, with a fuel ratio of 0% petcoke and 100% lignite, petcoke is excluded from the calciner, and the lignite ratio stands at 3.63%. Petcoke is not utilised in the main burner, whereas the lignite proportion stands at

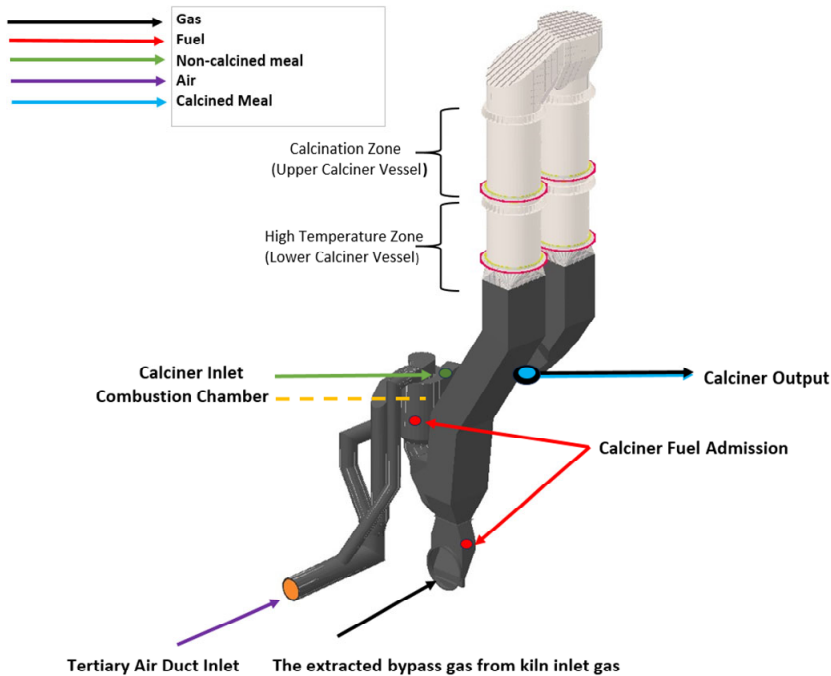
44.34%. In scenario 3, with a fuel ratio of 15% petcoke and 85% lignite, the calciner utilises 0.54% petcoke and 3.09% lignite, whereas the main burner employs 8.33% petcoke and 42.22% lignite. In scenario 4 (fuel ratio 25% petcoke and 75% lignite), 0.91% petcoke and 2.72% lignite are used in the calciner, while 13.92% petcoke and 41.75% lignite are used in the main burner. In scenario 5 (fuel ratio 35% petcoke and 65% lignite), 1.27% petcoke and 2.36% lignite are used in the calciner, and 19.45% petcoke and 36.18% lignite are used in the main burner. In scenario 6 (fuel ratio 45% petcoke and 55% lignite), 1.63% petcoke and 2% lignite are used in the calciner, and 25.02% petcoke and 30.58% lignite are used in the main burner. In scenario 7 (fuel ratio 55% petcoke and 45% lignite), 2% petcoke and 1.63% lignite are used in the calciner, 30.56% petcoke and 25% lignite are used in the main burner. In scenario 8 (fuel ratio 65% petcoke and 35% lignite), 2.36% petcoke and 1.27% lignite are used in the calciner, 36.18% petcoke and 19.48% lignite are used in the main burner. In scenario 9 (fuel ratio 75% petcoke and 25% lignite), 2.72% petcoke and 0.91% lignite are used in the calciner, 41.75% petcoke and 13.92% lignite are used in the main burner. In scenario 10 (fuel ratio 85% petcoke and 15% lignite), 3.09% petcoke and 0.54% lignite are used in the calciner, and 47.26% petcoke and 8.34% lignite are used in the main burner. In scenario 11 (fuel ratio 95% petcoke and 5% lignite), 3.45% petcoke and 0.18% lignite are used in the calciner, and 52.82% petcoke and 2.78% lignite are used in the main burner. In scenario 12 (fuel ratio 100% petcoke and 0% lignite), 3.63% petcoke and 0% lignite are used in the calciner, and 55.6% petcoke and 0% lignite are used in the main burner. In alternative model 2, different amounts of petcoke and lignite mixtures are used. In this model where 4 scenarios are examined; in Scenario 13, no petcoke and lignite mixture is used in the calciner, while 78 tons of mixture is used in the main burner. In this case, the RDF ratio is 72.65% and the TDF ratio is 27.35% in the calciner, while the main burner contains 40.83% petcoke, 22.02% lignite and 37.10% RDF. In scenario 14, 78 tons of petcoke and lignite mixture is used in the calciner, while none is used in the main burner. In this case, the calciner contains 20.46% petcoke, 11.02% lignite, 47.74% RDF and 20.78% TDF, while 100% RDF is used in the main burner. In scenario 15, a daily mix of 39 tons of petcoke and lignite is utilised in the calciner and main burner. The calciner comprises 10.22% petcoke, 5.50% lignite, 47.98% RDF, and 36.29% TDF, whereas the main burner utilises 20.45% petcoke, 11.0% lignite, and 68.54% RDF. Finally, in scenario 16, no petcoke and lignite mixture is used in the calciner and main burner, in which case the calciner contains 72.65% RDF and 27.35% TDF, while the main burner contains 100% RDF.

2.1.1 Fuel Properties and characterisation

The ultimate analysis (C, H, O, N, S) of proximate analysis (moisture, volatile matter, ash, fixed carbon, and calorific value) alternative fuels provided by Türk Çimento Sanayicileri Birliği are analysed for as wt(%). When we examine the components of fossil and alternative fuels such as lignite, petcoke, RDF, TDF, and waste oil, the carbon (C) content is 73.78%, 87.8%, 34%, 74.3%, and 40.8%, respectively. In terms of hydrogen (H), lignite has 4.74%, petcoke 3.76%, RDF 5.97%, TDF 6.88%, and waste oil has 7.8% hydrogen. While the highest sulphur (S) content is 6.73% in petcoke, RDF contains 0.25%, TDF 1.59%, waste oil 2%, and lignite 0.42% sulphur. Nitrogen (N) content was determined as 2.01% in lignite, 1.4% in petcoke, 1.23% in RDF, 0.3% in TDF, and 2% in waste oil. In terms of oxygen (O) content, RDF has the highest value

with 17.08%, while lignite contains 13.74%, TDF 6.52%, waste oil 8%, and petcoke 0.12% oxygen. When evaluated in terms of moisture content, lignite and petcoke contain almost no moisture (both 0.01%), while RDF and waste oil have 33% and TDF has 1.61% moisture content. Lignite has 10.61% ash content, RDF and waste oil 6.4%, TDF 8.8%, and petcoke 0.18%. The fixed carbon content was recorded as 55.46% in lignite, 90.17% in petcoke, 6.87% in RDF, and 26.55% in TDF. The volatile matter content was 33.93% in lignite, 9.64% in petcoke, 53.7% in RDF, and 60.3% in TDF. The fixed carbon and volatile matter content of waste oil was not specified. Several variables need to be considered when fuels are selected. The quality of the product, emission values, and the operating process can be affected by these variables.

Figure 1 Geometry and boundary conditions of the existing calciners (see online version for colours)



2.1.2 Combustion gas compositions

According to these data, the A_{min} (minimum air) and V_{min} (minimum combustion gas) formula is calculated and the kiln gas composition comes from the main burner. In the calciner of a cement plant, 'minimum air' refers to the minimum amount of air required to achieve complete combustion of the fuels used. This value is essential for ensuring that all the combustible components in the fuel are fully oxidised, which helps optimise fuel efficiency and minimise unburned residues. 'Minimum combustion gas' refers to the least quantity of combustion gases required to sustain the optimal temperature and reaction parameters within the calciner. This guarantees excellent management of the heat and chemical processes within the calciner, resulting in optimal performance and minimised emissions. Both factors are essential to the functioning of the calciner. Maintaining

acceptable minimum amounts of air and combustion gas is essential for optimising combustion efficiency, minimising emissions, and enhancing overall energy efficiency (Gasser, 2000).

The kiln and calciner combustion gas composition calculation steps are demonstrated by the following equations. Where C, H, S, N, O, H₂O are the weight fractions (kg/kg fuel) of carbon, hydrogen, sulphur, nitrogen, and water in the fuel.

The minimum air $A_{\min}$ (Nm³/kg fuel) can be calculated by given following equation (1):

$$A_{\min} = 8.89 \times C + 26.5 \times H + 3.3 \times S - 3.3 \times O \quad (1)$$

The combustion gas emissions released can be given by the following equations (2), (3), (4) and (5):

$$0.79 \times A_{\min} + 0.8 \times N \rightarrow N_2 \quad (2)$$

$$1.87 \times C \rightarrow CO_2 \quad (3)$$

$$0.7 \times S \rightarrow SO_2 \quad (4)$$

$$11.2 \times H + 1.24 \times H_2O + A_{\min} \times H_2O_{\text{air}} \rightarrow H_2O \quad (5)$$

Then, $V_{\min}$ can be obtained by the following equation (6):

$$V_{\min} = (0.79 \times A_{\min} + 0.8 \times N) + (1.87 \times C) + (0.7 \times S) + (11.2 \times H + 1.24 \times H_2O + A_{\min} \times H_2O_{\text{air}}) \quad (6)$$

The volume percent of each gas can be calculated as a proportion of volume (vol.%) divided by $V_{\min}$.

These data were converted to proportion of weight (wt.%) and utilised for the NASA-CEA and Chemkin-Pro boundary conditions. In existing model, the percentage distribution of gas components is calculated at 1,473.15 Kelvin for calciner and main burner. Average gas composition is follows: 67.56% N₂, 22.67% CO₂, 9.45% H₂O, and 0.33% SO₂. The results align with the existing literature. Zhang et al. (2024) reported the kiln gas composition as 80.87% N₂, 15% CO₂, 2% H₂O, and 0.12% NO.

2.1.3 Raw meal properties

Equation (7) shows that the calcination process is a significant endothermic reaction in which limestone (CaCO₃) undergoes decarbonisation to produce lime (CaO) and carbon dioxide (CO₂) through thermal breakdown at around 900°C (Khadka, 2021).



The chemical composition of raw meal and hot meal analysis results [SiO₂, CaO, MgO, and loss on ignition (LOI)] supplied in wt.% by the cement factory; the raw meal is 12.93%, 41.66%, 0.64%, and 33.42% while the hot meal is 20.82%, 55.2%, 1.16%, and 2.5%.

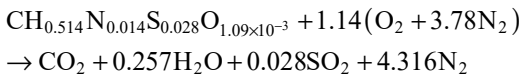
2.2 Temperature and gas species measurements

The temperature data and outlet gas composition was collected by MRU-S type thermocouples and optima MRU type exhaust gas analyser. The sampling point for data was the outlet of the calciner at three different points. To ensure the accuracy and stability of the test data, the operating parameters of the calciner were protected unchanged during measurement. The average value was taken for accurate take measurement in every 10 and 15 minutes during test period and no significant fluctuations were found in the measurement data. Measured values of average gas concentration and temperature is as follows: 2.45% O₂, 0.17% CO, 17.9% CO₂, 240 PPM NO, 252 PPM NO_x, and 300 PPM SO₂. The measurement temperature was averagely of 1,173.15 Kelvin. Our measurements are consistent with the literature. Li et al. (2024) obtained the measurement data at the end of the rotary kiln. The observed values were as follows: O₂ at 3.25%, CO₂ at 15.88%, and NO_x concentration at 1,095 PPM. The temperature was measured at 1,332 Kelvin. Wang et al. (2024) reported the variation in average sectional area concentrations of three principal gaseous components (CO₂, O₂, and NO) along the height of the calciner. The measurement data indicated 392 PPM NO, 5.8% O₂, and 25% CO₂ at 1,170 Kelvin.

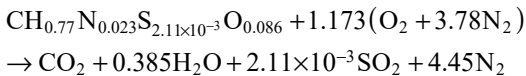
2.3 AFT of fuels

The AFT for air-lignite/RDF/TDF/waste oil is determined. The results indicate AFTs related to fuel characteristics including volatile matter, ash content, and moisture content. The moisture content of RDF and waste oil is a key indicator of its performance as a fuel because moisture is not flammable. Excessive moisture in RDF and waste oil can inhibit ignition, reduce flame temperature, slow down the rate of combustion, extend the burn time, lengthen the flame envelope, and increase the risk of flame instability. Ash content affects fuel reactivity, diminishing calorific value and postponing ignition. Lignite possesses the highest ash content, whereas petcoke exhibits a low ash concentration, rendering petcoke more combustible than lignite and RDF. The ignition and combustion of volatiles are essential phases in the combustion process; TDF, possessing the largest volatile content among fuels, exhibits superior flammability, whereas the little volatile content of petcoke renders it challenging to ignite (Sharma, 2023). The modelled simplified single-step reaction calculations (Khadka, 2021), for air-petcoke/lignite/RDF/TDF/Waste oil complete combustion are defined as 2,355.8, 2,407.62, 2,269.35, 2,419 and 2,303.71 Kelvin, respectively.

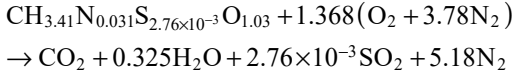
The complete combustion of air-petcoke can be represented by a modelled reaction:



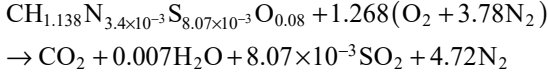
The complete combustion of air-lignite can be represented by a modelled reaction:



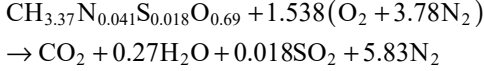
The complete combustion of air-RDF can be represented by a modelled reaction:



The complete combustion of air-TDF can be represented by a modelled reaction:



The complete combustion of air-waste oil can be represented by a modelled reaction:



3 Numerical calculations

The combustion gases from the calciner and primary burner were evaluated utilising equilibrium models created with NASA chemical equilibrium with applications (CEA) and Chemkin-Pro software. However, it is essential to acknowledge that equilibrium models lack the precision of kinetic models. To fully understand the impact of parameters such as time on the system, kinetic model studies are necessary. The CEA assumes that all gases behave ideally and that phase interactions can be disregarded. The equation of state for the mixture is represented by equation (8):

$$Pv = nRT \quad (8)$$

For a mixture with the number of species, the Gibbs energy per kilogram of the mixture, denoted as g , is represented by equation (9):

$$g = \sum_j^{j=NS} (n_j \mu_j) \quad (9)$$

where n_j and μ_j are the number of moles and chemical potential of species j , respectively. The chemical potential per kilogram-mole of species j is defined to be by equation (10):

$$\mu_i = \frac{\partial g}{\partial n_{i,T,P,n_i \neq j}} \quad (10)$$

The condition for chemical equilibrium is achieved by minimising free energy, which is typically constrained by mass-balance equations. Helmholtz free energy is minimised when the volume (or density) is held constant as a thermodynamic state. The Lagrange multipliers method is utilised to minimise Gibbs free energy because of its better efficacy relative to alternative techniques. Due to the non-linear nature of the equations required to ascertain the composition variables, an iterative method is typically essential. In this iterative procedure, treating n as an independent variable is advantageous. The Newton-Raphson method is used to adjust the initial estimates of composition n_j Lagrange multipliers λ_j and moles of gaseous species (Yucel and Aydin, 2023).

In Chemkin-Pro software, the combustion process of various fuels is simulated by first inputting the chemical compositions of the selected fuels. Essential process parameters, such as temperature, pressure, kiln gas flow rate, and tertiary air duct mass

flow rate, are subsequently established to configure the simulation. Following configuration of these inputs, Chemkin-Pro performs calculations and produces results predicting the distribution and concentration of gaseous products arising from fuel combustion. This facilitates a comprehensive examination of the combustion process, aiding in the optimisation of fuel consumption and the reduction of pollutants.

3.1 NASA CEA reaction modelling

This study will utilise NASA's CEA computational tool to determine the gas emissions produced by the fuel. This software provides the computation of all requisite parameters pertinent to the analysis (NASA CEA, 2024).

The following is a comprehensive overview of the input selection procedure in CEA:

- Initially, it is essential to identify the sort of problem to be solved. The option 'assigned temperature and pressure' is selected to define the reaction mechanism of the current model.
- The subsequent phase involves selecting the working conditions for the current model, based on literature data, which include a temperature range of 973.15 to 1,473.15 Kelvin and a constant pressure of 1 bar. These settings are selected because the calciner functions within this temperature range and pressure.
- Subsequent to selecting this data, the following stage is to determine the type of fuel. Emissions produced from the fuel (N_2 , CO_2 , H_2O , SO_2) are classified as fuel, whilst the raw material limestone ($CaCO_3$) is categorised as the oxidiser. Emissions' weight percentage and enthalpy values are input into the system based on proximate and ultimate analysis results, as well as calciner output temperature.
- The oxidiser/fuel ratio is determined to be 0.15.
- Combustion is represented as a process with a constant enthalpy by assessing the total enthalpy of the air-fuel combination and keeping it invariant during the calculation of the chemical equilibrium composition. The total enthalpy calculation is crucial for the combustion model in the new code; hence, the relevant CEA studies are established using temperature (T) and pressure (P) utilising the enthalpy data from the individual situation.
- Following completion of the simulation, CEA presents the results in various parts by examining the emissions produced within the temperature range of 973.15 to 1,473.15 Kelvin, alongside other parameters. The species are included: calcium oxide (CaO), limestone ($CaCO_3$), nitrogen (N_2), nitrogen monoxide (NO), sulphur monoxide (SO), sulphur dioxide (SO_2), carbon monoxide (CO), carbon dioxide (CO_2), O_2 (oxygen), H_2 (hydrogen), and moisture (H_2O).

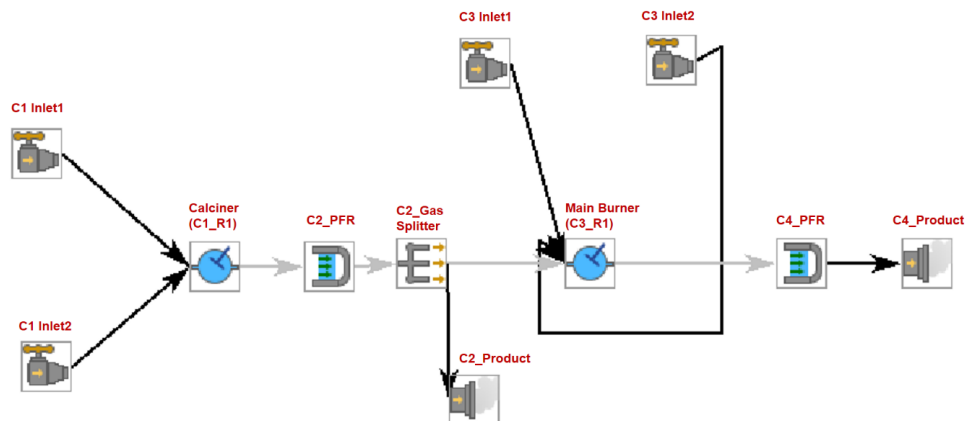
Based on the data, the emissions occurring in the temperature range of 973.15 to 1,473.15 Kelvin were calculated by applying the existing model boundary conditions. The boundary conditions required for NASA CEA were calculated as % wt proportion of nitrogen (N_2), CO_2 , H_2O , and sulphur dioxide (SO_2) major combustion gases for 16 scenarios. The enthalpies (ΔH) of the gas components in these scenarios were calculated by NASA CEA. In scenario 1, the percentage distribution of gas components is as follows: 67.56% N_2 , 22.67% CO_2 , 9.45% H_2O , and 0.33% SO_2 . In scenario 2, there are

65.92% N₂, 21.88% CO₂, 12.12% H₂O, and 0.08% SO₂. For scenario 3, these rates are calculated as 65.97% N₂, 21.89% CO₂, 12.01% H₂O, and 0.13% SO₂. In scenario 4, there are 66.01% N₂, 21.89% CO₂, 11.94% H₂O and 0.16% SO₂. In scenario 5, the distribution of gases is 66.04% N₂, 21.90% CO₂, 11.87% H₂O, and 0.19% SO₂. In scenario 6, 66.07% N₂, 21.90% CO₂, 11.81% H₂O, and 0.22% SO₂ are seen. In scenario 7, the gas rates are the same, 66.07% N₂, 21.90% CO₂, 11.81% H₂O, and 0.22% SO₂. In scenario 8, 66.13% N₂, 21.91% CO₂, 11.68% H₂O, and 0.27% SO₂ are seen, while in scenario 9, 66.17% N₂, 21.91% CO₂, 11.62% H₂O and 0.30% SO₂ are seen. In scenario 10, 66.20% N₂, 21.91% CO₂, 11.56% H₂O and 0.33% SO₂ rates were calculated. In scenario 11, 66.23% N₂, 21.92% CO₂, 11.50% H₂O, and 0.35% SO₂ were included, and in scenario 12, 66.25% N₂, 21.93% CO₂, 11.45% H₂O and 0.37% SO₂ were included. In scenario 13, the gas distribution was 67.52% N₂, 22.70% CO₂, 9.47% H₂O and 0.31% SO₂. In scenario 14, these rates were calculated as 67.11% N₂, 22.44% CO₂, 10.15% H₂O and 0.30% SO₂. Finally, scenario 15 has 67.94% N₂, 23.01% CO₂, 8.70% H₂O and 0.34% SO₂, while scenario 16 has 73.63% N₂, 16.94% CO₂, 9.31% H₂O and 0.12% SO₂. The obtained of simulation data are compared and only major combustion gas (CO₂, H₂O and SO₂) are focused.

3.2 Chemkin-Pro reaction modelling

Numerical computations of combustion gas products for the cement calciner and main burner were conducted utilising Chemkin-Pro. Chemkin-Pro, the most recent iteration of the commercial program, has grown from the Chemkin II code created at Scandia National Laboratories. This program models and simulates intricate chemical reactions, facilitating the assessment of chemical kinetics for diverse industrial processes and combustion systems in the conceptual design phase (Sieradzka et al., 2020).

Figure 2 Diagram of calciner and main burner for calculation combustion gas composition with Chemkin-Pro (see online version for colours)



The gaseous combustion products for both fossil and alternative fuels were computed using Chemkin-Pro, based on their chemical compositions. It is necessary to designate the raw materials as a system input for computations in Chemkin-Pro. Simulation was conducted in the existing calciner for bypass gas extracted at rates of 25.2 kg/sec and

14.01 kg/sec from the kiln inlet gas and tertiary air duct, respectively. In the main burner, simulation is performed for 9.84 kg/sec and 17.46 kg/sec for secondary air and cooler exhaust air, respectively. The required boundary conditions of existing model calculation equations are demonstrated using mass balance. Calculations for the existing model materials in the calciner were conducted at five distinct temperatures: 973.15, 1,073.15, 1,173.15, 1,273.15, 1,373.15, and 1,473.15 Kelvin. The main burner was consistently maintained at 1,873.15 Kelvin. Ultimately, varying quantities of fossil fuels and alternate fuel compositions were utilised to create various models, with the results at 1,473.15 Kelvin in the calciner emphasised as they offered the most favourable contrast for these models. The boundary conditions required for Chemkin-Pro were calculated as % wt and the major gas (CO_2 , CO , N_2 and NO_x) is focussed. The flow diagram is illustrated in Figure 2.

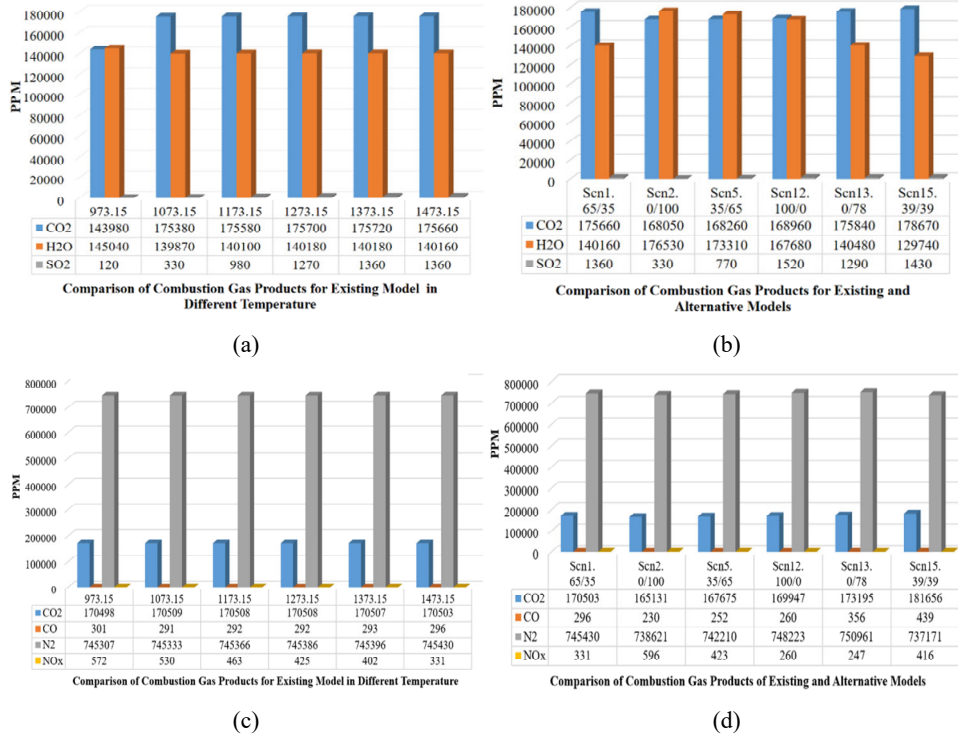
4 Result and discussion

4.1 Validation of the accuracy of the model

Concentrations of combustion gases were quantified and corroborated by juxtaposing them with simulation outcomes derived from NASA-CEA and Chemkin-Pro at temperatures of 973.15 K, 1,073.15 K, 1,173.15 K, 1,273.15 K, 1,373.15 K, and 1,473.15 K, respectively. At 1,173.15 K, the recorded values were 2.45% O_2 , 0.17% CO , 17.9% CO_2 , 252 PPM NO_x , and 300 PPM SO_2 . NASA-CEA simulation results at 1,173.15 K yield gas concentrations of 0.055% CO , 17.57% CO_2 , and 980 PPM SO_2 in given bar chart Figure 3(a). The CO_2 concentration indicates strong correlation with our results, suggesting that the simulation's CO_2 values closely match our experimental data. However, the concentrations of CO and SO_2 from NASA-CEA exhibit considerable discrepancies compared to the measurements. While our measurement shows 0.17% CO and 300 PPM SO_2 , the NASA-CEA simulation predicts only 0.055% CO and 980 PPM SO_2 , which indicates an estimation of these gas components. Chemkin-Pro simulation results at 1,173.15 K for the major gas compounds are as follows: 17.05% CO_2 , 0.029% CO , 2.80% O_2 and 463 PPM NO_x in given bar chart Figure 3(c). The concentrations of CO_2 and O_2 align closely with our results, so confirming the validity of the CO_2 simulation. However, the NO_x and CO measurements from Chemkin-Pro exhibit more deviation. Our observations indicate 240 PPM NO_x and 0.029% CO , while Chemkin-Pro simulates 463 PPM NO_x and 0.029% CO , revealing a significant overestimation of CO and an underestimating of NO . In the literature, Li et al. (2024) simulated the following gas concentrations at the end of the rotary kiln: 3.20% O_2 , 15.14% CO_2 , 1,096 PPM NO_x , and a temperature of 1,320 Kelvin. Wang et al. (2024) reported simulation results of 5.8% O_2 , 25% CO_2 and 392 PPM NO , and a temperature of 1,170 Kelvin in the calciner. Additionally, the verified NO concentration was 412.21 PPM, and the verified temperature was 1,167.42 Kelvin. In a nutshell, the calculations directly determine the maximum possible emissions based on the elemental composition because NASA CEA and Chemkin software do not include a volatilisation model. However, when considering mass transfer limitations, we may obtain different results from the actual emissions since not all elements are released. For validation, the closest data to the temperature and gas concentration measurements obtained from the calciner outlet points ($\text{NO} = 10$ PPM) occurred at 1,473.15 Kelvin (1,200°C), therefore alternative models were simulated at

1,473.15 Kelvin temperature. Nakhaei et al. (2021) reported a temperature range of 1,150–1,200°C for the existing calciner fuel inlet point in their study.

Figure 3 Combustion gas products of prediction, (a) (b) NASA CEA (c) (d) Chemkin-Pro software respectively (see online version for colours)



Notes: Figures 3(a) and 3(c) – comparison of combustion for existing model in different temperature; Figures 3(b) and 3(d) – comparison of gas products for existing and alternative models.

4.2 Comparison of NASA CEA and Chemkin-Pro

The existing model and alternative models demonstrated gas species such as CO, H₂, NO, and O₂ gas in the almost same ratio of 80, 30, 10 and 50 PPM, respectively since this data is present in all the scenarios, not included in the comparison. In the given bar chart in Figure 3(b), the all models are compared. The existing model indicates a concentration of SO₂ gas at 1,360 PPM. In alternative model 1, where the petcoke rate was elevated by 40%, the maximum SO₂ gas concentration reached 1,520 PPM in the 100/0 scenario. In alternative model 2, a 30% increase in the TDF rate in scenario 15 (39/39) resulted in the highest SO₂ gas concentration of 1,430 PPM. The closest SO₂ gas to the existing model was scenario 10 (85/15) and scenario 13 (0/78) as 1,350 and 1,290 PPM, respectively. In scenario 13 (0/78) and scenario 15 (39/39) where only alternative fuels (RDF and TDF) were supplied to the calciner, there was a potential for reducing CO₂ emissions because of the lower carbon percentage in RDF compared to coal and TDF. However, CO₂ emissions increased. This was attributed to an approximately 10% increase in the lignite

and petcoke mixture rate, even though the RDF rate increased by 6% in the calciner, compared to scenario 1 (65/35). Scenario 8 (65/35) had the same petcoke/lignite ratio as the scenario 1(65/35). In alternative model 1, without TDF, CO₂ emissions can be reduced by increasing the RDF rate in the calciner by 30% compared to the existing system.

In scenario 16 (0/0), using only alternative fuels (TDF and RDF) reduces CO₂ emissions, while scenario 15 (39/39) has the highest CO₂. The calorific value, influenced by the ash and moisture content in fuels, is essential for achieving full combustion. In scenario 1, it was 5,402 kcal/kg, whereas in alternative model 1, it fluctuated between 4,591 and 4,982 kcal/kg. In alternative model 2, the scenario values from 13 to 16 were 5,472, 4,672, 5,318, and 4,173 kcal/kg, respectively. Elevating RDF decreased the calorific value due to elevated moisture content, whereas petcoke enhanced it.

Luo et al. (2024) observed that utilising RDF in cement manufacturers can decrease CO₂ emissions by 1.61 kg for every 1 kg of RDF utilised, in comparison to traditional fuels. This shows that RDF provides carbon dioxide reduction but at different rates depending on the material it is produced from, its carbon content, and its moisture content. It has been observed that when RDF is co-combusted in cement factories, more combustion air is needed and it reduces the thermal efficiency of the kiln. This elevates the specific heat consumption of the kiln, potentially resulting in production loss. The RDF sourced from the calciner possesses lower caloric value and greater particle size, whereas the RDF from the flame pipe may exhibit smaller particle size and higher caloric content, since it is required to generate elevated temperatures in the sintering zone (Hasanbeigi and Bhadbhade, 2023). However, since waste feeding systems will differ, it has been reported in the literature that it would be beneficial to choose the RDF size according to the feeding. In scenarios 14 and 16 where RDF is fed from a 100% main burner, CO₂ gas decreases while the moisture rate increases. Considering that RDF has an AFT of 2,269.35 Kelvin; due to RDF being a non-homogeneous fuel with high volatility, variable particle size distribution, and high moisture content, difficulties may be experienced in maintaining a stable flame and complete combustion cannot occur. The ignition of RDF in the main burner may lead to coating issues and affect clinker quality due to variations in heat value, particle size, and moisture content. It may lead to increased extra air relative to other scenarios. It may result in a reduction of calorific value (Hercog et al., 2023). In alternative 1 scenarios and scenarios 13 and 15; in the cases of co-firing of petcoke and RDF in the main burner, considering that the AFT of petcoke is 2,407 Kelvin; it can be expected to improve ignition and combustion in general, but in this case, attention should be paid to the larger particle size and moisture content of both fuels. According to the literature, the moisture content should be reduced to approximately 10–15% before feeding RDF to the main burner. In addition, a significant amount of pulverised coal should be fed from the main burner to maintain a sufficiently high temperature in the combustion zone of the rotary kiln and thus facilitate the necessary chemical reactions. In the alternatives 1 and 2 models, an increase in the RDF ratio within the fuel mixtures resulted in a decrease in SO₂ emissions, due to the reduced sulphur content in RDF relative to TDF and fossil fuels. In the alternative 2 model scenarios, where RDF substitutes fossil fuel, the sulphur concentration in the system decreased considerably (Hasanbeigi and Bhadbhade, 2023). The current investigation revealed that RDF-based production gas had a low calorific value of 2.67–4.34 MJ/Nm³, rendering it the most appropriate source for gas firing from the calciner (Sharma, 2023). The alternative models demonstrate a larger quantity of RDF,

indicating elevated moisture content. Conversely, studies involving TDF show a decrease in humidity. According to the literature, it has been stated that to offset carbon by substituting RDF instead of coal, the moisture content of RDF should be lower than 15%, and thus a 0.4 ton CO₂/ton coal emission reduction can be achieved (Chatziaras et al., 2014), SO₂ can be generated from sulphur compounds in the clinker (CaO) as well as from sulphur content in petcoke and TDF. Petcoke and TDF generate elevated SO₂ levels relative to RDF, while lignite yields reduced SO₂ emissions. The findings of the study were analogous to those of the research conducted by Hasanbeigi and Bhadbhade (2023). The utilisation of TDF either diminishes or exerts a negligible effect on the emissions of diverse pollutants from cement kilns. Nevertheless, TDF may pose difficulties when directly introduced into the kiln because of the elevated zinc concentration in the ashes, which can substantially modify the cement composition. To reduce this issue, it is suggested to maintain replacement rates for kiln fuel below 20–30% (Hasanbeigi and Bhadbhade, 2023). Thus, introducing TDF into the calciner is regarded as a more suitable method.

The chemical composition of combustion gas products was evaluated using Chemkin-Pro for the materials under investigation, with a detailed analysis presented for the principal combustion gas products at varying temperatures. Figure 3(c) illustrates the principal gases (CO₂, CO, N₂, and NO_x). As the temperature increased, the CO₂ and N₂ concentrations rose slightly, but the NO_x and CO concentrations dropped even slightly. In our study, the tertiary air inlet velocity was taken as 14.01 kg/s and the temperature as 780°C, and the kiln temperature was determined as 1,400°C. The following explanation applies to this situation: fuel combustion is typically regarded as the primary source of NO_x emissions during the cement production process. The two primary types of NO_x emissions in the rotary kiln are fuel NO_x, which is formed from nitrogen in the fuel, and thermal NO_x, which is produced from N₂ in the air. The temperature in the pre-calciner is generally between 850°C and 1,200°C, which is lower than the temperature in the rotary kiln. The majority of the NO_x produced in these circumstances is NO. Therefore, only fuel-based NO was considered in our study, and thermal NO_x and prompt NO_x production were ignored. There are volatile N and char N in pulverised coal. After being transformed into HCN and NH₃ intermediates, the volatile N is oxidised to NO. N₂ is generated when the unoxidised intermediates react with NO as reduction agents. The char N undergoes direct oxidation to NO. Because the char is reductive, some of the NO is converted to N₂. Volatile substances instantly oxidise in the pre-calciner under high temperatures and sufficient oxygen. Therefore, the reduction reaction between hydrocarbons and NO is challenging. The calciner system prompts the NO produced in the rotary kiln to enter the pre-calciner, where some of it is reduced by the powdered coal. The remaining NO is discharged from the system together with the NO produced in the pre-calciner. Yang et al. (2020) reported NO formation in the pre-calciner depends on the nitrogen content in the fuel and the oxygen level in the ignition zone. Sufficient oxygen ensures complete combustion of the fuel and increases NO production accordingly. An increase in the tertiary air temperature can encourage more intermediate products, HCN and NH₃, to react directly with NO. As a result, the amount of NO produced can be decreased in the pre-calciner. This situation was also confirmed in our study: most of the NO_x formed in the calciner is in the form of NO, and the decrease in the NO_x level with the increase in temperature is because the temperature promotes fuel combustion and more HCN and NH₃ react with NO. Therefore, the reduction in NO levels within the calciner can be

attributed to these processes. Zhang et al. (2024) utilised ANSYS FLUENT software to analyse the structure and parameters of a pre-calciner with a capacity of 4,500 t/day, aiming to mitigate NO_x emissions during combustion. This study examined the impact of raw material angle, tertiary air velocity, and tertiary air temperature on NO concentration. The concentration of NO at the pre-calciner outlet increased from 124 ppm to 220 ppm when the tertiary air velocity escalated from 22 m/s to 38 m/s. When the temperature reached 1,123 K, the NO concentration reached its highest value of 211 ppm at the pre-calciner outlet. In our investigation, the insufficient oxygen, temperature, and tertiary air duct speed can be the causes of this behaviour.

Comparing gas concentrations in different scenarios by Chemkin-Pro is presented in the bar chart Figure 3(d). In our existing system, in scenario 1 (65/35), NO_x concentration was calculated as 331 PPM. However, in our modelling and calculations, it was determined that in scenarios where RDF and lignite were fed to the calciner at the highest rate and volatility was high, NO_x concentrations increased to 596 PPM and 423 PPM for scenario 2 (0/100) and scenario 5 (35/65), respectively. In scenario 12 (100/0), where RDF and petcoke were utilised at the maximum rate, the NO_x content diminished to 260 PPM, despite petcoke's lower volatility. Luo et al. (2024) documented that the utilisation of alternative fuels (such as MBM, tyres, RDF, and plastics) lowers NO_x emissions. The decline is elucidated by the conversion of nitrogen compounds emitted during the burning of alternative fuels or the pyrolysis process into N₂ gas via chemical processes. The significant volatility of alternative fuels facilitates the conversion of NO_x into N₂ gas. Furthermore, NO_x production is significantly influenced by the nitrogen content of fuels. Contrary to the literature, we obtained different results. Although petcoke has 1.4% N and RDF has 1.23% N content, in our analyses, RDF with high volatility has higher NO_x emissions despite its lower nitrogen content. The low volatility (9.64%) and low oxygen concentration (0.12%) of petcoke restrict NO_x emissions, but the high oxygen content (17.08%) and volatility (53.7%) of RDF may have elevated NO_x generation by accelerating the combustion rate. The low volatility and high carbon content of petcoke may have diminished NO_x generation by stabilising the combustion process. In scenario 13 (0/78), when only 72.65% RDF and 27.35% TDF were fed through the calciner, the NO_x concentration was calculated as 247 PPM at the lowest level with 0.3% N content, 60.3% volatility and 6.52% O₂ content of TDF. In scenario 15 (39/39), when the highest rate (36.29%) of TDF was fed through the calciner, the NO_x concentration was calculated as 416 PPM. In contrast to research, the criteria that determined emissions were not the amount of nitrogen in fuels but rather their volatility and oxygen content. Kinetic simulations and Chemkin-Pro complex system modelling were employed to explain these variations.

5 Conclusions

The research concluded that CO₂ emissions in cement kiln operations might be significantly decreased by including RDF and TDF as alternative fuels. RDF, owing to its reduced sulphur concentration, decreases SO₂ emissions; yet, it requires meticulous management due to its elevated moisture level. Scenario 2, featuring the highest lignite use, exhibited elevated NO_x emissions, whereas scenario 12, characterised by increased petcoke and RDF content, demonstrated reduced CO₂ emissions but heightened SO₂ emissions. Scenario 13 (0/78) is distinguished for optimal emission control, utilising RDF

and TDF in the calciner, and achieved the greatest reduction in SO₂ and NO_x emissions. Nonetheless, the divergent calculation methodologies employed by NASA CEA, emphasising chemical equilibrium, and Chemkin, advocating kinetic analysis, may result in discrepancies in emission forecasts. Therefore, additional research is necessary to standardise these methodologies and enhance the accuracy of emission predictions in the complex processes of cement manufacturing.

Future work: incorporating CFD modelling in future study could produce more accurate predictions of emission dynamics and heat distributions, especially in intricate industrial environments such as cement kilns. Although NASA CEA and Chemkin-Pro offer accessible and dependable tools for preliminary assessment, integrating them with CFD simulations could enhance the precision of geographic assessments, including temperature distributions and flow dynamics. Additional investigation into hybrid modelling methodologies will enhance the efficacy of emission control techniques and process optimisation in cement manufacturing facilities.

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