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Use of scrap tires as an alternative fuel source at the Lafarge cement kiln, Brookfield, Nova Scotia, Canada

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Scarth MacDonnell Lafarge Canada Inc.
Plant Manager
Cement, Eastern Canada
87 Cement Plant Road
Brookfield, Nova Scotia, B0N 1C0 Canada

Submitted By
Dr. Mark D. Gibson MRSC C.Sci C.Chem P.Chem
Associate Professor
Department of Process Engineering and Applied Science
Dalhousie University

Authors
Ebenezer Asamany, Dr. Mark D. Gibson P.Chem, Courtney Wilson, Ellen Patrick and Dr. Michael J. Pegg P.Eng.
Department of Process Engineering and Applied Science
Dalhousie University

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EXECUTIVE SUMMARY

The use of Tire derived fuel (TDF) obtained from used tires in the Lafarge Brookfield cement kiln as a locally appropriate tire disposal strategy in Nova Scotia, Canada is examined and presented in this report.

Previous works on the composition, recycling and combustion mechanisms of used tires have been reviewed and summarised in a Literature review section. Considerations made by various authors in selecting used tire management strategies; and in using tires as alternative combustion fuel have been reviewed and presented as a basis for the case to be made for TDF in the long dry kiln at Lafarge Brookfield. Emissions, their health impacts and mitigation strategies for the general case of fuels and specifically for TDF as discussed by the literature were collected and reviewed to give the reader a useful background to the study of used tires as a fuel in cement kilns.

On the basis of equivalent heat content, expected gaseous emissions are theoretically obtained for TDF and coal-coke used in two scenarios. The first was a comparison of emissions on a 50,000kJ equivalent heat basis for TDF only and coal-coke only. The results showed an expected 71% reduction in fuel related SO_2; 77% reduction in fuel based NO_x emissions; 3% reduction in CO_2 and a 58% increase in H_2O switching from 100% coal-coke to TDF. Predictions show no significant change in the total mass of gaseous products. The second study theoretically calculated emission changes for a practical substitution rate of 30% TDF and 70% coal-coke. Fuel SO_2, CO_2, and fuel NO_x saw reductions of 21%, 1%, and 23% respectively. H_2O emissions are expected to increase by 17%. In light of the theoretical results and the literature, predictions on potential changes in particulate matter, metals, VOCs, products of incomplete combustion and PCDD/Fs are also discussed for the given scenarios.

Based on the results, the environmental and economic benefits of the diversion of used tires to cement kilns compared to other alternatives currently available in Nova Scotia is presented. In 2007 a landmark report cited that among the many alternatives for scrap tire usage, TDF option was second to high value tire derived products developed and generated for markets within and around Nova Scotia. To date, no industry manufacturing such high value products for a corresponding market has been established: Only the low value solution of replacing relatively inexpensive aggregate with a portion of the used tires in the province for Tire Derived Aggregate (TDA) as base and fill for construction projects is currently being practiced to a notable degree. Aside the low desirability of this low value TDA, the current practice also raises concerns of long term fire hazards associated with burying large amounts of such a high potency fuel in the proximity of dense human activity.

The urgent need for a high value solution; and present state of tire recycling within the province are thus touted as significant boosters for the proposal to consider displacing a fraction of fossil fuels such as coal and coke with used tires in the cement kiln currently available at Brookfield, Nova Scotia, Canada as a premium option.

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1 INTRODUCTION

The intense heat requirement and associated cost of clinker manufacture has caused many cement plants to evaluate alternative fuels to displace coal and petroleum coke in their cement kilns. In many cases, depending on the composition of the alternative fuel, cement kilns have been able to decrease their environmental footprint. Lafarge cement, Brookfield like many other cement manufacturing plants across the world has explored the use of alternate fuels and is currently permitted to process glycerol, waste roofing shingles, used oil and plastics as alternative fuels.

Approximately 1.4 billion tires are produced worldwide annually. 1 billion tires are disposed of yearly and it is estimated that 4 billion waste tires are currently in stockpiles and landfills (Martínez, Puy et al. 2013). Given that the annual rate of production far outweighs the annual rate of disposal, it is expected that the need for better tire disposal strategies will increase in the near future. Due to the complex composition of tires, recycling is difficult. In Canada, approximately 22 million tires are disposed of each year. Of these, 75% are used for material recovery, 20% for energy recovery, and 5% are not recycled (WBSCB 2008). The challenge and costs of collecting and disposing of tires in environmentally responsible ways have been studied and well discussed in the literature and more specifically in Nova Scotia, Canada. Many re-use and recycling approaches have also been studied and are in use world-wide. These approaches include retreading used tires, using shredded tires in civil engineering applications and incorporating tire rubber into new products. High value products from pyrolysis of scrap tires and upgrade of its char to retrieve valuable carbon black have been limited by the cost of the products compared to competing processes.

In comparing the various avenues for responsible tire disposal, the literature (research journal manuscripts, government reports and industry reports) does not consider them as competing interests but as complementary interests given the quantity and projected future increase in number of used tires disposed of annually. Stakeholders must decide which alternative use is beneficial under prevailing circumstances and given current available technology.

In the case of Nova Scotia, reference is made to a pertinent report completed by the Advisory Committee on Used Tire Management on a review of alternatives to Tire Derived Fuel for the province of Nova Scotia in 2007. The report ranks the recycling of tires into new products a preferable alternative to TDF for Nova Scotia. The committee's report did not discount the technical feasibility of TDF in cement kilns. It sought to comprehensively evaluate alternative disposal options for used tires within Nova Scotia. Their findings however consider the unavailability of a large crumbing and shredding facility in Nova Scotia, a challenge to the short term implementation of such in-province alternative to TDF. Likely competition from already established facilities in New Brunswick, and Quebec, Canada for the present market for manufactured products from recycled tire also poses an economic challenge to having such a facility within Nova Scotia, Canada in the long term. The Resource Recovery Fund Board (RRFB) reports that an estimated 1million tires (approximately 75% of tires collected) are shredded to 50-300mm pieces called Tire Derived Aggregate (TDA) and used for the construction of roads as base and fill (RRFB 2015). The use of scrap tires in civil engineering works is widely accepted however there is risk of fire when tires are stored in large quantities during the construction off-season. There is also the long term fire hazard associated with burying such a high potency fuel in the proximity of dense human activity. The continuous dependence on TDA, a low value product with limited desirability, which consumes only 75% of used tires generated within the province falls short of the expectations espoused by both the RRFB and the report of the Advisory Committee on Used Tire Management. In fact deducing from the committee's report TDF is ranked a better alternative to this current practice. Other alternatives to TDF presently available such as retreading used tires do not provide enough consumption for the vast numbers of used tires produced annually. As a cost effective, in-province and sustainable method of tire disposal; and given the current state of used tire disposal in Nova Scotia, Canada, the present report discusses the use of TDF to displace non-renewable coal-coke and to potentially reduce emissions in a local cement kiln as high value solution.

Cement is a high-value, high-demand product manufactured to meet rigorous standards. The fuel used in providing the high temperatures in cement kilns contributes to the components of the final clinker since there is no waste collected from fuel combustion. To meet accepted market standards therefore, a cement plant needs to cautiously regulate and optimize its use of alternative fuels necessarily to avoid undesirable clinker properties. This presents an inherent check on the indiscriminate use of cheaper waste derived fuels in cement kilns. On the other hand successfully producing standard quality cement at lower costs will positively impact infrastructural development and increase job opportunities within proximate jurisdictions. Considering currently available alternatives to the use of tires as TDF in Nova Scotia, it is possible to adopt the TDF approach while expanding the potential for re-use and recycling of used tires within the province.

The considerations made in the literature regarding used tire management include the value, demand and market for the resulting products; accessibility to technology; tire consumption efficiency, tire storage risks, environmental impacts and overall energy efficiency. Based on these criteria TDF used in cement kilns to produce an essential commodity and to reduce dependence on coal is considered a formidable avenue for responsible disposal of used tires. Effects of TDF on cement kilns operation and stack emissions have been studied; with many concluding that while it is hard to come to an actual overall emission factor, the emission levels are acceptable and in some cases better than those of primary cement kiln fuels.

The objective of this report is to theoretically evaluate what changes could occur in gaseous combustion and related emissions when TDF is used in a long dry process rotary cement kiln based on equivalent heat. The theoretical predictions are made referring to ultimate analysis data of a sample of used tires. The predictions are discussed in light of the literature and focused on assessing the need for TDF applications within Nova Scotia, Canada.

2 LITERATURE REVIEW OF TIRES AS FUEL

2.1 <u>Brief overview of used tire-recycling approaches</u>

Prior to disposal, tires can be retreaded to extend their life. This practice is common for truck tires. Unfortunately it is not common to retread passenger tires due to the danger of the retread coming loose and the decline in cost of purchasing new passenger tires.

Waste tire rubber can be shredded or further processed into crumb rubber. When shredded only, recycled tire rubber can be used in various ways especially in civil engineering applications. There are two methods to produce crumb rubber. The first process occurs at ambient temperature. The tires are first shredded, and then reduced in size through a series of different milling processes including the use of magnets to remove metal and a fiber separation process. The second method involves cryogenically freezing the shredded rubber to a temperature of -80°C. The frozen rubber then easily breaks apart into crumb rubber. Although more expensive, the cryogenic method produces smoother particles which can be advantageous in some applications (Dondi et al. 2014). While solely shredding of tires is more cost effective than the production of crumb rubber, the tire crumbs have more uses including making sports surfaces, vehicle products, molded products, and asphalt additives. 50-60% of one standard vehicle tire can be produced as crumb rubber. To be defined as a tire crumb, the particles must be 3/8” or less (Sunthonpagasit and Duffey 2004).

As an alternative fuel tires are used in cement kilns, paper and pulp mills, electric utilities, and industrial boilers in parts of Europe, Asia, United States and Canada. Tires as fuel are most effective in cement kilns and paper and pulp mills since no pre-treatment of the tires is required. In electric utilities and industrial boilers, the tires must be shredded prior to being processed for fuel. Specific facilities for converting tires to energy are cost prohibitive due to the initial investment costs (EPA 2012).

Devulcanized rubber is used in the rubber industry as an additive to new rubber mixtures. During devulcanization, the vulcanized rubber's structure is decomposed so the rubber does not regain the same chemical composition as natural rubber and cannot be used as a natural rubber substitute (Sienkiewicz, Kucinska-Lipka et al. 2012). The de-vulcanization process involves rubber crumbs being exposed to strong shearing and compressing forces, a mechanochemical process, to alter the structure (Zhang, Lu et al. 2013).

Pyrolysis of tires is a method where whole tires are heated above 400°C in a reactor without oxygen. This thermochemical process breaks chemical bonds in the material thus producing syngas and char. The gas produced is used to fuel the reactor and therefore there should be no resultant emissions. The pyrolysis of tires however is still under research and not yet used industrially (Martínez, Puy et al. 2013).

Gasification is another thermal process where a shredded tire feedstock is heated at 850°C through steam gasification to produce syngas and char. This process is very costly and is still under research (Molino et al. 2013).

2.2 General considerations of fuel emissions and their impacts.

Carbon dioxide (CO_2) is the major oxide produced from the combustion of carbon containing fuels. Carbon monoxide is formed in the case of incomplete combustion as an intermediate product, which could be converted to CO_2 in the presence of oxygen.

In the absence of sulphur bearing materials, sulphur dioxide (SO_2) generated as a result of the combustion of a fuel is governed by the sulphur content of the fuel: low sulphur coals have occasionally been blended with traditional coals to reduce SO_2 emissions: several major utilities and the U.S Department of Energy have also considered the co-firing of biomass with coal in utility boilers for the same purpose (Tillman 2000). Results of these studies suggest that given the lower sulphur content in used tires-see **Table 2**, it is likely to reduce sulphur emissions when blended with coal. This reduction may not reflect in an overall reduction in process emissions in cases where process materials other than the fuel also bear significant amounts of sulphur as in the cement making process.

Particulate matter (PM) emissions are influenced by fuel composition and extent of combustion, especially PM with a median aerodynamic diameter ≤ 10 µm (PM_{10}) (Gibson, Heal et al. 2009). Total suspended particulates (TSP) which include all airborne PM (~ <60 µm) are a function of the percentage of ash, or mineral matter, in the fuel, coupled with the unburned carbon resulting from incomplete combustion and firing method used (Tillman, Duong et al.). Pulverized coal firing, for example, typically yields 80% solid products of combustion as fly ash compared to 30% from cyclone firing (Tillman, Duong et al.). It is also expected that a higher volatile content will reduce unburned carbon in the products of combustion.

Gases such as SO_2, NO_x, and VOCs can transform in the atmosphere to form secondary fine PM and ozone (O_3) by a number of chemical reactions (Tillman, Duong et al. , Gibson, Guernsey et al. 2009, Gibson, Heal et al. 2013, Gibson, Pierce et al. 2013, Gibson, Haelssig et al. 2015). Therefore, the combustion of used tires with low sulphur and nitrogen content coupled with complete combustion of VOCs in the kiln should theoretically produce significantly lower fuel

SO_2 and NO_x emissions. This would have the knock on effect of reducing secondary PM and O_3 formation in the emission plume from the Lafarge cement kiln (Gibson, Guernsey et al. 2009, Gibson, Kundu et al. 2013, Gibson, Pierce et al. 2013). Wang, Zhang et al. (2008) however suggests that the presence of certain elements such as calcium in the fuel's mineral matter or ash may cause particles to coalescence leading to lower levels of $PM_{2.5}$ than expected and causing changes in the PM size distributions.

Volatile organic compounds as a combustion product is discussed by Choi and Yi, 2000 (Choi and Yi 2000): the extent of thermal degradation of produced VOCs, such as benzene, xylene and toluene, is dependent on temperature and residence time. At temperatures above 1000°C and favourable retention time within this zone, the mixture of organic vapour from devolatilization of the solid fuel; and air is oxidized to form CO, CO_2, NO_x and H_2O thereby reducing the presence of harmful VOCs in emissions.

$$C_nH_m + \left(\frac{n}{2}+\frac{m}{4}\right) O_2 \rightarrow nCO + \frac{m}{2} H_2O;\ \text{Then}\ CO + \frac{1}{2}\ O_2 \leftrightarrow CO_2\ \text{(Choi and Yi 2000)}$$

NO_x formation increases exponentially with temperature because the combustion process requires air, which also provides the nitrogen (N_2) and oxygen (O_2) that react to form thermal NO_x reaction combustion. However NO_x formed by the oxidation of organo-nitrogen compounds found in the fuel is dependent on the reactivity of the fuel. Highly reactive fuels promote early release of nitrogen in the fuel mass: the release of nitrogen in the early, fuel rich stages of combustion reduces the formation of NO_x at the later, high-temperature stages of combustion. For a fuel blend to have an effect on reducing NO_x, it must contain less nitrogen and/or constitute a more reactive fuel than was previously the case. The nitrogen content in fuels is generally low, therefore, fuel derived NO_x should form a small fraction of total NO_x expected after combustion in excess air (79% nitrogen). Reactivity of fuels is not directly discussed in this report. Other hazardous pollutants, such as trace metals and mercury, may also be sources of concern if they are present in the fuel mix being used (Tillman 2000).

The general agreement on polychlorinated dibenzo dioxins (PCDD/dioxin) and polychlorinated dibenzo furan (PCDF/Furans) is that their formation depends on kinetic factors beyond the presence of certain elements present in a fuel (Stanmore 2004). The distribution of the toxic fraction of the dioxin and furan species is fairly similar for different conditions (Tan, Hurtado et al. 2002). The suggestion that dioxins and furans are better off being controlled by controlling the rate of formation and depletion of precursors and suppressors has been adopted in many combustion scenarios. Yazawa, Nakazawa et al. (1999) discuss kinetic factors and thermodynamic trends, relying on available thermodynamic data, in the formations of PCDD/Fs have been for the gaseous C-O-H-Cl system at 300°C. They conclude that PCDD/Fs decompose at high temperature, at high oxygen (O/C>1) or low chlorine content. Interestingly, they also indicate that high hydrogen or water vapour content and the deposition of carbon could suppress the formation of these toxic gases. Increased concentrations of chlorine led to more PCDD/Fs but at higher concentrations, chlorine-carbon compounds were formed preferentially to PCDD/Fs. The predominant species of chlorine in combustion gases is HCl, and its removal could enhance PCDD/Fs due to the removal of hydrogen. Fortunately in usual practice, chlorine is removed preferentially to HCl as a molecule, leaving hydrogen. An example of this reaction is given here:

$$2HCl_{(g)} + CaO_{(s)} \rightarrow CaCl_{2(s)} + H_2O_{(g)}$$ (Yazawa, Nakazawa et al. 1999)

The effect of HCl is also supported by Duo and Leclerc (2007) who also indicates that a theoretical molar ratio of Cl/S of 2 and above creates an inhibitive effect to the formation of

PCDD/Fs in boilers. According to their observations, NO_x has no effect on PCDD/Fs formation and the effect of carbon monoxide (CO) could not be ascertained by thermodynamic analysis alone. Duo and Leclerc (2007) also propose a simplified stack emission model for boilers, which shows that stack dioxin emission increases linearly with decreasing ESP efficiency and exponentially with increasing ESP temperature.

Effects of different gaseous emissions on the health of humans have been studied by various authors in very diverse work environments: for example the presence and impact of soluble transitional metals exposure has been investigated for welding fumes (McNeilly, Heal et al. 2004). The literature shows that even very delicate cutting and shredding activities may contribute to changes in particulate matter emission and distribution (Brace, Stevens et al. 2014). Under household operating conditions, changes in kitchen fuel were seen to affect potential exposure of people to certain VOC species (Dohoo, Read Guernsey et al. 2015). Studies also suggest an association between short- and long-term exposure to SO_2, NO_2 and O_3 and increased morbidity, mortality, and hospital admissions for cardiovascular and pulmonary diseases. They are also associated with acid deposition and photochemical smog (Bari, Curran et al. 2015). Overall the actual impact of emissions on the environment and receptor populations is dependent on the mode and scope of operation as well as the consistency of emission monitoring and modelling. Keeping emissions within the regulated limits would ensure minimal adverse impact on downwind receptor populations and the environment.

2.3 Composition of tires

Tires are composed generally of vulcanized rubber, reinforcing fillers and fibres; and petroleum oils which improve low temperature flexibility of vulcanized rubber (Amari, Themelis et al.

1999). Co-polymers, styrene-butadiene (SBR) or a blend with natural rubber tires are used as raw materials. The process of vulcanization introduces additives such as zinc oxide, stearic acid and amounts of sulphur into the tires. Carbon black is most widely used as a reinforcing filler to strengthen and improve the abrasive resistance of finished tires. Various fibres are also used as reinforcement: steel based fibre and tire cords; and textiles such as rayon, nylon and polyester. Of the rubber compounding components of tires SBR and carbon black make up approximately 90%, extender oils, zinc oxide and sulphur make up 1.9%, 1.2% and 0.7% respectively. Reinforcing fibre could make up 13% or less of the final tire. The scrap tire management council of the Rubber Manufacturers Association (RMA) reports the composition of tires by weight as shown in **Table 1**.

Table 1: Composition of tires by weight from Rubber Manufacturers Association (RMA).

Component	Passenger Tire (%)	Truck tire (%)
Natural rubber	14	27
Synthetic rubber	27	14
Carbon black	28	28
Steel	14 – 15	14 – 15
Fabric, fillers, accelerators, antiozonants, etc.	16 – 17	16 – 17
Average weight:	**New 25 lbs, Scrap 20 lbs.**	**New 120 lbs, Scrap 100 lbs**

For this report, ultimate analysis of used tires was conducted at EXOVA laboratory, Quebec, Canada. The results are displayed in **Table 2**, along with that of 50-50 coal-coke for comparison. The used tire ultimate analysis conducted compares very well with the data published by scrap tire management council of the Rubber Manufacturers Association.

Table 2: Analysis of used tires and 50-50 coal-coke mixture showing elemental and ash compositions as reported by Exova laboratory.

Component	Unit	Used tire	Coal-coke
Chlorine	mg/kg	752	183
Fluorine	mg/kg	15.1	85.2
Carbon	dry %	87.79	69.67
Hydrogen	dry %	6.52	3.18
Oxygen	dry %	1.8	7.11
Nitrogen	dry %	< 0.5	1.68
Sulphur (S)	%	1.34	3.52
Moisture	%	0.88	0.37
Ash at 900°C	%	2	13.43
Calorific Value	KJ/kg	38453	29631
Aluminium Oxide	%	2.65	17.05
Calcium Oxide	%	4.79	2.5
Iron Oxide	%	6.18	36.49
Magnesium Oxide	%	1.07	1.2
Phosphorus Oxide	%	1.93	0.57
Potassium Oxide	%	0.532	0.92
Silica	%	14.55	34.32
Sodium Oxide	%	0.41	0.07
Titanium Oxide	%	0.26	0.059
SO_3	%	3.35	8.8

2.4 Combustion mechanisms of tires as fuel

The effect of particle size, heating rates and temperature on the thermal decomposition mechanism of tires during combustion and pyrolysis has been discussed extensively (Leung and Wang 1998, Aylón, Callén et al. 2005, Larsen, Schultz et al. 2006, Nielsen, Aniol et al. 2011, Antoniou and Zabaniotou 2013).

In their pyrolysis study of tire conversion for tire particles 2 mm and lower, Aylón, Callén et al. (2005) indicate that the size of particles did not determine the extent of conversion, with total tire conversion being achieved. Their observations agree with those of Leung and Wang (1998) who conclude that heating rate plays a more influential role for process and kinetic parameters while studying 40 mesh tire rubber. The mechanisms in thermal degradation of tires is summarized as follows: moisture loss by 150°C; oil, plasticizer and additive loss between 150°C and 350°C; natural rubber, butadiene rubber and styrene-butadiene loss between 340°C and 550°C with two observable peaks at 380°C and 450°C (Leung and Wang 1998). The devolatilization characteristics of larger particles of tire as studied using a macro-thermogravimetric analysis (TGA) reactor by Larsen, Schultz et al. (2006), shows that for tire sizes between 7.5 mm to 22 mm, devolatilization times increased with increased particle size for a 490°C to 840°C temperature range. They however report a more significant effect of surrounding temperature on devolatilization rates. In another study Nielsen, Aniol et al. (2011) discussed the effect of mixing larger fuel particles in a pilot scale rotary kiln: large fuel particles placed on the top on the bed of kiln material will predominantly be covered by raw material after less than 30 s in the rotary kiln. This may affect the heating and combustion mechanisms for the fuel particles.

Work done on pyrolysis of automobile tires by Antoniou and Zabaniotou (2013) shows that product yields generally increase with increasing temperature, indicating better thermal cracking at higher temperatures. Gas yields could be as high as 73wt% at 830°C. Their observations also show that conversion of char from tires to CO_2 increased significantly with an increase in temperature from 800°C to 900°C- 950°C.

Caponero, Tenório et al. (2004), (2005) in seeking to lower products of incomplete combustion (PIC) such as soot and polyaromatic hydrocarbons (PAH) generated from tire chips used in batch combustion processes suggested that proper temperature regulation, proper mixing of effluent with air and hot flue gas filtration played a major role in reducing the emission of CO, PAH and

PM. They operated their bench scale furnace between 500°C and 1000°C, far lower than is expected in industrial kilns and still observed major reduction in PIC by employing these strategies.

According to Takeshi et al, in a comparison of scrap tires to coal, tire samples had less moisture, more combustible matter, less fixed carbon and higher heat content. Ash residue of 1.25 cm rubber, 5 cm rubber tire pieces with steel, 5 cm rubber tire pieces without steel and coal were reported as seen in **Table 3**. Ash from rubber tire pieces with steel was made mostly charred steel. The rubber and tire pieces produced gaseous emissions containing zinc oxide, lower quantity of heavy metals and lower NO_x.

Table 3. Ash residue percentage from four tested samples reported in (Amari, Themelis et al. 1999)

Sample	**Ash residue** (%)
1.25 cm rubber pieces	16
5 cm rubber tire pieces with steel	23
5 cm rubber tire pieces without steel	9
Coal	11

The combustion mechanism, ignition and burnout characteristics of blends of waste tires with high ash coal were studied by Li, Ma et al. (2006) using thermogravimetric analysis. They note that the combustion of waste tire is characterized by more complex emissions of volatile compared with the coal. Blending waste tires with high ash coal improved combustion characteristics of coal especially the ignition performance and the peak weight loss or extent of combustion: ignition temperatures decreased with an increase in waste tire fractions in the blend. Their observations show a coupling effect between the two fuels in the blend and a general feasibility of blending waste tires with coal.

2.5 Use of Tire Derived Fuel

Based on considerations needed to be made before introducing alternative fuels into cement kilns and the combustion characteristics of tire rubber, changes in cement kilns using TDF as fuel in cement kilns have been studied and published. These works vary with location, scale and length of study, type of cement kiln, type of primary fuel, percent of used tires in fuel mix and change parameters analysed.

Pipilikaki, Katsioti et al. (2005) studied the effect of TDF on clinker: 6% of total fuel was TDF. The authors conclude that no apparent problems were noticed in clinker in terms of strength. There was the presence of zinc which the paper gave as the main constraint limiting TDF to 30% by weight of the fuel mix in most cement kilns. They mention that metals such as zinc and chromium present in TDF chemically combine with clinker and therefore there is no risk of these metals leaching from the clinker, once produced. The authors compare this phenomenon to silica not leaching from glass once it has been produced.

Data published by the Rubber Manufacturing Association (RMA) on bottom and fly-ash from 100% TDF combustion showed iron as the main component of bottom ash (96%) whereas zinc, carbon, silicon and iron make up over 95% of the fly ash. Elements such as lead, arsenic and cadmium were present in bottom ash to approximately 0.001% by weight each; and in fly ash at 0.22%, 0.02% and 0.05% respectively. Hower and Robertson (2004) studied the chemistry and petrology of fly ash derived from co-combustion of coal and 1.25-1.8% TDF at an energy plant. They evaluated the fly ash collected by emission control devices using petrographic analysis and x-ray fluorescence. Based on characteristic morphology, they determined that the coarse carbon fly ash collected contained carbon attributable to TDF. Their work also observed that a decrease in flue gas temperature was accompanied by an increase in the concentration of chlorine, iodine, zinc and lead in the fly ash collected by electrostatic precipitators. However for elements which could be present in both coal and TDF such as lead and arsenic, increases were largely allocated to coal. The effectiveness of the ESP as an emission control device is implicitly highlighted in these results.

Carrasco, Bredin et al. (2002), Conestoga-Rovers&Associates (2007) report a broad variation of expected changes in gaseous emissions such as SO_2, NO_x and CO in their literature review of other studies on effects of TDF on cement kiln emissions. They attribute the variation in results to the fact that SO_2 and NO_x emission do not only depend on the quantity of their parent elements in the fuel but also on their presence in raw materials; and the combustion efficiency, which is also important in CO formation. Carrasco, Bredin et al. (2002) report slight increases in PM, SO_2, and CO; and a decrease in NO_x after collecting data from cement kiln stacks in Quebec, Canada. In terms of metal emissions, the most increases were seen in zinc (Zn) and iron (Fe), which are both components of tires. Lead (Pb), chromium (Cr), aluminium (Al) and manganese (Mn) also saw some increase though at very low concentrations. Emissions of organic compounds including dioxins and furans decreased with the use of scrap tires. The presence of higher amounts of chlorine in tires than in coal resulted in an increase in HCl emissions. This seems to agree with earlier referenced chemistry literature that an increase in HCl could suppress the formation of dioxins and furans. Carrasco concludes that even though certain pollutants increased while using tires as a source of fuel, environmental standards were still well respected.

2.6 Summary of the Literature

The cited literature highlighted the relative importance of surrounding temperature and heating rates; tire size; and the presence of additives in the performance of used tires in thermal degradation processes. Surrounding temperature and heating rates seem to be most significant in determining the rate and extent of thermal decomposition of tires.

The literature has also given credence to the feasibility of TDF in combustion processes based on its composition and combustion mechanism. The effects of TDF substitution in cement kilns are varied: there is not a consistent conclusion and results are widely dependent on individual kilns and prevailing conditions. Furthermore, the literature presented observations made when TDF was introduced into different cement kilns using varying approaches to maintain and improve combustion efficiency. The influence of coupling effects within fuel blends, raw materials, kiln operating parameters and kiln delivery methods have been shown to be peculiar to each kiln and must be studied in terms of local benefits to reach optimum TDF delivery and fractions.

It has also been concluded from the literature that impacts of emissions on downwind populations and the environment are kept minimal when regulatory emission standards are adhered to. The role of adequate emission control devices, such as ESP's, have also been emphasized as having been successfully applied in reducing emissions from cement kiln stacks regardless of the fuel choice or type of kiln.

3 ANALYTICAL PROCEDURE

A preliminary comparison is conducted on the mass of gaseous products expected from complete combustion of 50,000kJ equivalent heat of 50/50 coal-coke and TDF burnt separately. Subsequently, using 4.5GJ/tonne of clinker as an average for a dry process cement kiln as estimated by Natural Resource Canada, the values for the gaseous combustion products were obtained on equivalent heat basis theoretically for 30% used tires blended with coal-coke for combustion using the following generalized equation where *X* is the element being considered and *n* is the stoichiometric mole ratio of *X* to its oxide:

$$mass\ of\ product\ \left(\frac{kg}{tonne\ of\ clinker}\right)$$

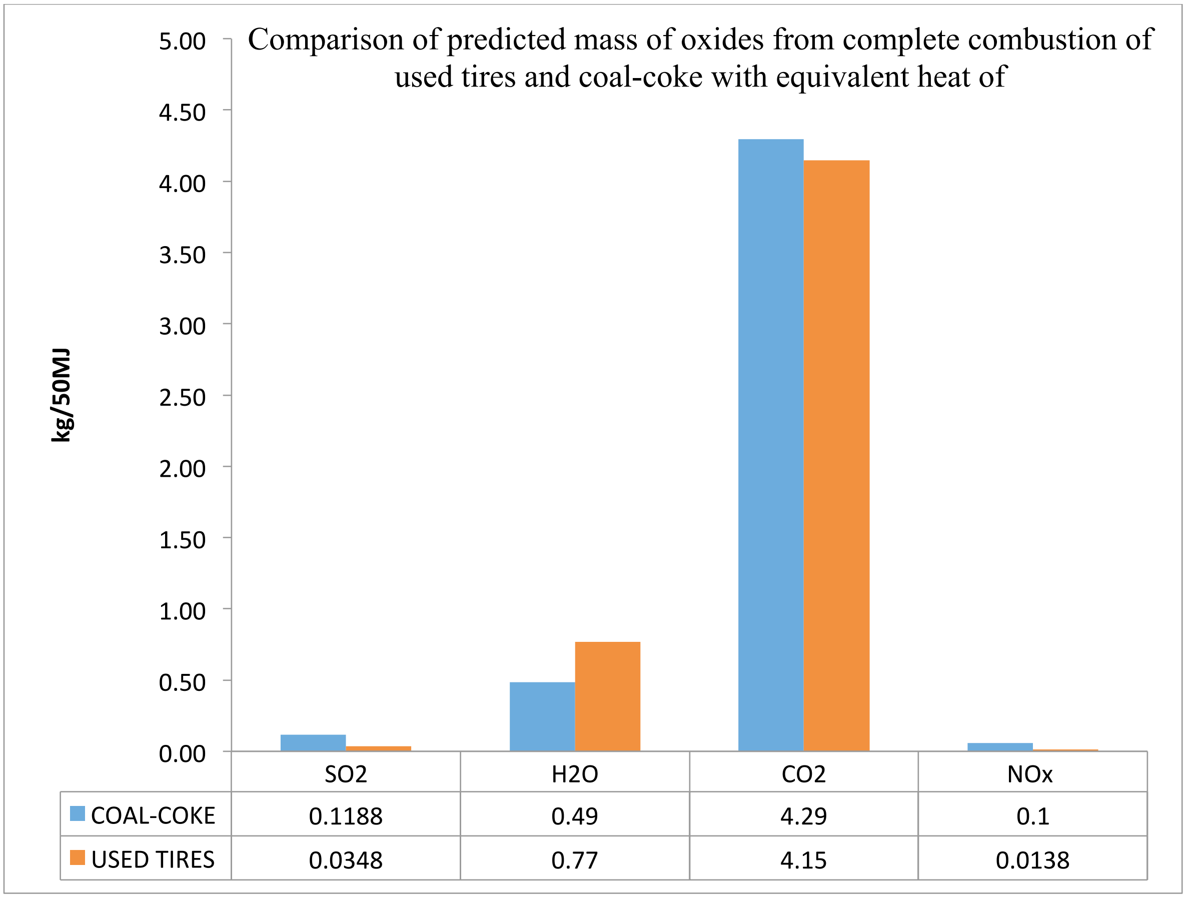
$$=$$

$$\frac{energy\ target\ (kJ)}{calorific\ value\ kJ/kg}\times\frac{\%\ of\ X\ in\ fuel}{molar\ mass\ of\ X}\times molecular\ mass\ of\ 'X'oxide\times n$$

Where the composition of the element was reported as a percentage of dry weight, the moisture content was subtracted from the obtained fuel weight before proceeding with further weight calculations. Elemental composition on equivalent mass basis obtained from EXOVA laboratory shown in Table 2 were used for these calculations. Predictions for a second scenario where heat required is split 30%- 70% between Tire Derived Fuel and coal-coke were calculated from the summation of products expected from the TDF and 50/50 coal-coke with respect to their equivalent heat contribution in the fuel blend.

Coal and petroleum coke samples used for comparison were oven dried at 50°C for 10 hours before being crushed to (80% ~200mesh) in a roll mill and mixed to a 1:1 ratio. The tire sample was obtained from a used tire collector. From Table 2 coal-coke generates more ash at 900°C than used tires. The halogen, chlorine is present in larger quantities in used tire while coal-coke contains more fluorine element than used tires. Again on equivalent mass basis, used tires contain more carbon and hydrogen and lower amounts of nitrogen, sulphur and oxygen.

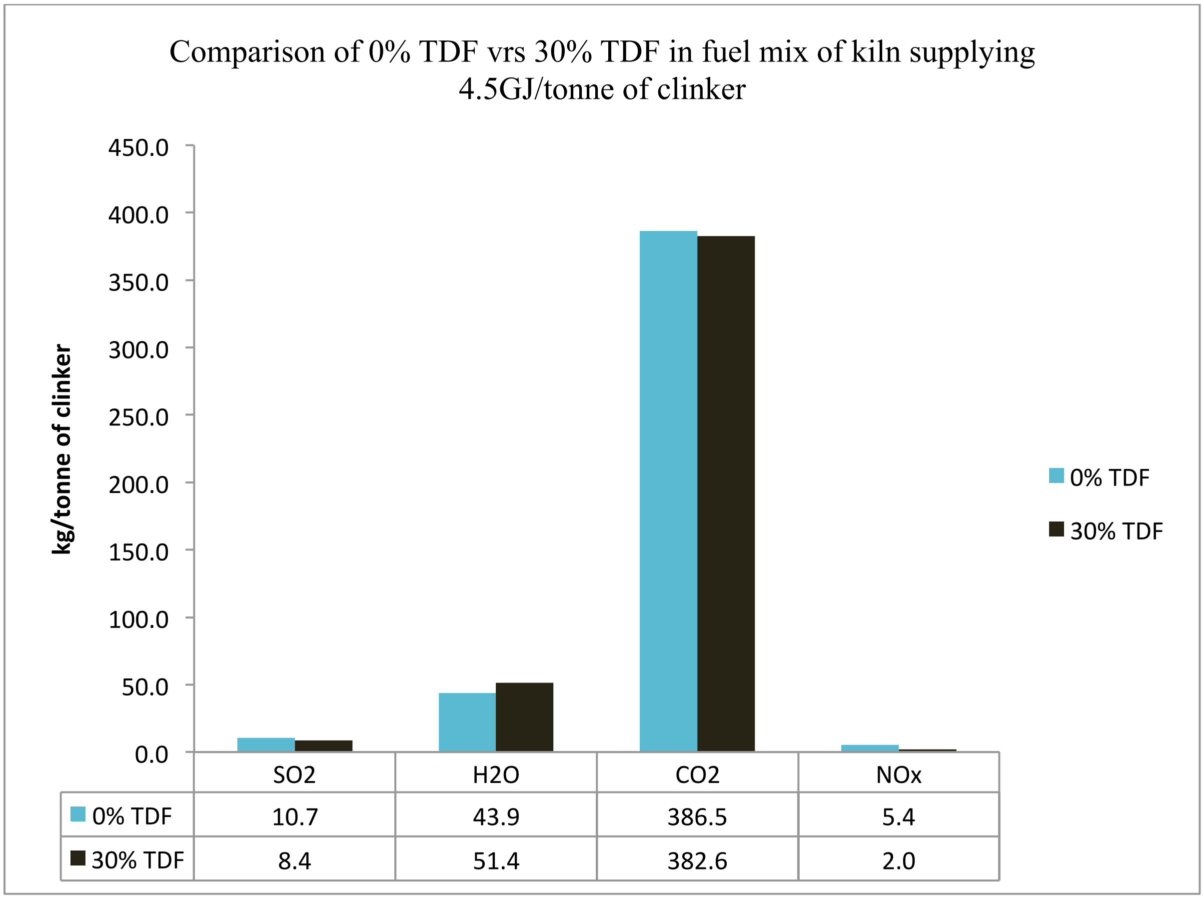
4 RESULTS


Comparison of predicted mass of oxides from complete combustion of used tires and coal-coke with equivalent heat of

	SO_2	H_2O	CO_2	NO_x
🟦 COAL-COKE	0.1188	0.49	4.29	0.1
🟧 USED TIRES	0.0348	0.77	4.15	0.0138

Figure 1: Graph showing gaseous emissions theoretically expected from the complete combustion of coal-coke and used tire

The results from theoretical calculations shown in Figure 2 show in terms of gaseous emissions, similar products are expected for used tires and coal-coke with the most noticeable reduction occurring for NO which was used to represent the entire NO_x species. On an equivalent heat basis, there is an expected 71% reduction in fuel related SO_2; 77% reduction in fuel based NO_x emissions; 3% reduction on CO_2 and a 58% increase in H_2O when coal-coke is replaced with used tire. Figure 1 shows a comparison of these emissions for used tire and 100% coal-coke.



	SO2	H2O	CO2	NOx
0% TDF	10.7	43.9	386.5	5.4
30% TDF	8.4	51.4	382.6	2.0

Figure 3: Chart showing theoretically predicted gaseous oxides from the complete combustion of 30:70 blend of TDF: coal-coke

Figure 2 shows the expected changes in gaseous emissions expected from the complete combustion of a fuel mix made up of 30% TDF and 70% coal-coke. Fuel SO_2 emissions are expected to reduce by approximately 21%, CO_2 by 1% and NO_x by an estimated 23% with a 17% increase in H_2O. Though there are reductions in three of all the major gaseous products of complete combustion there is little change in total mass of gaseous emissions expected when the theoretical fuel blend is made up of 30% TDF. A summary of predicted increase and decrease with respect to fuel blend percentage is shown in Table 4.

Table 4: Summary of changes expected in gaseous emissions for two coal-coke displacement scenarios

Gaseous product	Per 50,000kJ	30:70 TDF: coal-coke for 4.5GJ
SO_2	decrease	decrease
H_2O	increase	increase
NO_x	decrease	decrease
CO_2	decrease	decrease
Total gaseous emission	No significant change	No significant change

5 DISCUSSION

5.1 Waste tire consumption

A 30% equivalent heat displacement of coal-coke by TDF, assuming no prominent coupling effect, is expected to reduce total emissions after complete combustion. To attain a 30% by heat substitution for an annual production of 300,000 tonnes of clinker at 4.5GJ/tonne of clinker, more than 1.3 million 8kg passenger tires will be consumed. This number is more than the quantity generated in Nova Scotia. This implies that TDF in the Brookfield cement kiln could adequately resolve the tire disposal challenge within the province.

5.2 Products of complete and incomplete combustion

In light of the theoretical basis of comparison, used tires perform better in overall emissions and result in decreases in fuel NO_x, SO_2 and CO_2 emissions. In practice, these emissions are affected by the combustion performance which depends largely on factors outlined in the literature review section of this report. For example the presence of products of incomplete combustion (PIC) such as poly aromatic hydrocarbons (PAH) and CO reduce with increases in surrounding temperature, residence time and air-to-fuel ratio. Although in general cement kilns provide the conditions required for the reduction of the potential PICs, there is a possibility of an increase in CO where large pieces of tires are placed in oxygen deficient regions of the kiln. This could be further tested in bench scale and field trials. Generally, improvement in combustion efficiency adds to the suitability of any given fuel in a cement kiln. In this case, better combustion places used tires in similar ranges for coal-coke in terms of total gaseous emission products: where there are certain deficiencies in actual operations, long residence times and high temperatures will limit the emission of PICs. The higher volatile matter content of TDF is also likely to positively affect the ignition performance of a coal-coke/ TDF fuel blend for better combustion. For a blend of TDF and coal-coke versus coal-coke only, there is a potentially slight change in total gaseous emissions expected per equivalent heat as seen from the results. The total mass combustion products to be handled by emission control systems remain very similar.

5.3 PCDD/Fs

The results from theoretical combustion may result in an increase in H_2O production. The elemental analysis also points to potential increased formation of HCl due to a higher hydrogen and chlorine content in used tires than in coal-coke. The presence of hydrogen bearing molecules reduces the potential for the formation of PCDD/Fs due to the increased competition for oxygen. The presence of higher levels of chlorine in used tires than in coal-coke as seen in Table 4 raises fouling concerns for the cement kiln and associated machinery. It may also suggest a higher potential for the formation PCDD/Fs however, this is countered by the presence of lower levels of fluorine compared to coal-coke which would suggest a reduced potential for the formation of PCDD/Fs. Given the complex mechanisms leading to the formation of PCDD/Fs it is useful to continuously monitor its presence and to ensure that emissions remain within regulatory limits as is the case for the many studies conducted on fossil fuel replacement with TDF.

5.4 Particulate matter and metals

Considering that, ash contributes to the suspended particles released via combustion, the lower content of ash from used tires seen in **Table 2**, reduces its potential to contribute to particulate matter emission. This agrees with observations in literature which reports reduced particulates with TDF. In any case, it has been shown that ESP is able to remove these released particulates from flue gas stream, keeping the stack emissions within allowable range.

The analysis in **Table 2** does not cover the presence of metals such as mercury, lead and zinc however the literature shows that higher levels of zinc and lower mercury content are expected for used tires. The abundance of lead in used tires and coal-coke may vary with respect to type and primary composition. The presence and abundance of particulate matter and heavy metals could be monitored and ascertained during kiln trials since their emergence depends on the effectiveness of the ESP.

6 CONCLUSION AND RECOMMENDATION

On an equivalent basis for 1 tonne of clinker, expected changes in gaseous products of complete combustion, switching from coal-coke to TDF, are reported: 71% reduction in fuel related SO_2; 77% reduction in fuel based NO_x emissions; and 3% reduction on CO_2. A slight reduction of gaseous emissions is expected for 30% equivalent heat replacement of coal-coke with TDF, with corresponding decrease in gaseous combustion products: 21%, 1%, and 23% decrease in fuel SO_2, CO_2, and fuel NO_x emissions respectively; and 17% increase in fuel H_2O.

Based on knowledge from the literature on combustion mechanisms and collected kiln emission data potential changes in emissions PICs, dioxins and furans and particulate matter have also been discussed. The effect of high temperature, residence times and air-to-fuel ratio of cement kilns on the emission of CO and PAH as PICs has been highlighted. Dioxin and Furans formation is expected to be suppressed with the introduction of TDF or at least remain the same as coal-coke. Particulate matter emissions are expected to reduce with coal-coke being replaced by TDF. In blends of coal-coke with TDF, ignition performance is expected to improve compared to coal-coke only. Consistent field monitoring and proper maintenance of ESP are as essential for cement kiln fueled by TDF as would be for other conventional fuels.

The necessity of tires for transporting people and goods in modern society means a continuous generation of used tires is inevitable. This must be countered and contained by cost-effective and rigorous waste valorization approaches. A case has been made for TDF usage in an already existing cement kiln as a viable option under current waste diversion goals within the province of Nova Scotia, Canada. In light of these findings and the urgent need to find a cost effective and environmentally sound solution to the challenge of tire disposal within the province of Nova

Scotia, it will be beneficial to introduce TDF into the Lafarge cement kiln, equipped with an ESP, as a supplementary fuel following trials to determine optimum TDF/coal-coke fractions and TDF delivery methods for the cement kiln. It is highly likely that substituting up to 30% of the heat requirement at the Brookfield kiln with TDF would decrease the overall environmental footprint of the plant and would significantly improve the provincial tire recycling program provided the emissions observed from continuous monitoring meet the provincial standards.

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