EXERGETIC AND CO_2 EMISSIONS ASSESSMENTS OF A CLINKER PRODUCTION SYSTEM APPLYING WASTE FUEL

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Abstract. *The finite nature of global fossil fuel resources, high prices and most importantly, their damaging effect on the environment underscore the need to develop alternative for industrial systems include the cement production process. This industry is an energy intensive industry and emits high quantity of carbon dioxide, so the use of the alternative fuels in cement production can extend fossil fuel supplies and help resolve air pollution problems associated with the use of conventional fuels. This paper proposed to analyze two Case Studies, one operating with fossil fuel combustion for producing clinker and other operating with a mixture of waste fuel and fossil fuel. The study foucused analysing energy and CO_2 emissions performance of both cases studied, apointing the advantages of use of waste fuels. The results show that the cement industry in Brazil can achieve a gain of US$ 1907 per day and avoid emitting 7847 ton CO_2 /year when the tires are applyied as fuel.*

Keywords*: clinker, waste fuel, exergy analysis, CO_2 emissions.*

1. INTRODUCTION

Increased public awareness with relation to global warming has led to greater concern over the impact of anthropogenic carbon emissions on the global climate. The CO_2 emissions are projected to increase to over to over 800 ppm by the end of the century (Huntzinger and Eatmon, 2009).

Approximately 5% of global carbon emissions originate from the manufacturing of cement. The calcination process (driving off CO_2 from $CaCO_3$ to form CaO) accounts for roughly half of the CO_2 emitted, while the remaining carbon results from energy usage during the production process (Hendriks et al., 2000). According to the International Energy Agency's (IEA) Greenhouse Gas R&D Program, cement production generates an average world carbon emission of 0.81 kg CO_2 per kg cement produced.

With respect to energy consumption, the cement industry has been one of the most energy intensive industries in the world with energy typically accounting about 30 – 40% of the production costs. Several studies and results obtained the production for each ton of cement consumes energy from 4 to 5 GJ/ton. This energy share of the cement industry in the industrial field is found to be ranging between 12% and 15%. For considering all kinds of industries, this share changes between 2% and 6% in terms of total consumption of energy (Sogut, 2005).

In this context, there is the preoccupation of the finite nature of global fossil fuel resources, high prices and most importantly, their damaging effect on the environment underscore the need to develop alternative fuels for many industrial systems that relay on fossil fuels. Increased use of renewable and alternative fuels can extend fossil fuel supplies and help resolve air pollution problems associated with the use of conventional fuels.

The use of alternative fuels in cement manufacturing, therefore do not only afford considerable energy cost reduction, but they also have significant ecological benefits of conserving non-renewable resources, the reduction of waste disposal requirements and reduction of emissions.

With the goal of proving the advantage of use of alternative fuel, the present work analyzed through two Case Studies the emissions of CO_2 and the efficiency exergetic when the clinker production use only fossil fuel and when use alternative fuel combined with fossil fuel.

2. CEMENT PRODUCTION

Cement industries typically produce Portland cement. This is a fine, gray powder comprised of dicalcium silicate, tricalcium silicate, tricalcium aluminate and tetracalcium aluminoferrite, with the addition of forms of calcium sulfate. The main stages of cement production at a Portland cement plant are:

1 – Procurement of raw materials
2 – Raw milling (preparation of raw materials for the pyro processing system)
3 – Pyro processing of raw materials to form Portland cement clinker
4 – Cooling of Portland cement clinker

5 – Storage of Portland cement clinker
6 – Finish milling
7 – Packing and loading

In cement production most of the raw materials used are extracted from earth through mining and quarrying and can be divided into the following groups: lime (calcareous), silica (siliceous), alumina (argillaceous), and iron (ferriferous). These raw materials go to milling process where the extracted raw material to obtain the correct chemical configuration and to achieve the proper particle-size to ensure optimal fuel efficiency in the cement kiln.

The next step is the pyro processing process that heats the raw material for producing Portland cement clinkers. Clinkers are hard, gray, spherical nodules with diameters ranging from 0.32 – 5.0 cm produced from the chemical reactions between the raw materials. The pyroprocessing system involves three steps: drying or preheating, calcining (a heating process in which calcium oxide is formed), and burning (sintering). The system uses a rotary kiln that contains the burning stage and some equipment has a part for calcining stage.

After of pyroprocessing, the clinker is cooled and ground with other materials (which impart special characteristics to the finished product) into a fine powder. Up to 5% gypsum and natural anhydrite is added to regulate the setting time of the cement.

3. CEMENT INDUSTRY EMISSIONS

The main emissions from cement production are nitrogen, carbon dioxide, water, oxygen, nitrogen oxides, sulfur oxides, carbon monoxide and hydrocarbons. Cement kiln dust (CKD) is also produced. CKD is the powder retrieved from the exiting gases and it is either all or partly returned to the operation or removed entirely. The handling, storage, and deposition of CKD can generate fugitive dust emissions. The methods used to control particulate emissions from the kiln system are reverse-air fabric filters, electrostatic precipitators and acoustic horns (Gibbs et al, 2011).

The control of the others pollutants as the SO_2 can be done by the kiln system that capture up to 95% of the SO_2 emissions. However, if sulfur (pyrites) is present in the kiln fed, this absorption rate can decline to as low as 50%. With respect to NO_x emissions, the control is possible there are stable kiln operation, recirculation of the flue gas and fuels with low nitrogen content.

Besides of the pollutants described, it is import to detach that the cement industry is a significant source of global carbon dioxide (CO_2) emissions. These are emitted during cement production by fossil fuel combustion, as well as the carbon dioxide is released as a by-product during calcination, which occurs in the upper, cooler end of the kiln, or a pre-calcinater, at temperatures of 600-900°C, and results in the conversion of carbonates to oxides (Fig. 1). According to the International Energy Agency's (IEA) Greenhouse Gas R&D Programme (Hendriks et al., 2000), cement production generates an average world carbon emission of 0.81 kg CO_2 per kg cement produced.

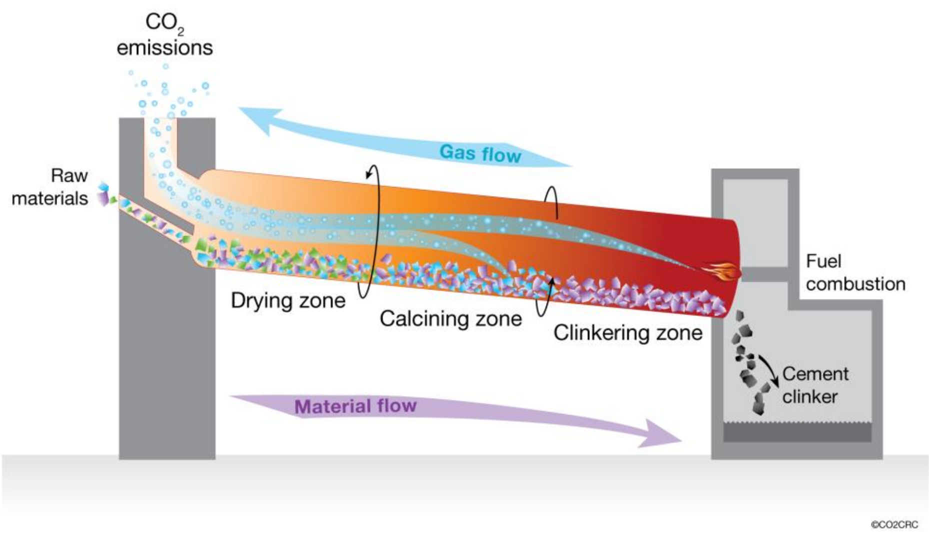

Figure 1. Sources of CO_2 emissions provide of cement industry (CO2CRC, 2012).

4. UTILIZATION OF TYRE AS FUEL IN CEMENT KILNS

Used tyres are material residual with a higher heating value of 28–32 MJ/kg, they are excellent sources of energy, mainly when used as secondary fuels. The high temperature, the high time of residence, the high effect of absorption of the raw material in the pre-heating and the incorporation of the ashes generated to the clinker are favorable conditions to it burns of tyres in rotary kilns of clinker production, so that, it is an adequate form to final disposition for these wastes. Besides, due to the high calorific value of the tyres, the co-processing contributes to a decrease in consumption of others fossil fuels utilized (as coal, petroleum coke and fuel oil), saving the natural resources. The tyres can be introduced in the system of feeding of fuel of the whole kiln, pricked, or in shavings. The typical characteristics and the chemical composition of tyres are presented in Tab. 1.

Table 1. Typical characteristics of tyres.

Typical Characteristics	
Component	% (mass)
Rubber	36
Stuffing (SiO_2)	37
ZnO	1.2
Stabilizer	3
S	1.3
Steel	18
Rest	3.5

Source: Souza (2000)

For the valuation of the pollutants generated by burn of used tyres in the clinker kiln, it is necessary to analyze the process of combustion in the rotary kiln. As the tyre doesn't possess a sustainable flame, it is indispensable to associate it with other fuel that possesses this characteristic. The fuel more utilized in the moment by the cement industry is the petroleum coke or coal, or fines or charcoal, or a mixture of both, with other industrial wastes.

5. EXERGY BALANCE OF CEMENT PRODUCTION

The cement production is a process that involves chemical reactions, so there are two main kinds of exergy: physical and chemical. The kinetic and potential exergy are negligible compared to other two.

Physical exergy also known as thermodynamic exergy is the maximum possible work that can be gained in a reversible process from an initial condition (T, P) to the environment states (To, Po). The specific physical exergy can be expressed as Eq. (1) (Kolip and Savas, 2010):

$$ex_{ph} = (h - h_0) - T_0(s - s_0) \tag{1}$$

For ideal gas, assuming ideal gas flow with constant specific heat, we have the Eq (2):

$$ex_{ph} = c_p(T - T_0) - T_0\left(c_p \ln\frac{T}{T_0} - R\ln\frac{P}{P_0}\right) \tag{2}$$

For the solid and liquid streams we write the Eq (3):

$$ex_{ph} = c_p\left((T - T_0) - T_0 \ln\frac{T}{T_0}\right) - v(P - P_0) \tag{3}$$

Where “v” is the specific volume at the specified T_0 temperature.

With respect to chemical exergy is the maximum possible work that can be acquired during a process that brings the system from environmental condition (T_0, P_0) to the dead state (T_0, P_0, μ_{0i}). The specific chemical exergy (ex_{ch}) of a substance in P_0 states is calculated by equating the components with the reference environment. The specific molar chemical exergy of the reference species having a partial pressure of P_{00} evaluated as Eq. (4):

$$ex_{ch,0i} = RT_0 \ln\left(\frac{P_0}{P_{00,i}}\right) \tag{4}$$

Now, the chemical exergy of the ideal gas and liquid mixtures is computed as Eq. (5).

$$ex_{ch} = \sum_i x_i \left[ex_{ch,0i} + RT_0 \ln(x_i) \right] \quad (5)$$

Where x_i is the molar ratio of the species i, and $ex_{ch,0i}$ is the standard chemical exergy. It is important to account that cement manufacturing process, each step includes the irreversibility generation and thus the losses of exergy (frequently called exergy destroyed). The exergy destroyed or the irreversibility of a system is then given in work of Kabir et al. (2010), present in Eq. (6):

$$ex_{total,in} - ex_{total,out} = T_0 s_{gen} \quad (6)$$

In this work, it was available the main inputs and outputs of cement production process (Fig. 2) for computing the exergetic balance and irreversibility, as shows the Eq. (7).

$$E_{raw\ material} + E_{fuel\ alternative} + E_{fuell} + E_{cooling\ air} - E_{pre\text{-}heater\ exhaust} - E_{hot\ air\ exhaust} - E_{clinker} - E_{stack\ dust} = E_{destroyed} \quad (7)$$

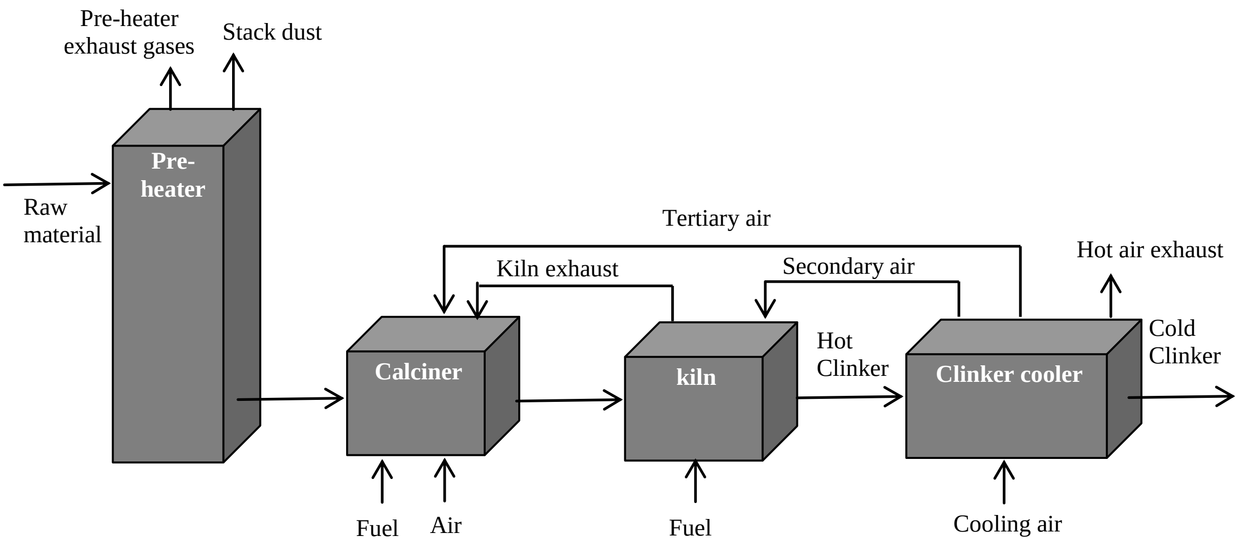

Figure 2. Scheme of main mass fluxes of cement production process.

6. CO_2 EMISSIONS ANALYSIS

The environmental analysis in cement industry takes to account that cement production results in the release of a significant amount of solid waste materials and gaseous emissions, besides the cement production involves the consumption of large quantities of raw materials, energy and heat (Van Oss and Padovani, 2002). For computing the environmental impacts the methodology Life Cycle Assessment (LCA) can be applied. The benefits of LCA including the ability to evaluate the material and energy efficiency of a system, as well as it provide benchmarks for improvement. The focus of this work is the global environmental impacts, particularly global warming potential (GWP), since the clinker production generates a great average world carbon emission.

Global Warming Potentials are a quantified measure of the globally averaged relative radioactive forcing impacts of a particular greenhouse gas. It is defined as the cumulative radioactive forcing – both direct and indirect effects – integrated over a period of time from the emission of a unit mass of gas relative to some reference gas (Van Oss and Padovani, 2002). Carbon dioxide (CO_2) was chosen by the IPCC as this reference gas and its GWP is set equal to one.

7. CASES ANALYZED

In this work were proposed two case studies, the Case Study 1 operated with only conventional fuels of cement industry (mineral coal, petroleum coke and charcoal). The proportion of each fuel was based on the tendency of the cement sector that had increased the use of petroleum coke and decreased the use of charcoal (EPE, 20011). The Case Study 2 operated with the same conventional fuels descripted added with waste fuel: scrap tires.

The scrap tires is a type of waste that has been used by the cement industries, not only for their energetic properties, but also by the fact that the burning of such material contributes to the preservation of the environment and also collaborates with the practices of sanitation avoiding diseases. Typically, used tires can replace up to 20% fuel demand required to produce the clinker, this limitation is due to high replacement rates can lead to overheating in the kiln, causing the formation of volatile sulfur compounds (Schmidthals, 2003).

Then with the considerations mentioned the proportions of each fuels was defined for the two Case Studies, the values are present in Table 2.

Table 2. Percentage of fuel used in the case studies.

Fuels	Percentage (%)	
	Case Study 1	Case Study 2
Mineral coal	20	10
Petroleum coke	60	60
Charcoal	20	10
Scrap tires	-	20

The chemical composition of the fuels used was searched in literature and they are presented in Table 3.

Table 3. Fuels components and its mass percentages

Component	**Scrap tires** (Islam et al., 2008) (%)	**Petroleum coke** (Furimsky, 2000) (%)	**Charcoal** (Villegas et al., 2010) (%)	**Mineral coal** (Vélez et al., 2009) (%)
C	86.40	87.8	90.06	82.4
H	8.00	1.9	1.70	5.1
N	0.50	2.0	1.30	0.8
S	1.70	5.7	0.06	1.4
O	3.40	1.5	4.82	10.3

With respect to raw material composition, the present work used the same mass composition of work Santos (2007): $CaCO_3$ (75.21%), SiO_2 (12.79%), Al_2O_3 (3.44%), Fe_2O_3 (1.86%), $MgCO_3$ (3.57%), SO_3 (0.92%), Na_2O (0.03%), K_2O (0.8%), P_2O_5 (0.13%), Cl (0.014%).

Finally the work considerate parameters referred to cement plant that operated with horizontal rotary kiln with four stage preheater cyclone calciner. The main parameters are presented in Table 4.

Table 4. Parameters used in Case Studies

Standard Parameter	**Value**
Mass flow of clinker (kg/s)	34.72
Mass flow of raw material (kg/s)	54.45
Specific fuel consumption (kJ/kg clinker)	3150
Initial fuel temperature (°C)	25
Clinker outlet temperature from rotary kiln (°C)	1450
Clinker outlet temperature from cooler (°C)	120
Pre-heater exhaust gases temperature (°C)	352
Hot air exhaust temperature (°C)	352
Cooling air temperature (°C)	25
Stack dust temperature (°C)	352
Oxygen free in calciner (dry basis) (%)	2.4
Oxygen free in rotary kiln (dry basis) (%)	1.7

8. RESULTS

8.1 Exergy analyze

With the assumption previously described the exergy balance was calculated. The results are presented in Table 5.

Table 5. Exergy Balance of Case Studies

		Case Study 1 Exergy (kW)	**Case Study 2** Exergy (kW)
Input	Fuels	118919	94252.69
	Alternative fuel	-	24750.89
	Raw material	8346.84	8346.84
	Cooling air	128.43	128.43
	Sub-Total	**127265.84**	**127350.42**
Output	Cool clinker	44979.19	45075.51
	Stack dust	2368.21	2368.21
	Pre-heater exhaust gases	21524.05	21421.24
	Hot air exhaust	8970.8	9105.79
	Sub-Total	**77842.25**	**77970.75**
Exergy destruction		49423.59	49379.67
Exergetic efficiency (%)		35.34	35.39

From the results in Table 6, it can be seen that the flow of exergy related to fuels have values very close, representing 93% of the input exergy, the main cause is that booth Case Studies had to meet the same specific fuel consumption (3150 kJ/kg). However, the mass flows were very different in each Case Study. In Case Study 1 the fuel consumption was: charcoal = 0.866 kg/s, mineral coal = 1.062 kg/s, petroleum coke = 2.09 kg/s. Adding the fuel consumption was of 4.02 kg/s.

In Case Study 2 the fuel consumption was: charcoal = 0.433 kg/s, mineral coal = 0.531 kg/s, petroleum coke = 2.09 kg/s and scrap tires = 0.883 kg/s). The total fuel consumption was of 3.94 kg/s.

Although of the input fuel exergy are similar, the chemical composition of the different fuels and their different ratios in Case Studies produced diverse output exergy flows due to combustion process of them. So for the second Case Study 2 was obtained a total exergy output 0.16% bigger than Case Study 1. The exergy destroyed of Case Study 2 was 0.09 % lower than Case Study 1.

However from the technical view point the exergy efficiencies were the same, but when considering the economic view point the Case Study 2 is more advantageous since 20% of fuel provide from waste (scrap tires), that represents low acquisition costs when compared to traditional fuels. Actually the mean price of scrap tires is around US$ 65-75 / ton, besides some industries of tires (Bridgestone Firestone, Goodyear, Michelin, Pirelli, Maggion, Levorin and Rinaldi) pay on average US$ 25 per ton of tire to cement industry in Brazil. Then, with the consumption of 0.883 kg/s of scrap tires the cement industry in Brazil can achieve a gain of US$ 1907 per day.

8.2 Environmental analysis

For the environmental analyze the paper focused the emissions of carbon dioxide during the clinker production, since these emissions are the main cause of global warming potential in cement industry case. Thus, it was computed the CO_2 emissions provide of fuel combustion and calcination process. The results are presented in graphic of Figure 3.

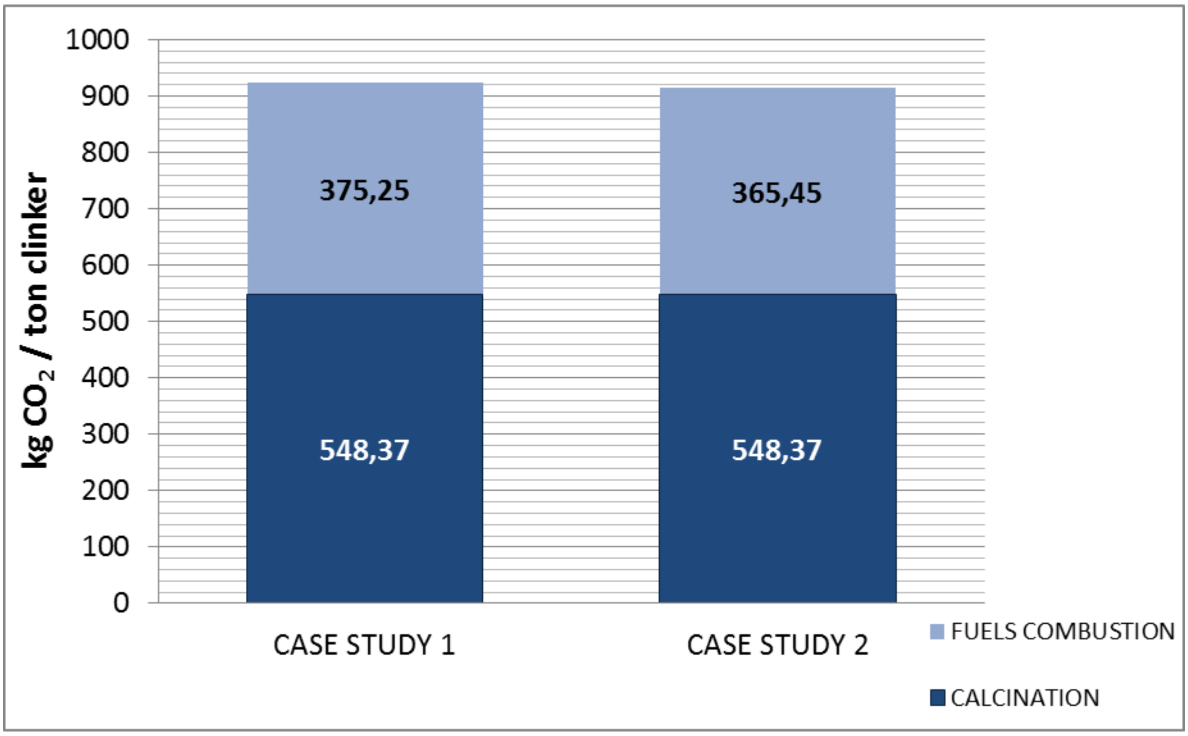

Figure 3. CO_2 emissions of the clinker production.

The results showed that the main source of CO_2 emissions provide of the calcination process (approximately 60%), where the $CaCO_3$ decomposed in CaO and CO_2. The results are equal for two case studies because the raw material did not change. With respect to fuel combustions, the emissions in Case Study 1 were 1.07 % higher than that obtained from Case Study 2. This percentage can be expressive for industries that produce great quantities, as example one industry producing 794 x 10^3 ton cement /year of cement avoid emitting 7847 ton CO_2 /year.

Therefore, the results appoint that the use of alternative fuels in cement industry shows as an advantageous alternative from environmental view point.

9. CONCLUSIONS

In this paper an environmental and exergy analyzes applied in cement industry was developed with goal to compare two Case Studies. One Case Study used only fossil fuels; the other used a mixture of fossil fuel and alternative fuel (scrap tires). The results of exergy and environmental analysis were similar in two Case Studies, however the Case Study that applied alternative fuel emitted a quantity of CO_2 lower than the Case Study that used only fossil fuels.

With respect to the exergy efficiency both Case Studies presented the same value, but the advantage of the use of the scrap tires is the low acquisition cost and the burning of this material contributes for the preservation of the environment and also collaborates with the practices of sanitation, preventing diseases.

10. ACKNOWLEDGEMENTS

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