Co-processing of Scrap Tires and Waste from the Re-refining of Used Lube Oil in Cement Kilns

Rogério José da Silva, Renata Vitor Chaves S. G. Francisco, Alexandre Oliveira Lopes

Abstract— **The cement industry has a high consumption of thermal energy through the burning of fuels. The use of wastes as alternative fuels allows, through co-processing, its destruction and the use of its calorific value in the production process. Scrap tires and the wastes generated in re-refining of used motor oil has been used in co-processing in cement kilns due the increase of automotive vehicles. Co-processing has multiple variations according to its location, the productive process and its facility. This way, it is possible to reach high thermal destruction efficiency and low emission of pollutants. This paper analysis the environmental and production restrictions that determine the use limits of waste in the kiln, when the main fuels are petroleum coke or coal and the waste co-processing occurs in rotary kiln with preheaters stages, precalciner with tertiary air and grate coolers.**

Index Terms— **Cement Kiln, Co-processing, Used tyres, Waste Lubricating.**

I. INTRODUCTION

Cement industry is characterized by its high energy consume, wherein half of direct production cost in a plant correspond to electrical energy and fuel [1].

Thermal energy costs of Portland cement production are directly connected with the type of process and technology used. The average thermal energy consumption of a cement plant with rotary kiln and preheater towers with six stages is about 3000 to 4000 MJ/t clinker in other installations. Reducing energy consumption can be achieved with the use of dry systems, rotary kiln with precalciner and preheaters, with high capacity to burn the raw meal. The specific fuel consumption of the cement sector is determined by: chemical composition, mineralogy and moisture of the raw material; production capacity and technologies used in the installation; properties of fuels and utilized mixtures; and rotary kiln operation [2].

Petroleum coke is currently the most used fuel by the cement industry in Brazil. It is resulting of coking, which process heavy residual oil from petroleum distillation, increasing the oil refinery production of light and intermediate products. Besides, petcoke has a high calorific value and low acquisition cost.

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There are two types of coke: green coke and calcined coke. The sulfur content in petroleum coke can range from less than 1% up to 6%, depending on the origin of the oil and the process. The sulfur content of Brazilian green petcoke is up to 1%, while some types of Mexico Gulf petcoke has a high sulfur content of about 5%. Among the combustion products of petcoke is SO_2, which reacts with several compounds that are present in the raw material. Consequently, it is incorporated into the clinker. Reference [3] discussed the diversity of petcoke.

Cement industry is responsible for 2% of total primary energy in the world [4]. Therefore, in order to reduce the fossil fuel consumption, the cement industry incorporated on its process the co-processing, which is the burning of industrial wastes that can be used as fuels, due its calorific value. The waste that is co-processed is called alternative or secondary fuel.

Fossil fuel has been replaced by alternative fuel successfully since 1970s decade in Europe, Japan, USA, Canada and Australia and its proportion varies depending on where it is used. European countries have replaced about 20% of conventional fuel for alternative ones. North America, Japan, Australia and New Zealand have an average rate of 11% of replacement. In addition, Latin America has an average rate of 10%. Lastly, Asia have replaced only 6% [5].

Recently, reference [6] showed that use of alternative fuels in rotary kiln in cement manufactories is 85% in Netherlands, 45% in Sweden, 41% in Switzerland (in 2012), more than 53% in Germany (in 2010), 60% in Belgium (in 2011), more than 22% in Spain, 8% in USA (with data of 2004) and 15.5% in Japan.

The characteristics of cement fabrication process assure the process viability, even though the co-processing varies according to the region in which the plant is located. According to [7], the process main characteristics that guarantee the complete consumption of alternative fuels are: in rotary kiln the maximum temperature is about 2000ºC (flame temperature); gas retention above 1200ºC and about 8 s; in the sintering zone material temperature of about 1450ºC; and oxidizing gas atmosphere. In secondary firing system the gas retention time of more than two seconds with temperature above 850°C and solids temperature of 800ºC. In precalciner the retention time is longer and temperature is higher (than secondary firing system) and solids temperature is the same as secondary firing system. The system has uniform firing conditions for load fluctuations, due to high temperatures and retention times sufficiently long. Likewise, the fluctuation of the load at high temperatures can not cause changes, so it is necessary to assure uniform conditions of burnout in long retention times, as well as the destruction of organic pollutants. It also has conditions for the destruction of organic compounds. There is a high absorption rate of gaseous compounds such as HCl, HF and SO_2 by the alkaline reagents, notably CaO. There is also a high retention capacity of heavy metal particles. The short gas retention time inhibit the de novo synthesis in temperature range known to lead to the formation of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). Finally, mineral parts of the fuel can be incorporated in the clinker components, and as result, occurs the energy recovery and recycling of materials. For that reason, it can be conclude that high temperatures and long retention time at rotary kiln assure destruction of organic compounds. Furthermore, the kiln alkaline environment guarantees acid and oxides absorption, and the conventional and alternative products of combustion recycling. Consequently, cement manufacturing is ideal for industrial waste energetic recycling.

II. Scrap Tires Co-Processing

Scrap tire is the most used waste as alternative fuel in Brazil. In 2009, 180 thousand tons were co-processed, which represents 36 million units [1]. For cement manufacturing, the major advantage of burning scrap tires is its high calorific value, which is, usually, higher than the calorific value of coal.

In 2013, 68.8 million tires were produced by Brazilian industry, according to [8]. It took 76 years between the first tire manufacturing installations in Brazil, until the creating of a disposal legal framework. During the period without a legally regulation, millions of tires were discarded inappropriately in landfill, wasteland, and others inappropriate areas. The real number of scrap tires that were discarded inappropriately in Brazil is unknown; however, it can be estimated between 100 and 900 million tires. These tires are a serious environmental and public health issue, since it can be vector-borne disease, such as dengue disease and leptospirosis [9].

The Brazilian National Waste Management Policy (Política Nacional de Resíduos Sólidos, PNRS) approved in August 2010, overlook the decrease of inappropriate disposal, considering that manufacturers are responsible for the adequate destination of its tires [10].

The National Tire Industry Association (ANIP, Associação Nacional da Indústria de Pneumáticos), has among its associates 59% of total companies in Brazil. It has a project of collection service and final disposal of scrap tires since 1999, called Reciclanip. The purpose of the project is to determine pickup points of tires located throughout the country. The steel wire is removed from the tired collected and sent to steel rolling mills, while the rubber is shattered. In 2012, Reciclanip had 743 pickup points in Brazil. Since 2010, when the Brazilian National Waste Management Policy was created, the number of collecting points increased 29%. According to ANIP, 270 million tires of passenger car have been collected since the beginning of the project [8]. More than half of the total collected tires is forwarded to cement manufacturing without additional cost for them, where they are burned as alternative fuel. The remainder is forwarded to be used for sheet asphalt and asphalt-rubber, multi-sports floor, rubber articles, carpet car and shoe sole manufacturing [11].

Germany has classified tire as a suitable material for alternative fuel, due a series of successful experiences using tire in the co-processing. Depending on location in the rotary kiln that the tire is burned, the emission of nitrogen oxide can be reduced [12].

According to [13], the composition of tire is about 88 % of carbon and oxygen, which results in fast combustion and high calorific value (about 31,400 kJ/kg). Consequently, the amount of coal used is reduced by 1.5 tons for each ton of tires. Table 1 shows the composition of several samples of tires and its respective LHV.

Table 1 – Chemical composition and LHV (in kJ/kg) of tire chips sample.

Fuel composition	Tire chips			
	Sample 1	Sample 2	Sample 3	Sample 4
Carbon	72.30	75.90	77.60	79.00
Hydrogen	7.10	6.50	5.90	5.40
Sulfur	1.54	2.00	1.10	1.47
Oxygen	5.00	0.50	0.30	1.80
Nitrogen	0.36	0.50	0.10	0.06
Moisture	0.14	0.07	0.40	0.09
Ash	13.70	14.60	15.00	12.20
Volatile	61.70	59.10	61.50	38.30
LHV (kJ/kg)	33650	38970	35118	36055

Source: Adapted from [14].

The opening interval of the feeding system is function of the fuel type and LHV. As the tire has a specific feed rate, a special tire feed system is necessary. So, adaptions might be necessary in the precalciner feed and the kiln feed to use entire tires. In Brazil, most plants have preheaters and precalciners. An example of feed system for entire tires is shown in Figure 1. In cases of feed in chips, other systems are necessary.

The feed rate control is very important because the way that tire is burned in the kiln influences the CO emission [15]. The tire feed system controls the inlet tire rate trough a vacuum chamber with a gate. When the gates open, the tires enter the precalciner or kiln.

The presence of zinc in the chemical composition of the tire can be disadvantage in hydration and hardening of cement. As a consequence, the use of alternative fuels can't be more than 20% of total fuel [6], otherwise it can affect negatively the cement physic-chemical characteristics.

Sulfur is another compound that must be analyzed carefully. Table 1 shows that sulfur content is about 1-2%, which is inferior to most coal used in cement kilns, which have less than 1% of sulfur content. The control of sulfur emissions is made by using calcium carbonate, which is the main raw material of cement and reacts with sulfuric gas, controlling the sulfur emission.

Besides the chemical composition, to determine if the tire can be used as a secondary fuel it is necessary to analyze sub

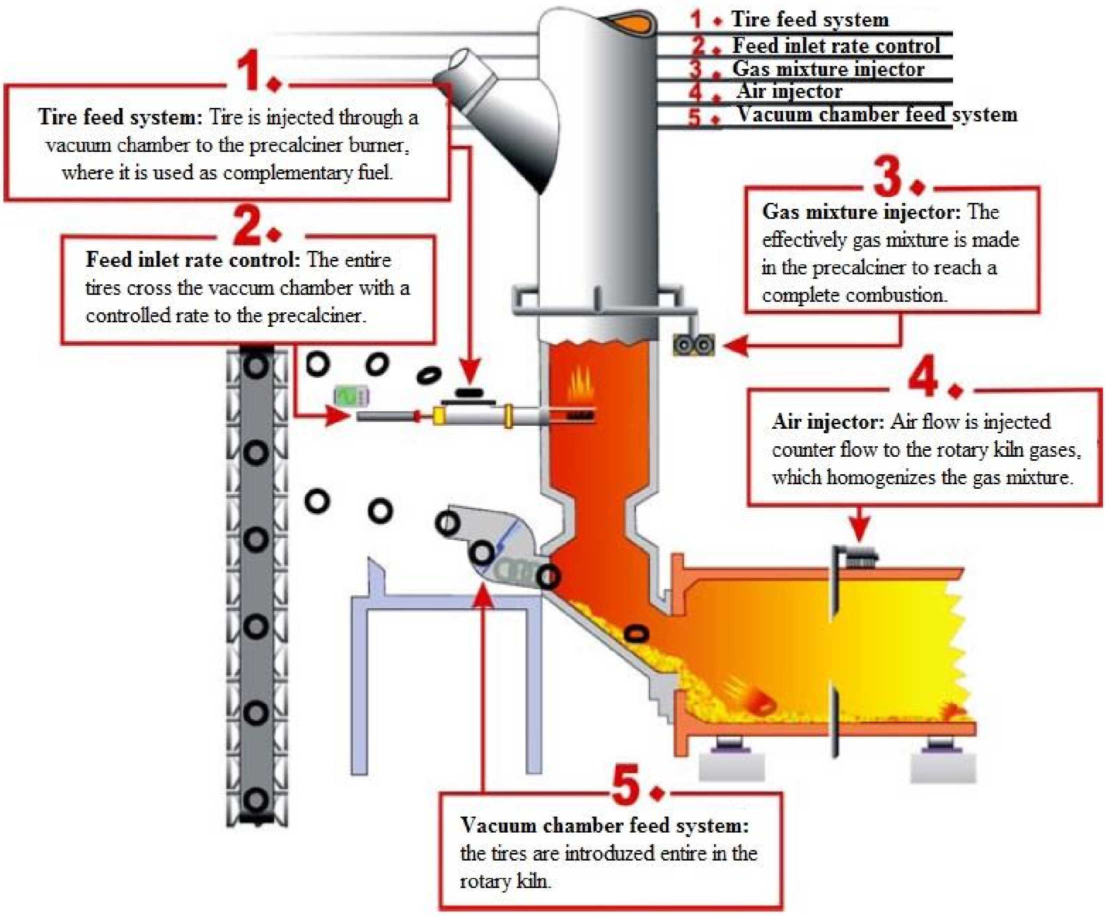

Figure 1: Tire feed system in pre-heater and precalciner [15].

products of combustion, which might contain pollutant gases. During the burning, the level of pollutants emitted cannot exceed the legislation limits. The key parameters are firing temperature and residence time in the rotary kiln or precalciner. Tires, just as another alternative fuels, have a maximum percentage that can be burned in the kiln, due to pollutant emission. Several studies have shown that this percentage cannot exceed 20% of total heat requested in the process, which already happens in most cement plant in Brazil [16].

III. Co-Processing of Used or Contaminated Waste Lubricating Oil

The lubricating oil used in automotive vehicles and industrial process contains a high content of additive, to increase efficiency and durability. It is classified as a hazardous waste, because it contains organic acid, aromatic polynuclear hydrocarbon, heavy metal such as cadmium, nickel, lead, mercury, chromium and copper (all considered carcinogenic). The lubricating oil consumption leads to waste generation, called used or contaminated lubricating oil. This waste has a high toxicity for environment and public health.

The reverse logistic of used lubricating oil occurs in Brazil since 1963, when National Petroleum Council (CNP, Conselho Nacional do Petróleo), which is already extinct, made compulsory to collect and destinate it to the re-refine process. The amount collected has been increased year by year. In 2005, CONAMA, the National Environment Council, determined that all the used or contaminated lubricating oil must be collected and it must have an adequate disposal, so it can be recovered as much as possible and it does not became harmful to the environment.

At the end of the re-refine process more than 80% of used or contaminated lubricating oil can be recycled and became basic oil of petroleum, which replace this importation, reducing the costs.

The re-refine process is the removal of contaminants, degradation products and additives from used lubricants oil, so it acquires the same characteristics as basic neutral oil, which is technically the same as the oil after the first refine that usually is imported. The industrial process has three different technological sets: a) acid and clay process with cracking (in this technology there is a predominance of heavy neutral basic oil); b) flash distillation (the predominance in this technology is light and intermediate neutral basic oil); c) propane extraction (the predominance is of intermediate neutral basic oil).

The most commonly used process in Brazil is the acid and clay process, which is not been used in several countries due to economic, technologic and productive reasons and the fact that this process yields acid waste. Nevertheless, this process has the lowest maintenance cost and it treats low quality used oils and oils with diverse contaminants. This process has a low production due to the fact that it is a batch process and that it has a high oil drag (about 10% of total volume). The oily residues generated by re-refine industries in Brazil is about 35,000 tons/month, in comparison with a volume of collected used lubricating oil of 405,000,000 liters. The typical composition of oily residue is shown in Table 2. Also, it LHV is 23,000 kJ/kg.

Table 2 – Heavy metals presents in oily residues

Heavy metal	Symbol	Concentration (ppm)
Antimony	Sb	25.1
Arsenic	As	0.34
Cadmium	Cd	1.27
Lead	Pb	163.82
Cyanide	CN	-
Cobalt	Co	5.3
Cupper	Cu	185.22
Chrome	Cr	33.05
Tin	Sn	0.61
Fluorine	F	0.01
Manganese	Mn	-
Mercury	Hg	0.06
Nickel	Ni	13.11
Palladium	Pd	-
Silver	Ag	-
Rhodium	Rh	-
Selenium	Se	-
Thallium	Tl	0.25
Tellurium	Te	3.17
Vanadium	V	0.98
Zinc	Zn	4520.02

IV. Control and Emission Limits

The waste co-processing in rotary kiln of cement plant must attend the maximum limits foreseen in law, as it is shown on Table III.

Table III – Maximum emission limits in waste co-processing

Pollutants	Maximum emission limit
HCl	1.8 kg/h or 99% of reduction
HF	5 mg/Nm³ corrected to 7% of O_2 (dry base)
CO*	100 ppmv corrected to 7% de O_2 (dry base)
MP	70 mg/Nm³ dry meal corrected to 11% de O_2 (dry base)
THC (expressed as propane)	20 ppmv corrected to 7% of O_2 (dry base)
Mercury (Hg)	0.05 mg/Nm³ corrected to 7% of O_2 (dry base)
Lead (Pb)	0.35 mg/Nm³ corrected to 7% of O_2 (dry base)
Cadmium (Cd)	0.10 mg/Nm³ corrected to 7% of O_2 (dry base)
Thallium (Tl)	0.10 mg/Nm^3 corrected to 7% of O_2 (dry base)
As, Be, Co, Ni, Se, Te	1.4 mg/Nm³ corrected to 7% of O_2 (dry base)
As, Be, Co, Cr, Cu, Mn, Ni, Pb, Sb, Se, Sn, Te, Zn	7.0 mg/Nm³ corrected to 7% of O_2 (dry base)

**The concentration of CO in chimney cannot exceed 100 ppmv in hourly average*

V. Conclusion

The adoption of efficient control methods of pollutant emissions by cement plants allows the use of alternative fuel and raw materials in clinker manufacturing. This process presents a solution for adequate disposal of industrial waste. This energetic recycling technique takes advantage of the waste LHV to generate energy and, simultaneously, to promote a thermal destruction and thermal treatment of waste.

The Brazilian National Waste Management Policy promotes an ideal political and juridical condition to increase the co-processing by cement plants in Brazil, especially in Minas Gerais, a state that has the larger number of cement plants in the country. However, the maximum emission limits of pollutant gases in Brazil are high in comparison with European limits. The limits adopted do not incentive the Brazilian cement plants to adopt more efficient techniques to control pollutant emissions, as it occurs in Europe.

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