

WASTE-DERIVED FUELS FOR CO-PROCESSING IN ROTARY CEMENT KILNS

by

Ebenezer Afram Asamany

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DEDICATION

I dedicate this to the memory of my dearly beloved friend Ntorbea Asamoah-Odei, whose passing on my birthday in 2016 will forever be etched on my heart. She knew of this day and cheered me all the way even through her own challenges. The care and hospitality she showed me made Halifax a place worth calling home for me. I also dedicate this work to the memory of Joshua Lawson, a friend who also hoped for achievements such as this but did not live to partake of this accomplishment. Rest well, I miss you both dearly!

I also dedicate this to the honour of my father, Raphael Asamany who has always showed me through challenging periods of his life that a handshake for a good job done was more valuable than the many luxuries associated with success.

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ABSTRACT

Co-processing waste as alternative fuel in cement kilns presents a two-pronged solution to cost and environmental concerns in resource utilization. It is the simultaneous recovery of energy and recycling of resources where waste from different sources are used in the manufacture of a valuable commodity such as cement. In this study, bench-scale and full-scale experiments have been used to identify and characterize examples of waste-derived fuels (WDF) available for co-processing in cement kilns in Nova Scotia, Canada.

Field trials were used to select optimum kiln delivery approaches which overcame practical operational challenges in the delivery of waste asphalt roofing shingles (WARS) into the local cement kiln. The consumption of shingles was improved from 5% to 17% by mass of total fuel combusted.

A bench-scale tube furnace was used to determine the volatile organic compounds (VOC) content and particle distribution of combustion products generated from WDF. Plastic-derived fuel (PDF) from low density polyethylene (LDPE) film, plastic containers and expanded polystyrene (EPS) were found to have better thermal performance compared to waste carpets and discarded clothing on an equivalent energy basis. With respect to calorific value, moisture content and ash content of the WDF, thermal performance indicators, observed in full-scale tests, such as clinker production rate, kiln gas flowrate and kiln gas temperature matched bench-scale trends in residual VOC emission from the combustion of WDF.

A heated grid reactor (HGR) was designed and constructed, and then used in conjunction with Thermogravimetric analysis (TGA) and emission measurements, in several combustion experiments on waste plastics, waste shingles and blends with coal and coke. Particulate emissions sampled from the combustion of the fuel blends containing WDF did not differ significantly from that of the mixture of coal and coke only. Indeed, blending with plastics and shingles was seen to improve the combustion efficiency by reducing the time to ignition (TTI) and the extent of devolatilization achieved in the coal and coke fuel samples over a 5 to 10 second fast heating period.

Using these experiments, a bench-scale screening procedure for WDF to be used as cement kiln fuel was applied to study, assess and to provide preliminary expectations for WDF application in a local cement kiln. The results also showed that the proper co-processing of WDF in Nova Scotia will not only result in macro-scale environmental gains, but also improve the efficiency of the combustion process on a micro level without significantly affecting particulate emissions.

LIST OF ABBREVIATIONS AND SYMBOLS

A [1/s]	Pre-exponential factor
B [°C/min]	Heating rate
E [kJ/mol]	Activation energy
R [kJ/kmol. K]	Universal molar gas constant
T [°C, K]	Temperature
α [-]	Reaction progress variable
ALCF	Alternative Low Carbon Fuel
ASMI	Athena Sustainability Materials Institute
C&D	Construction and Demolition
CAC	Cement Association of Canada
CPIA	Canadian Plastic Industry Association
EFR	Entrained flow reactor
daf	Dry ash free
EPS	Expanded Polystyrene
ESP	Electrostatic precipitator
FC	Fixed Carbon
GCMS	Gas Chromatography Mass Spectroscopy
HDPE	High Density Polyethylene
HGR	Heated grid reactor
HMA	Hot Mix Asphalt
LDPE	Low Density Polyethylene
LHW	Liquid hazardous waste
MRF	Material Recovery Facility
MSW	Municipal Solid Waste
NRC	Natural Resources Canada
PC	Pulverized coal
PF	Pulverized fuel
PCA	Portland Cement Association
PCDD	Polychlorinated dibenzodioxin
PCDF	Polychlorinated dibenzofuran
PDF	Plastic-derived fuel
PM	Particulate Matter
PP	Polypropylene
RDF	Refuse-derived fuel
RMA	Rubber Manufacturers Association
RRFB	Resource Recovery Fund Board
SHW	Solid hazardous waste
SRF	Solid recovered fuel
TCLP	Toxicity Characteristic Leaching Procedure
TDA	Tire-derived aggregate
TDF	Tire-derived fuel
TGA	Thermogravimetric analysis
TSP	Total Suspended Particles
TTI	Time to ignition

LIST OF ABBREVIATIONS AND SYMBOLS

VM	Volatile matter
VOC	Volatile organic compound
WARS	Waste asphalt roofing shingles
WDF	Waste-derived fuel
WMR	Wire mesh reactor

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CHAPTER 1. INTRODUCTION

Population growth and the expansion of access to urban living has, over the years, led to waste management issues which are environmentally challenging and expensive for municipalities to handle effectively. As a result, the '4R' approach (Reuse, Reduce, Recycle and Recover) as a way of reducing the impact of waste has been widely accepted and is being used as a tool in optimizing waste disposal. The fourth 'R'(Recovery), a recent addition, represents recovery of energy from waste materials from diverse sources destined for landfills. For example, the roofing industry in Canada alone generates an estimated one and half million tonnes of asphalt-related roofing waste [1]. Similar reports on the quantity of unrecyclable waste headed to landfills from household and industrial sources are readily available for Europe, North America and parts of Asia, which have rigorous waste sorting, and modernised disposal systems. Though heterogeneous in energy density, physical properties and size distribution, unrecyclable waste could be recovered as valuable fuels for the production of energy. Therefore, energy recovery as a waste management practice has become an important component of discussions on sustainable development. These fuels are commonly referred to as waste or refuse-derived fuels (W/RDF). Some proponents of this category of alternative fuels are reluctant to use the term 'waste' in describing these fuels because it seems to connote a loss of usefulness which distorts public perception and unfairly affects their acceptability. Labels such as Process Engineered Fuel (PEF) and Solid Recovered Fuel (SRF) have been used. More recently Alternative Low Carbon Fuels (ALCF) has been used by Ontario regulation 79/15 under the Canadian Environmental Protection Agency Act to define a fuel that has a carbon dioxide emission intensity that is less than the emission intensity of the coal or coke in the place of which the fuel is combusted per equivalent energy [2].

The description WDF is however maintained for the purposes of this work to encompass a broad spectrum of potential fuels.

Another consequence of the current trends of population growth is the increased demand for energy. Demand for materials for infrastructural expansion such as cement, which are made from energy-intensive processes, have also risen. Cement manufacturers are in continuous search for cheaper ways to increase production, these efforts have been directed primarily at energy, and raw material cost reduction. The energy requirement for the production of clinker in dry rotary cement kilns is approximately 3–4 MJ/kg of clinker [3]. Over the years, the cement industry has relied heavily on coal and petroleum coke, which apart from meeting the high-energy demand, are pulverisable at ambient temperature and produce ash, which may contribute positively to cement properties. In the first place, steep dependence on coal has resulted in increased uncertainty in the cost of production due to fluctuating coal prices. In addition to this uncertainty, the classification of coal as a non-renewable fossil fuel also negatively affects sustainability ratings of the cement production process, which is already considered to have a large carbon footprint [3]. The cement industry has sought to reduce cost and the carbon footprint by displacing coal with different kinds of alternative fuel in cement kilns. Alternative fuels derived from waste generally have a lower carbon dioxide emission intensity than conventional fuels. Co-processing waste as alternative fuel in cement kilns therefore presents a two-pronged solution to cost and environmental concerns for sustainable production of an essential commodity. Co-processing refers to the practice where waste materials are used in a cement kiln as a means to simultaneously recover energy and recycle resources.

1.1 GLOBAL STATE OF CO-PROCESSING IN CEMENT KILNS.

The rotary kiln cement manufacturing process involves high temperature, an alkaline environment, an oxidizing atmosphere, the absence of residual waste (since all metallic and non-metallic incineration products undergo a complete absorption by the clinker), a large heat-exchange surface, good mixing of gases and cement kiln products and sufficient residence time. These kiln parameters create favourable conditions for the use of waste, or even hazardous materials as co-fired fuel [4]. In many cases, since alternative fuels are co-fired or co-processed with coal in cement kilns, the effect of the alternative fuel on the performance of coal has been of interest in recent literature. The combustion of alternative fuels in cement kilns offers an alternative method of waste utilization, which is environmentally sustainable and profitable to the cement industry and society. Many years of experience have shown that such use of waste is both ecologically and economically justifiable [4]. In Australia, for example, alternative fuels are estimated to have reduced the cement industry's dependency on coal by over 800,000 tonnes since 1999 [5]. According to a 2002 report from CEMBUREAU, the European Cement Association, the greatest usage of alternative fuels in European countries are in Holland (72%), Switzerland (34%), Germany (30%), and Belgium (30%), and solid alternative fuels have the biggest share of the alternative fuels used in the cement kilns [5]. CEMBUREAU further reports that in 2011, the average fossil fuel replacement rate among EU member states was 34.3% and some individual cement plants report obtaining 100% of their fuel requirement from alternative fuels. The equivalent of 6.6 million tonnes of coal is displaced each year and the mining requirements for other non-renewable resources such as crude oil and natural gas are also reduced [5]. CEMEX, a cement manufacturer, re-

ports that certain European plants have successfully reached 70% equivalent-energy substitution rates. Cement manufacturers in so-called developing countries have also assessed and applied alternative fuels in their rotary kilns to various degrees. For example, a 2005 feasibility study, conducted in line with Promotion of Renewable Energy, Energy Efficiency and Greenhouse gas Abatement in the Philippines [6], successfully maximized utilization of agricultural wastes in cement kilns. In Canada, the cement industry is concentrated in Ontario and Quebec with 10 of 17 plants operating in these two provinces. British Columbia and Alberta have 3 and 2 plants, respectively. Single plants operate in Nova Scotia and Newfoundland [3]. The thermal energy substitution rate for cement kilns with alternative fuels in Canada is shown to have reached 11.3%, and there was a 3.3% fully carbon-neutral biomass rate in 2008 [7]. The thermal energy source distribution across Canadian cement kilns by year 2008 is shown in Figure 1. Waste-derived fuels accounted for 8% of thermal energy input. Heavy fuel oil and natural gas which constituted 3.6% of the thermal input are usually combusted in a nozzle separate from the solid fuel mix within the kiln chamber. On a global scale, Nielsen [8] indicated that the share of alternative fuels in the total energy input on cement plants producing about 20% of world cement, ranged between 0.7 to 22%. Table 1 shows the thermal energy share for alternative fuels in cement plants owned by the major cement production companies producing a combined 20% of the world's cement, as reported by ICR from Nielsen [8]. Operators of cement kilns that make use of alternative fuels have, over time, developed criteria for the suitability of such fuels for their kilns. This is discussed in later chapters of this work. In general terms however, the use of waste and low-grade fuels as alternatives in cement kilns leads to reductions in the overall cost of production. This reduction is largely a result of the comparatively lower cost of waste-derived alternatives to equivalent heat amounts of coal.

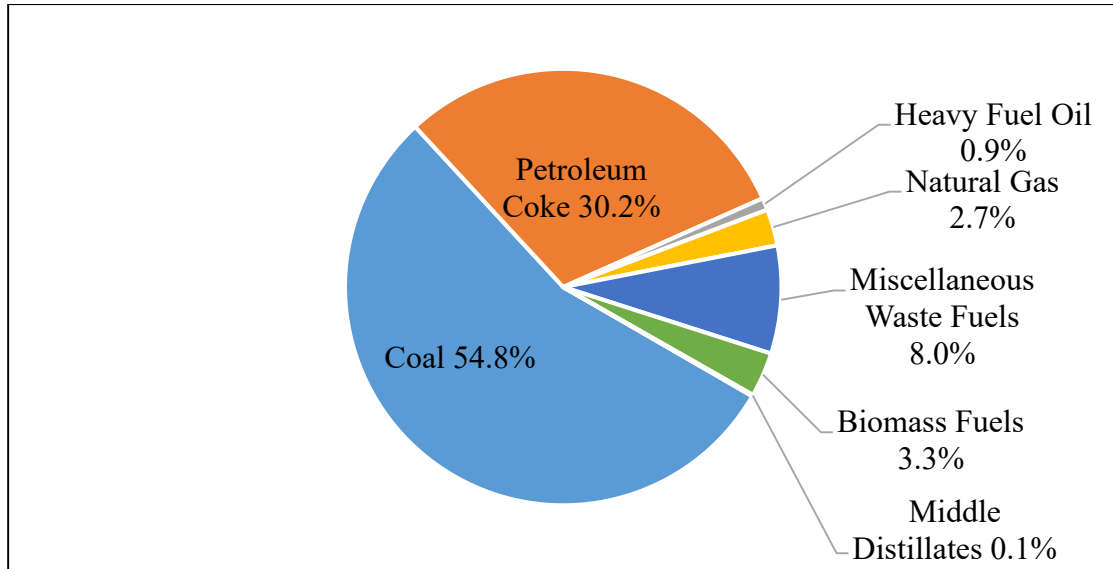


Figure 1. Thermal energy inputs for the cement production in Canada by fuel type for 2008 [7].

Additional costs may arise in the application of the alternative fuels, from secondary processing and kiln delivery system modifications. However, the savings as a result of fuel cost are usually more significant. There are also a number of environmental benefits to the use of alternative fuels in cement kilns. First, the re-direction of the waste from waste incinerators or landfills presents a sustainable solution to the disposal of unrecyclable waste streams. In addition, the coal replaced by alternative fuels represents a reduction in the consumption of a non-renewable resource. Depending on an alternative fuel's chemical composition and energy content, blending it with coal could also lead to the reduction in emissions of CO₂, NO_x and SO₂, and impact positively on the combustion efficiency. Nevertheless, the diversion of waste as an alternative fuel in cement kilns is confronted with a number of technical challenges and knowledge gaps, some of which this research attempts to address.

Table 1. Alternative fuel use by leading cement manufacturers supplying 20% of the demand across the globe reported within the last decade [6]

Cement producer	% Thermal energy share covered by alternative fuels	Global share of cement production in % (million tonnes)
Lafarge	12	4.5 (136)
Holcim	12	4.4 (132)
CEMEX	20	3.2 (96)
Heidelberg Cement	22	2.6 (78)
Taiheiyo Cement	12	1.4 (43)
Grasim	0.8	1.1 (33)
SCG	14	1.0 (32)
ACC	0.72	0.7 (21)
Siam City Cement	5	0.5 (15)
CRH	14	0.4 (13)
Cementir	6	0.3 (10)

1.2 RESEARCH DEMAND FOR A HIERARCHY OF CHALLENGES

Some of the factors that inhibit the use of alternative fuels in cement kilns and have created subjects requiring further research are summarized as follows.

1. Technical modifications for fuel handling.

For a cement kiln to successfully adapt to alternative fuels, it must have the capacity to handle the incoming fuel stream safely and efficiently. The kiln, burner and fuel delivery system may have to be modified to handle the physical properties of the alternative fuel. This modification could introduce additional capital and personnel cost. Conducting these modifications with minimal economic loss is an area of concern being looked at by researchers.

2. Fuel performance and emissions testing.

A big challenge to the co-processing of alternative fuels in cement kilns is the need to ensure that fuels are used to their optimum potential without increasing harmful emissions. Given the heterogeneity of available alternative fuels, there is a demand for continuous performance

testing to first justify the choice of an alternative fuel to the permit-issuing regulatory bodies, and second, to reliably predict the effect of fuel blending with traditional fuels on cement kiln parameters (temperature, gas flowrates and oxygen consumption), cement quality and stack emissions. This knowledge will enable operators to design optimum fuel blends for different loads of alternative fuel.

3. Competing waste management interests.

Introducing energy recovery as a waste management practice may, according to one school of thought, induce the creation of waste for the purposes of profit. This poses a threat to public acceptance. A much larger challenge is the public perception that industrial innovation in the re-use and recycling of presently challenging waste materials will be stalled by the potential demand for these materials as alternative fuels for energy recovery processes. Even though evaluations of the quantitative, economic and risk assessment of various waste management options continue to be in the favour of co-processing, energy recovery is yet to be fully accepted as a viable waste disposal strategy within some environmental circles. Life cycle analysis of waste diversion into cement kilns as opposed to incineration or landfilling is therefore of continuous interest, as different potential WDF emerge.

4. Gaps in knowledge due to variations in local content.

One would expect that the development of a universally applicable model of waste to fuel diversion would be the ultimate driver for an increased use of alternative fuel of all kinds in cement kilns. Interestingly, however, as observed from the literature, strategies focusing on locally available alternatives have proven to be much more beneficial to the expansion of the use of alternative fuels than generic approaches.

As a result of this, gaps exist on a local scale for new alternative fuels regarding combustion characteristics, delivery system design and potential changes in emissions. In one case, progress made overcoming the challenge of design, for example, may deliver critical information for the use of a given fuel, but in a slightly different scenario of waste management and financial limitations, the identified fuel may require significant modifications to become fully applicable. To drive the overall increase of alternative fuels in cement kilns, there is a need for continued research into the handling and combustion behaviour of newly identified families of potential fuels within the local context of regulations and waste management policy targets.

In light of the background and clearly identified need for research on local WDF, the hypothesis of the current work is that proper co-processing of locally available WDF in a cement kiln will not only result in reduced environmental and human health impacts, but will also lead to macro-scale waste diversion. In addition, it is anticipated that using bench-scale experiments, the combustion behaviour on a micro level can also be studied as a comparative and predictive tool for full-scale application.

1.3 OBJECTIVES

This research focused on three main objectives:

1. To test and apply on a full-scale, case-study basis, fuel handling strategies that result in the direct increase of alternative WDF in a local cement kiln without adversely affecting kiln performance.

2. To develop and apply a simple and practical screening protocol for WDF for co-processing in cement kilns using modified bench-scale emissions tests to comparatively determine expected changes from the combustion of selected WDF and conventional fuels.
3. To expand the body of knowledge on the co-combustion of solid fuels by using bench-scale characterization techniques to study the effect of blending with local WDF on the combustion characteristics of coal and coke.

1.4 METHODS

The potential for co-processing of selected WDF, namely plastic-derived fuel (PDF), waste asphalt roofing shingles (WARS) and tire-derived fuel (TDF) in Nova Scotia, was reviewed to assess specific challenges and opportunities. A preliminary discussion of the potential changes in gaseous emissions expected from the co-processing of these WDF based on ultimate analysis and theoretical calculation was then conducted. This quantified and compared the emission intensity of the selected WDF to that of the displaced fuel.

An attempt was also made in this work to simplify performance testing by using emissions detection devices attached to a bench-scale tube furnace to determine the chemical composition and particle distribution of combustion products generated from selected WDF. This setup was designed and used in combustion experiments on a selection of plastic-based waste to be used as PDF. The trends in the emissions detected on bench-scale were compared with published full-scale trends for similarities, and to validate predictions.

Plastic-derived fuels from different plastic sources were studied using the relatively simple set-up that has been proposed by this study as a preliminary evaluation tool for kiln operators and policy makers on waste with combustion potential.

A heated grid reactor (HGR) with a computer controlled feedback system capable of reaching heating rates of 10^3 K/s was designed and built in-house, and was used in combustion experiments on PDF, WARS and blends with coal and coke. The HGR was used in conjunction with a thermogravimetric analyzer, a particulate matter detection device and a high-speed camera to investigate micro-scale effects of fuel blending on the combustion of coal and coke. A comparison of these observed characteristics was used to determine the potential impact of co-processing PDF and WARS on combustion efficiency and by extension, fuel delivery and kiln performance.

In reaching the objective to increase the use of WDF, the challenge of improving the delivery of WARS into a cement kiln was studied. Field trials were used to select optimum kiln delivery approaches to overcome practical operational challenges in the cement kiln. Lessons learnt from the testing and selection of appropriate fuel handling and delivery methods for WARS were used to evaluate waste-to-fuel scenarios which translate into an increased diversion of waste from landfills. The observations made on the impact of WARS characteristics on fuel delivery and kiln performance were used to discuss the potential impact of other WDF characterized on bench-scale, in the absence of full-scale trials.

These experiments, aside from fulfilling the desired objectives, also hold the ultimate goal of developing a framework of repeatable methods to improve the screening of WDF for co-processing. This would be potentially used by policy makers and regulators, researchers, the cement industry and resource and waste managers.

1.5 STRUCTURE OF THESIS

Chapter 2 contains a literature review on co-processing fuels in different cement kilns. Technical considerations suggested by other workers and regulatory bodies on the subject of co-combustion generally, and co-processing of WDF in cement kilns specifically, are summarized. The chapter also reviews the lessons acquired from experiences of practical applications of various WDF. In addition, expectations in cement production, fuel handling, emissions and clinker quality with the use of alternative fuels are also presented.

Chapter 3 reviews the literature on fuel characterization and the techniques used in various studies that are applicable to the objectives of the present work. Mathematical and experimental approaches to obtain information on kinetic behaviour, particle ignition and char combustion using thermal analytic apparatus are highlighted in the chapter. Limitations and inadequacies of the techniques of characterization are discussed and the foundation for their use in the experimental work is thus laid.

Chapter 4 contains results and discussion of the experimental work conducted for this research. It begins with expected, combustion-related emission changes based on theoretical calculations conducted on potential WDF available in Nova Scotia. Preliminary arguments in favour of the use PDF, WARS and TDF in the local cement kiln are presented together with the present status, opportunities and challenges facing the co-processing of these WDF. The materials, apparatus and experimental work used in this research on coal-coke and WDF are then described. The chapter will show results and discussions obtained from the following experimental work:

1. Laboratory-scale, emissions experiments conducted to comparatively study and select suitable PDF to be used in co-processing applications in a cement kiln.

2. Heated grid reactor and thermogravimetric bench-scale experiments showing co-combustion behaviour of fuel blends with coal-coke.
3. Field-scale trials conducted to determine optimum fuel delivery methods for WARS as guide for other WDF's.

Chapter 5 concludes the findings of the thesis and suggests aspects for future studies on the subject matter.

CHAPTER 2. CONSIDERATIONS IN CO-PROCESSING WASTE

The chapter discusses considerations developed over years of experience using WDF in cement kilns. It discusses in detail, a selection of works which describe the classes of alternative fuels and the impact of waste to alternative fuels applications on: (1) The cement manufacturing process and the product, (2) Emissions, environment and health, (3) Waste management.

2.1 CEMENT PRODUCTION

The work of Murray and Price [9] and Bhad [10] provide a detailed description and chemistry of the cement production process. In summary, cement is manufactured through a chemical combination of calcium (Ca), silicon (Si), aluminum (Al), and iron (Fe), which is then mixed with additives such as gypsum. Clinker, the major component of cement, is a pyro-processed product made in a kiln that operates a countercurrent flow system as seen in Figure 2.

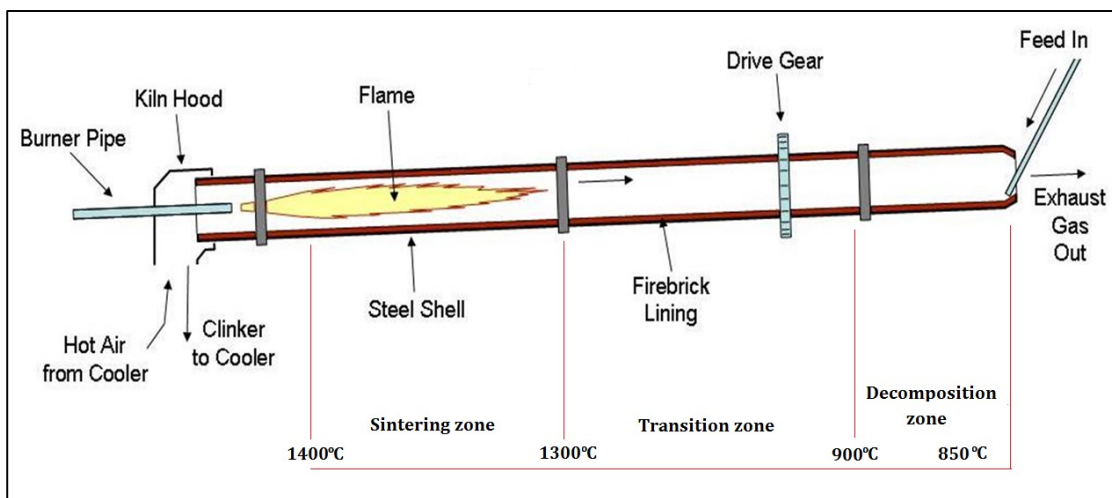


Figure 2. A view of the cement kiln depicting various temperature zones, and showing countercurrent flow of flue gas and feed after Bhad [10].

A mixture of limestone, clay and other raw materials bearing the elements mentioned earlier, flows down the kiln and hot gases flow up the kiln. Clinker production typically occurs in kilns heated to about 1450 °C. The estimated energy required for cement manufacture in different types of kilns is shown in Table 2. In rotary kilns, raw materials are introduced into the slightly elevated end of large rotating drums inclined downward towards an exit which holds a burner. Fuel is fed through the burner and combusted to supply heat by direct radiation and by convection via hot flue gases flowing by induced draft through the rotary kiln. The flue gases are passed through emissions control devices before exiting the kiln through the stack.

Table 2. The average fuel requirement for the production of clinker in the US based on size and type of process at cement plant [9].

Kiln type	Clinker production (GJ/tonne)
small wet plants (< 0.5 Mt/year)	6.51
large wet plants	5.94
small dry plants (< 0.5 Mt/year)	5.13
large dry plants	4.35
dry plants, no preheater	5.40
dry plants, preheater only	4.29
dry plants, precalciner	4.03

2.1.1 The kiln

The rotary cement kiln is long and cylindrical with an outer steel shell. To withstand high temperatures, the inner cylindrical surface includes a contiguous insulating refractory lining comprised of hollow bricks, and a refractory lining concentric with and over the insulating lining [11]. It is typically between 40–100 m in length and approximately 3–6 m in diameter. Cement kilns rotate at 1–5 rpm and are tilted up to 5° to enable the steady movement of the hot material bed.

In the design of a cement kiln the dimensions are directly related to the volumetric output expected [8]. Nielsen [8] discussed the benefits of different arrangements of preheaters and

precalciners to the efficient use of energy in cement plants. Temperatures in the kiln system range from ambient temperatures up to 2000 °C, and oxygen levels range from 2 vol.% –21 vol.% depending on the position in the kiln system. Solid and gas retention times vary in the different sections of the kiln system. In the rotary kiln, gas retention times may be in the order of 5–10 seconds, while solid retention times may be as long as 15–30 minutes [8]. In recent years, dry process kilns have been made more energy efficient by equipping them with grate and suspension preheaters where the kiln raw materials are heated with the exhaust gases before entry to the kiln. Some plants also have specially made precalciners where calcination of the raw materials takes place after preheating and before kiln entry. In the absence of preheaters, and precalciners, all heat dependent stages of the clinker production process occur along the entire length of the rotary kiln. The components of the feed such as calcium oxide, alumina, ferric oxide, silica, and other metal oxides interact with each other and finally form the four main components of the cement clinker: $3\text{CaO}\cdot\text{SiO}_2$ (C_3S), $2\text{CaO}\cdot\text{SiO}_2$ (C_2S), $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ (C_3A), and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ (C_4AF). The formation temperatures of these clinker components are different. According to the temperature requirement of different components formed, the dry process rotary kiln can be divided into four zones, namely the decomposition zone, the transition zone (temperature increasing and exothermic reaction zone), the sintering zone, and the cooling zone. The thermal effects for the different exothermic and endothermic reactions taking place in the different zones are presented in Table 3 after Bhad [10].

Table 3. The stages of chemical transformation in a cement kiln with associated temperatures and heat of reaction after Bhad [10].

Reaction Zone	Reaction	Reaction Temperature (°C)	Heat of Reaction (ΔH)
Decomposition	CaCO ₃ decomposition	900	+1660 kJ/kg of CaCO ₃
Transition	C ₂ S formation	900-1300	-603 kJ/kg of C ₂ S
Transition	C ₄ AF formation	900-1300	-109 kJ/kg of C ₄ AF
Transition	C ₃ A formation	900-1300	-37 kJ/kg of C ₃ A
Sintering Zone	C ₃ S formation	1300-1400	-448 kJ/kg of C ₃ S

2.1.2 The burner

The chemical and physical transformations of the raw materials are driven by the heat from the combustion of fuel injected into the kiln with accompanying axial and swirl air through a burner. Burners are designed to deliver short, narrow and highly radiative flames of a turbulent diffusive nature. In pulverized coal burners, a channel exists for the delivery of pulverized coal with channels for primary air injection. Modern cement kilns, where a variety of fuels could be used, rely on multi-channel burners which are designed to suit the size and nature of the new fuel. Generally, the selection of a fuel to be used in a cement kiln is largely constrained by burner channel design which is identified as a major challenge to the use of alternative fuels [8].

2.1.3 The kiln stack and emission controls

There are three main sources of potential emissions from cement production plants: kiln systems, clinker coolers and cement mills. The cement kiln stack conveys the exhaust gases generated in the cement kiln. The dispersion factor for a kiln is the ratio between the stack emission concentration and the maximum annual mean ground level concentration. This is influenced by stack height, exhaust gas temperature and flowrate, atmospheric conditions and topography around the plant [12].

Various control devices have been used in the past to control emissions from these sources and to keep them within regulatory limits. For the mitigation of dust emissions, bag filter houses and Electrostatic Precipitators (ESP) are usually installed. The bag filters separate the dust particles from the exhaust gas. As the exhaust gas passes through the bag tissue the dust particles are captured on the bag surface by impaction as the air flow moves around the filter fibre. Electrostatic Precipitators use electrostatic force to separate the dust from the gas. Discharge electrodes under high negative voltages (50–100 kV) emit electrons which settle on the dust particles. The now negatively charged particles are directed towards and separated on the collecting electrodes because of the electrical field between the discharge and the collecting electrodes. The dust particles accumulated on the collecting electrodes are discharged to the dust hoppers by electrode rapping. Other abatement techniques such as cyclones are employed for emissions at the clinker cooler, but are not effective in removing dusts from the exhaust gases prior to exiting the stack [12].

The release of NO_x , SO_2 and VOC depends on the nature of the raw materials and the production process; hence, it could be reduced with process, material and fuel modifications. However, secondary or post-combustion gas removal systems, including Circulating Fluidized Bed Absorbers (CFBA) or dry scrubbers, wet scrubbers and activated coke, have been used to remove SO_2 and VOC's from exhaust gases before they exit the kiln stack [12]. Post-combustion techniques can be costly and so many operators first resort to modifying fuel combustion and raw material selection to reduce gaseous emissions from the stack at the source.

2.2 CLASSIFICATION OF FUELS FOR CEMENT KILNS

2.2.1 Coal and petroleum coke

Coal is a complex polymer made up of carbon, hydrogen, oxygen, nitrogen and sulphur. It is a compact, aged form of biomass containing volatile matter, moisture and mineral matter. The chemical properties of coal depend upon the relative proportions of the chemical constituents present at deposition, the nature and extent of changes over time, and the presence of inorganic matter. Coal rank indicates the relative proportions of volatile matter (VM) and fixed carbon (FC) present in the coal. Coal rank increases with decreasing VM. Typically, a medium rank coal consists of 40% VM and 60% FC, while a high-rank coal has about 10% VM [13]. Petroleum coke is a high carbon content (90–95%), low hydrogen content, black solid residue obtained from the thermal decomposition and carbonisation of petroleum-derived feedstock. It is a product of additional processing of the crude residue collected after refining crude oil. Coal and petroleum coke are the conventional solid fuels used in cement kiln burners for pulverized fuel combustion.

2.2.2 Alternative fuels

Most alternative fuels for cement kilns are received as solids, liquids or gases. Liquid alternative fuels include tar, liquid chemical wastes, distillation residues, waste solvents, used oils, wax suspensions, petrochemical waste, asphalt slurry, paint waste and oil sludge [13]. Solid alternatives include paper waste, rubber residues, pulp sludge, used tires, battery cases, plastic residues, wood waste, domestic refuse, rice chaff, nut shells, oil-bearing soils and sewage sludge.

Landfill gas (mix of N_2 , CH_4 and CO_2) and pyrolysis gas (mix of C_xH_y , N_2 , H_2 , CO , CO_2 and H_2O) are examples of gaseous alternative fuels [14, 15]. Other classifications can be made based on physical properties of the fuel as received.

CEMBUREAU classifies alternative fuels based on the size of a representative particle of the sample, beginning from gaseous alternative fuels (Class 1) to lump-size solid alternative fuels such as whole tires and plastic pails (Class 5). Class 2 represents liquid alternative fuels and classes 3 and 4 represent solid fuels with pulverized particles and coarse particles respectively. This classification is similar to that given for RDF in the review conducted by Lockwood and Ou [16]. They grouped RDF into coarse: 95 % < 150 mm, fluff: 95 % < 50 mm, powdered: 95% < 1.7 mm, densified (compressed into pellets, briquettes, or a similar form) and pulp. Derived fuel refers to mechanically or chemically processed derivatives of biomass, refuse or waste. Due to the prohibitive costs of secondary processing, most cement kiln-bound, derived fuels are materials that have just been sorted or minimally processed for direct combustion. Murray and Price [9] and CEMEX [17] have categorized WDF based on their sources and chemical composition: agricultural biomass, non-agricultural biomass, industrial waste and hazardous chemical waste. Table 4 shows examples under each of the categories available from the literature [9]. Classification by source and classification by physical properties are the most widely used in the literature.

2.3 CO-PROCESSING IN CEMENT KILNS

A review of the literature points to a basic rule of thumb summarized in the statement that the fuel used in cement manufacturing should add value to the process, while meeting applicable regulations and permit requirements.

Table 4. Categorization and examples of waste-derived fuel based on sources and composition after Murray and Price [9].

Agricultural biomass	Non-agricultural biomass	Industrial	Chemical and hazardous waste
Rice hulls	Sewage sludge	Waste oils- bunker oil	Spent solvents
Bagasse	Saw dust	Crude glycerol	Electronic
Coconut residue	Paper	Rubber tires	scraps
Wood chips	Waste wood	Packaging material (Plastics and paper)	Pesticides
Animal waste and bone meal		Construction and Demolition waste	Paint residue

The criterion agrees with those of the United Nations Environment Programme (UNEP). Specific considerations for fuel blending with coal for economic, environmental and chemical benefits have been discussed to a large extent in the literature [18-20]. The parameters mostly affected, and which need to be managed during fuel blending for co-firing, include (1) moisture, (2) calorific value, (3) volatility and reactivity, (4) pollution potential, (5) slagging and fouling, and (6) corrosion. The potential for alternative fuels can therefore be measured by the tendency of their energy and volatile content to affect the reactivity of a fuel blend, and to reduce the formation of harmful emission products [20-22]. There appears to be an agreement in literature that whether or not a cement kiln uses a given alternative fuel successfully depends on the plant's access to, and ability to handle the particular fuel stream efficiently. After years of alternative fuel use, the German technical cooperation agency (GTZ) presented broad considerations in the use of waste as alternative fuel for cement kilns in the principles shown in Table 5.

Table 5. Summarized principles governing the use of alternative fuels in cement production by GTZ [4].

Principle	Description
The waste management hierarchy should be respected	<ul style="list-style-type: none"> • Waste should be co-processed in cement kilns where more environmentally and economically robust methods of recovery are not available • Co-processing should be considered an integrated part of waste management • Co-processing should be in line with the Basel and Stockholm Conventions and other relevant international environmental agreements
Additional emissions and negative impacts on human health must be avoided	<ul style="list-style-type: none"> • Negative effects of pollution on the environment and human health must be prevented or kept at a minimum • Air emissions from cement kilns co-processing waste cannot be statistically higher than those not involved in co-processing waste
The quality of the cement must remain unchanged	<ul style="list-style-type: none"> • The product (clinker, cement, concrete) must not be used as a sink for heavy metals • The product must not have any negative impacts on the environment (for example, as determined by leaching tests) • The quality of the product must allow for end-of-life recovery
Companies that co-process must be qualified	<ul style="list-style-type: none"> • Assure compliance with all laws and regulations • Have good environmental and safety compliance records • Have personnel, processes, and systems in place committed to protecting the environment, health, and safety • Be capable of controlling inputs to the production process • Maintain good relations with public and other parties involved in local, national and international waste management schemes
Implementation of co-processing must consider national circumstances	<ul style="list-style-type: none"> • Country-specific requirements and needs must be reflected in regulations and procedures • Implementation must allow for the build-up of the required capacity and the set-up of institutional arrangements • Introduction of co-processing must be in line with other change processes in the waste management structure of a country

For sustainable use of a given material as a waste-derived alternative fuel in a cement kiln, it must first be satisfactorily proven, based on cost, hazards and the prevailing need and standards of a jurisdiction, to be more beneficial as a WDF than as a reusable product. Furthermore, it must also be shown that its potential effect on the optimal operation of the cement kiln, the cement quality and cement stack emissions is within acceptable limits.

2.3.1 Effect of co-processing on clinker and product quality

Solid alternative fuels contain ash in such amount that they can affect the mineralogical composition of clinker and so the cement quality [23]. High levels of alkalis such as (K_2O and Na_2O) in cement can, in the presence of moisture, give rise to reactions with certain types of aggregates to produce a gel which expands, leading to cracking in concretes and mortars [24]. The characteristics of certain alternative fuels may also introduce changes in process parameters of the kiln, resulting in changes in clinker composition. It must be noted that all equipment, especially the induced draft fan that handles the extraction of combustion gases, has an optimized ability and capacity. For example, Lockwood and Ou [16] studied W/RDF with low calorific value and high volatile content and found that it will produce more flue gases than the conventional fuels for the same heat input. In this case it will reduce the thermal efficiency and negatively affect the formation of clinker. To maintain clinker quality, production capacity may have to be reduced to counter the thermal inefficiency. In fact, according to Ariyaratne, et al. [25], in order to maintain the kiln exhaust gas temperature and hence keep the clinker quality unchanged when replacing around 45% of the primary coal energy, production capacity may have to be reduced by 1.2% to 14.7%. The waste materials used were (1) solid hazardous waste (SHW), (2) RDF, (3) waste wood and (4) liquid hazardous waste (LHW).

These changes were attributed to the change in flue gas flowrates with changes in the fuel ultimate analysis. This thesis discusses their observations further, and uses them in the experimental section in a bid to correlate ultimate analysis and bench-scale results to full-scale kiln parameters.

The proportion of heavy metals in the fuel is also of great importance to the quality of the clinker. The heavy metal content of produced clinker is thought to be proportional to the heavy metal content of the fuel fired. Lockwood and Ou [16], however, observe from trials that even when firing 50% RDF which contained more heavy metals than coal, no difference was detected in the chemical and physical properties of the clinker produced. The results were the same for the cement and concrete. There are claims that since some of the metals contained in the wastes combusted in cement kilns become part of the cement or concrete product there may be instances of leaching which poses an environmental and health hazard. In light of these claims, the Portland Cement Association (PCA) carried out extensive leaching tests and found no significant leaching of toxic elements from clinker using waste as supplementary fuel in cement kilns. Even in cases where the aggressive Toxicity Characteristic Leaching Procedure (TCLP) described by Hillier, et al. [26] was applied, concentrations of metals in mortar cubes from kilns burning hazardous waste as fuel were not significantly different from kilns using conventional fuels [27].

2.3.2 Effect of co-processing on emissions, and the health impact

Carbon dioxide (CO₂) is the major oxide produced from the combustion of most fuels. Carbon monoxide is formed in the case of incomplete combustion as an intermediate product, and converted to CO₂ in the presence of oxygen. Potentially harmful acid gases, particulate matter

and VOC are also associated with the combustion of fuels in cement kilns. A substantial amount of these emissions are due to the organic content of raw materials introduced into the kiln. Emissions expected as a result of fuel combustion are addressed in this section.

2.3.2.1 Emission of sulphur dioxide

Sulphur dioxide (SO_2) is generated from the combustion of fuels containing sulphur. Its formation and abundance are 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 utility providers and the U.S Department of Energy have also considered the co-firing of biomass with coal in boilers for the same purpose [22]. There is a direct link between sulphur content in fuel and SO_2 emissions. Primary reduction resulting from changes in the content of sulphur in the fuel may not translate to an overall reduction in process emissions because raw materials for clinker production bear significant amounts of organic sulphur that contributes to the total SO_2 emitted. SO_2 can be removed, post-combustion, from the exhaust going through the kiln stack, by the use of scrubbers and adsorbents as discussed in section 2.1.3.

2.3.2.2 Emission of oxides of nitrogen

Formation of oxides of nitrogen (NO_x) increases exponentially with increasing temperature and excess air because air contains N_2 and O_2 , which react to form thermal NO_x . 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 N_2 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 the

reference case. The nitrogen content in fuels is generally low; therefore, fuel derived NO_x for cement kilns forms a small fraction of total NO_x expected after combustion in excess air (79% N₂). Many techniques outside fuel substitution exist to reduce NO_x formation and emission [12] but these are outside the scope of the thesis.

Calculations using Eq. (1) which is based on a simple stoichiometric mass balance of oxidation reactions, estimate the expected mass of a gaseous product from combustion. The expected mass in kilograms (m_e) of gaseous oxide (xO) with molecular mass (MM_{xO}) produced from the oxidation of x with molecular mass (MM_x) where $x = (N, C, S \text{ or } H)$, is given by:

$$m_e = \left[\frac{n \times Y_x \times MM_{xO}}{E_f \times MM_x} \right] \times E_t \quad (1)$$

Where n is the stoichiometric mole ratio of x to xO

E_t is the energy required for the process [kJ]

E_f is the energy content of the given fuel [kJ/kg]

Y_x is the percent composition of the x in the fuel on a dry basis from the ultimate analysis.

The EPA Ontario 79/15 refers to the term in square brackets as carbon dioxide intensity where xO is CO₂.

2.3.2.3 Emission of particulate matter

Particulate matter (PM) emissions are influenced by fuel composition and extent of combustion, especially PM with a median aerodynamic diameter $\leq 10 \mu\text{m}$ (PM₁₀) or $\leq 2.5 \mu\text{m}$ (PM_{2.5}) [28]. Recent field experimental campaigns by Rotatori, et al. [29] on four cement plants have gone further to measure changes in sub-micron PM when cement kilns use alternative fuels.

Total suspended particulates (TSP) which include all airborne PM ($\sim < 60 \mu\text{m}$) are a function of the percentage of ash or mineral matter in the fuel, coupled with the unburned carbon resulting from incomplete combustion and the firing method used [20]. In pulverized coal firing for example, fly ash typically composes 80% of the solid products of combustion but for cyclone firing it makes up 30% of the solid combustion products [20]. It is also expected that a higher volatile content will reduce unburned carbon in the products of combustion leading to reduced TSP. Gases such as SO_2 , NO_x , and VOC's can also transform in the atmosphere to form secondary fine PM and ground-level ozone (O_3) by a number of chemical reactions [20, 30-33]. Therefore, the combustion of alternative fuels with low sulphur and nitrogen content coupled with complete combustion of VOC's 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 cement kiln [30, 31, 34]. Wang, et al. [35], have also suggested that the presence of certain elements such as calcium in the mineral matter or ash may cause particles to coalesce, leading to changes in the PM size distributions.

2.3.2.4 Emission of volatile organic compounds

Volatile organic compounds as products of incomplete combustion have been discussed by Choi and Yi [36]. The extent of thermal degradation of produced VOC's, such as benzene, xylene and toluene, is largely dependent on the prevailing temperature and residence time. At temperatures above $1000 \text{ }^\circ\text{C}$, 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 removing harmful VOC's in emissions. Emissions of VOC's from the kiln stack are therefore more attributable to the release of the organic content of raw materials

before reaching the high temperature zone of the kiln than to incomplete combustion of the fuel [12]. The discussion on VOC's gives rise to considerations on polychlorinated dibenzodioxins (PCDD/dioxins) and polychlorinated dibenzofurans (PCDF/Furans). The general consensus is that the formation of these species depends on kinetic factors beyond the presence of certain elements in a fuel [37]. The distribution of the toxic fraction of the dioxin and furan species is fairly similar for different conditions [38]. The suggestion that dioxins and furans are better off being controlled by regulating the rate of formation and depletion of precursors and suppressors has been adopted in many combustion scenarios. Yazawa, et al. [39] discussed kinetic factors and thermodynamic trends, relying on available thermodynamic data, in the formation of PCDD/F's in a gaseous C-O-H-Cl system at 300 °C. They concluded that PCDD/F's decompose at high temperature, and at high oxygen (O/C >1) or low chlorine content. Interestingly, they also indicated that high content of hydrogen or water vapour and the deposition of carbon could suppress the formation of these toxic gases. In their study, increased concentrations of chlorine led to more PCDD/F's at low concentrations of chlorine but at higher concentrations, chlorine-carbon compounds were formed preferentially to PCDD/F's. The predominant species of chlorine in combustion gases is HCl, and its removal from the gas phase could enhance PCDD/F formation due to the loss of hydrogen. Fortunately, in usual practice, chlorine is removed preferentially to HCl, leaving the hydrogen which suppresses PCDD/F formation. Another reaction which could lead to the suppression of PCDD/F's by the removal of chlorine from the gas phase in a cement kiln is the interaction of HCl gas with calcium oxide solid [39]: $2HCl_{(g)} + CaO_{(s)} \rightarrow CaCl_{2(s)} + H_2O_{(g)}$. The role of HCl gas in supporting the formation of PCDD/Fs is supported by Duo and Leclerc [40],

who however, indicated 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/F formation and the effect of carbon monoxide (CO) could not be ascertained by thermodynamic analysis alone. Duo and Leclerc [40] also proposed a simplified stack emission model for boilers, which shows that stack dioxin emissions increases linearly with decreasing ESP efficiency and exponentially with increasing ESP temperature. The ESP efficiency of a cement kiln thus becomes of more significant concern regarding PCDD/F's. Other hazardous pollutants, such as volatile metallic oxides, trace metals and mercury, may also be sources of concern if they are present in the fuel blends being used [22].

2.3.2.5 Health and environmental impact of emissions

The effects of different gaseous emissions on the health of humans have been studied by various authors in very diverse work environments. The presence and impact of soluble transitional metal exposure has been investigated for welding fumes [41].

The literature shows that even very delicate cutting and shredding activities may contribute to changes in particulate matter emission and distribution [42]. Because of their size, PM_{2.5} have been known to remain attached to respiratory tissue, making organisms more prone to respiratory ill health. Under household operating conditions for example, changes in kitchen fuel were seen to affect potential exposure of people to certain VOC species [43]. Studies have shown an association between short and long-term exposure to SO₂, NO₂ and O₃ and increased morbidity, mortality, and hospital admissions for cardiovascular and pulmonary diseases. They are also associated with acid deposition and photochemical smog [44]. 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 the

efficiency of the available control. Keeping emissions within the regulated limits would ensure minimal adverse impact on downwind receptor populations and the environment in all cases. The products of the chemical changes in the cement kiln make up the most significant impact of cement production on the environment. At the rate of 200 kg of coal per tonne of cement, the process produces approximately 900–1000 kg of CO₂, a greenhouse gas (GHG). Approximately 50–60% of the CO₂ is related to calcination of CaCO₃, and the rest is as a result of fuel combustion [45, 46].

2.3.3 Effect of co-processing on firing design and process engineering

Need, regulatory demands and local targets have been the main drivers of the advancements in the use of alternative fuels in cement kilns. Years of experience have led to specific operator recommendations based on the chemistry of the fuel. In a study of Murray and Price [9], reference is made to accepted guidelines on process parameters such as optimum temperature and O₂ supply for a given category of WDF for co-processing, shown in Table 6. Other changes to the process because of alternative fuels have been implemented to cement kiln burner design and fuel handling over the years. Advancements in the efficiency of emissions control devices and the design of the cement kiln itself have seen much study and have been key in the current increase in alternative fuel use in cement kilns.

Finally, there has been progress in the development of chemically processed WDF. Pyrolysis and gasification processes have been used to produce energy dense alternative fuels which are easier to handle and more homogenous.

Table 6. Guidelines on operating conditions for hazardous waste used as fuel in cement kilns in USA and European Union [8].

Jurisdictional directive	Temperature (°C)	burning time (s)	Oxygen (%)
USA on Polychlorinated Biphenyls	1200	2	3
EU (Directive 2000/76/EU) non-chlorinated hazardous waste	850	2	-
EU (Directive 2000/76/EU) chlorinated hazardous waste (>1 %)	1100	2	2

2.4 REPORTED TRIALS IN CO-COMBUSTION OF WASTE-DERIVED FUEL

Liquid wastes such as crude glycerol from the production of bio-fuels have been studied and used in a local cement kiln by Pegg and Fels [47] who discussed the behaviour of crude glycerol under kiln-like temperature conditions and advanced a method of delivery into the cement kiln. Solid WDF's however, make up most of the alternative fuels being used in the cement and energy industries. Over the past two decades, the use of plastics, mixed fractions of municipal waste, biomass, sewage sludge, tires, meat and bone meal, animal fat, textile waste and scrap wood have been studied for use as a supplement or substitute to coal and other fossil fuels for blast furnace and power generation applications [15, 48]. The Portland Cement Association has compiled a bibliography of practical studies conducted in Europe and Asia on waste including plastics, waste oil and scrap tires as fuel for cement kilns [49].

Pipilikaki, et al. [50] studied the effect of TDF on clinker of with 6% of total fuel as TDF. The authors concluded that they noticed no apparent problems in the clinker in terms of strength. There was, however, the presence of zinc (Zn), which the authors assert as the main constraint limiting TDF to 30% by weight of the fuel mix in most cement kilns. Metals such as Zn and chromium (Cr) present in TDF chemically combine with the clinker, and present

no risk of leaching from the clinker, once it is produced. This occurrence is analogous to silica not leaching from glass after pyro-processing. Data published by the Rubber Manufacturing Association [51] on bottom and fly-ash from 100% TDF combustion showed that iron (Fe) was the main component of bottom ash (96%), whereas elements Zn, C, Si and Fe make up over 95% of the fly ash. Elements such as lead (Pb), arsenic (As) and cadmium (Cd) 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 [52] 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 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 the elements Cl, I, Zn and Pb in the fly ash collected by ESP's. However, for elements which were present in coal and TDF such as Pb and As, increases were allocated to coal. These trials highlight the effectiveness of the ESP for emission control. Carrasco, et al. [53] and a report by Conestoga-Rovers and Associates in 2007 show a broad variation in expected changes in gaseous emissions such as SO₂, NO_x and CO in their literature reviews on the effects of TDF on cement kiln emissions. Both groups attributed the variation in results to the fact that SO₂ 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 on the combustion efficiency, which is also important in CO formation. Carrasco, et al. [53] reported slight increases in PM, SO₂ and CO, and a decrease in NO_x after collecting data from cement kilns using TDF as a constituent fuel in Quebec, Canada. In terms of metal emissions, the highest increases were seen in Zn and Fe, which are both components of tires. Pb, Cr, Al and Mn also saw some increase though at very low

concentrations. Emissions of organic compounds including PCDD and PCDF decreased with the use of scrap tires whereas the presence of higher amounts of chlorine in tires than in coal resulted in an increase in HCl emissions. Increased HCl emissions may however increase the risk of acid rain formation. Carrasco, et al. [53] concluded in their studies that even though there were variations in gaseous emissions while using tires as a source of fuel, these variations remained within the emission regulatory limits.

In a study by Rovira, et al. [54], on a cement plant in Catalonia, Spain, petroleum coke was replaced by up to 20% with RDF from Municipal Solid Waste (MSW). The RDF mixture consisted of (1) plastics (35%), (2) paper and cartons (30%), (3) wood (20%), and (4) textiles (15%). Environmental monitoring was conducted to investigate the effects of the different fuels on emissions. While no significant increases were encountered in PM₁₀ emissions and gaseous pollutants, there was a significant decrease in metals and polychlorinated PCDD/Fs present in soil, herbage, and PM samples collected around the facility. Jeschar, et al. [21], in obtaining information on combustion behaviour, compared various plastics in preliminary tests to a bituminous coal as fuel in a calciner of a cement kiln. Jeschar, et al. [21] reported that a method of targeted staging of air and raw materials, and the use of plastic materials could lead to a reduction in NO_x emissions. Their work showed that the limitations of size and the challenge of replicating actual kiln conditions might sometimes lead to emissions results that do not conform to theoretical expectations. These deviations could be explained in similar fashion as the variations observed in the previously discussed work of Carrasco, et al. [53]. Apart from difficulties in simulating actual kiln temperature and oxygen profiles on a bench-scale, emissions under full-scale conditions could also deviate from expectations because more emissions sources, including raw materials, are present in actual kiln tests than are replicable on smaller scales. To be confident about actual kiln predictions deduced from

small-scale trends, certain conditions must be present in the experimental work. (1) Reasonable simulation of the actual kiln conditions by the smaller scale tests; and (2) a focus on kiln parameters that are not easily masked by the presence of other materials, and could be directly linked to properties of the fuel. Examples of these parameters are flue gas temperatures and flowrates. Predictive methods based on flue gas flowrates have been used successfully by Ariyaratne, et al. [25] to study the effects of fuel composition, moisture content, calorific value and state on actual kiln performance.

In conclusion, a review of the literature reveals that, of the WDF currently of interest to this research and to Nova Scotia, there are more reported trials on the use of TDF and WDF's associated with plastics than are available for WARS in cement kilns.

CHAPTER 3. CONSIDERATIONS ON FUEL CHARACTERIZATION

3.1 SOLID FUEL COMBUSTION MECHANISMS

The combustion products of biomass and solid WDF are similar to that of coal, but different fuel structure and particle size influence the extent of their formation reactions. When a solid fuel particle is heated, moisture existing as free water within the particle pores and as bound water in the fuel molecules is evaporated and transported via the pores out of the particle. Biomass and some WDF's generally contain more moisture than hard coals. This is however not the case with most waste plastics. The presence of excess moisture can affect particle ignition due to the loss of heat to vaporization. In burners, this can affect combustion performance [55].

The next stage is pyrolysis or devolatilization. During devolatilization, volatile components are rapidly released as gaseous compounds. Pyrolysis is typically completed in 10–200 ms for micron-range pulverised coal particles [9]. For coal and solid fuels with notable fixed carbon content, as pyrolysis proceeds, the structure of the solid residue continuously changes, becoming more porous, and may collapse at a point. The rapid pyrolysis step may not directly limit particle burnout, but it significantly affects the reactivity and porosity of the remaining char. For solid fuels with very low to no fixed carbon and ash content, little to no solid residue char may be formed during pyrolysis and the mechanism for the release of volatiles may differ significantly due to the absence of a skeletal carbon frame [55]. The released volatile compounds which, are composed of lighter hydrocarbons (CH_4 , C_2H_4 , C_2H_6) and heavier tar for coal, diffuse into the particle environment, where they homogeneously ignite as they meet an oxidising agent.

In woody biomass, for example, pyrolysis yields CO, CO₂, CH₄ and H₂ as major products along with other organic compounds. The volatiles oxidise in a sheet surrounding the char particle, thus hindering oxygen diffusion to the solid char and limiting heterogeneous combustion. The volatile yields of biomass and other WDF's are considerably higher than those of coal and coke which is typically 40% for medium coals [13] while most reported for biomass for example are 60–100% volatile, similar to plastics. This is an important difference between coal and WDF. Fuels with more volatile matter would lose more weight during rapid devolatilization, which is expected to lead to a more complete conversion in combustion systems. In some cases, this expectation may however, be counterbalanced by the size-reduction limitations of fuels with such high volatile content.

Devolatilization leaves behind a solid char, which is predominantly fixed carbon in the case of many solid fuels. Subsequently, char oxidation reactions take place. If oxygen is present, char gasification rates by reactions with H₂O and CO₂ are negligible and it is sufficient to consider only the char combustion with oxygen. The time required for the oxidation of pulverized coal (PC) char particles in utility scale applications is typically between 0.3–1 s, which is considerably longer than that required for devolatilization [55]. Therefore, in practice, the char combustion rate determines the extent of burnout or combustion efficiency for a given residence time depending on the particle size and temperature. In cases where different solid fuels are blended for use, the overall combustion efficiency depends on the burnout achieved in each of the components with considerations for any synergistic effect. Sami, et al. [13] proposed a combustion efficiency relationship (Eq. 2) based on the ratio of the fraction of burnout of the blend (η_{blend}) to that of the reference coal (η_{coal}) for coal-biomass blends with respect to volatile matter content. They assume the same degree of char burnout and loss of all volatiles in the individual fuels.

A modified form of their relationship without the assumption of equal char burnouts, generalized for WDF with significant volatile matter content to be used for discussions in this thesis, is given as:

$$\frac{\eta_{blend}}{\eta_{coal}} = \frac{VM_b Y_b + VM_c (1 - Y_b) + \eta_{b.char} (1 - VM_b) Y_b + \eta_{c.char} (1 - VM_c) (1 - Y_b)}{VM_c + \eta_{c.char} (1 - VM_c)} \quad (2)$$

Where VM_b and VM_c are the volatile matter content of the WDF and coal respectively. Y_b is the mass fraction of the WDF in the blend. $\eta_{b.char}$ and $\eta_{c.char}$ are the fraction of completely burnt out char for WDF and coal respectively. From the relationship, it can be seen that the presence of large amounts of volatile matter in WDF or an increase in char burnout of either fuel will increase the overall combustion efficiency of the blend as compared to coal only.

3.2 FUEL CHARACTERIZATION EXPERIMENTS

Thermal analytical studies of coal and alternative fuels for co-combustion and results available in the literature address different aspects of the combustion phenomena. Researchers have investigated the effect of fuel composition, size distribution, blend fractions, temperature, and heating rate on combustion products, volatile yields and char burnout or reactivity. These are important in analysing high temperature kinetics of thermal processes such as pyrolysis, gasification and combustion. Kinetic parameters obtained from thermochemical experiments that are conducted under conditions, which reasonably mimic industrial conditions yield better predictions in full-scale models [56]. Thermal analytical studies on fuels published in the literature differ widely in their approach, and in fuel selection, scale, experimental apparatus, application (gasification, pyrolysis or combustion) and full-scale equipment (blast furnace, cement kilns and boiler plants). In cases where the goal is industrial application, industrial

conditions to be simulated largely determine the design of the experimental study and the choice of apparatus. Apparatus that provide different temperatures, heating rates and ambient environments have been used. In addition, for cases where full-scale conditions are difficult to simulate, bench-scale studies have been used for the comparative analysis of thermal behaviour. The following sections presents a review of fuel characterization studies based on different experimental parameters.

3.2.1 Types of fuels characterized

Thermal analytical studies have been conducted mostly on coal [57, 58] and on biomass of various kinds and sources [56, 59-61] as solid fuels for diverse applications. Pegg and Fels [47] conducted and reported on the thermal analysis of waste liquid fuels such as crude glycerol for cement kiln combustion. Thermal analyses also can and have been conducted on materials not considered traditional fuels as a tool for evaluating the thermal stability of materials. For example, thermal decomposition kinetics of polypropylene composites filled with graphene nano-platelets have been reported by Liang, et al. [62] and Kissinger [63] also conducted experiments on kaolin using differential thermal analysis (DTA) to obtain kinetic data. Under the current regime of waste to energy research, the thermal behavior of these previously unused energy resources is applied to discuss their potential as fuels where appropriate. Despite the growing interest in WDF and its applicability in rotary cement kilns, there appear to be gaps in the literature for thermal analysis of non-biomass, non-hazardous, solid WDF. Due to extensive use of waste plastics in blast furnaces, however, the Japanese steel industry over the years, has published studies on combustion of plastics under blast furnace conditions using bench-scale apparatus [64].

3.2.2 Scales of investigation

In terms of scale, bench-scale thermal analyses of fuels make up a large portion of the available literature. They are relatively simpler and less cumbersome to carry out. Due to the smaller sample weights used in small-scale experiments, they may require extensive mixing to create representative samples where blends of fuels are to be investigated. Despite the inability, in certain cases such as Jeschar, et al. [21], to match bench-scale results with full-scale observations on emissions, results obtained by researchers such as Ariyaratne, et al. [25] show links between bench-scale analysis and full-scale burner parameters. Ariyaratne, et al. [25] studied the effect of substituting coal with RDF, waste wood, SHW and LHW using models on overall heat and mass balances of the cement kiln, and validated these with full-scale WDF trials. The characteristics of the fuels as received are shown in Table 7. These fuel properties (moisture, ash content and elemental composition) obtained from the proximate and ultimate analysis have been used to explain trends in temperature, flue gas flowrates and their consequent effect on clinker production rates. For example, kiln gas temperatures were 24°C, 28°C, 22°C and 95°C lower than the temperature in the coal reference case for RDF, waste wood, SHW and LHW respectively. The higher the heating value, and lower the ash content for the solid fuels, the higher the kiln gas temperature. There is a relatively larger fall in temperature for LHW because of the relatively higher moisture content. An increase in the required mass of fuel increases gaseous combustion products and leads to an overall increase in flue gases. This increase in the total flue gas leads to a reduction in thermal efficiency, which translates to a reduction in kiln gas temperature. Furthermore, the kiln gas temperature is impacted by the air requirement for fuel combustion and this can also be deduced from the ultimate anal-

ysis of the fuel [65]. The fuel-air requirement is affected by a combined effect of the concentration of O and the molar H/C ratios for the given fuel [65]. Generally, the higher the molar H/C ratio of a fuel, the lesser the molar air requirement.

Table 7. Ultimate analysis of fuels used as received for experiments conducted by Ariyaratne, et al. [25]

Parameter	Unit	Coal	RDF	Waste wood	SHW	LHW
Net Calorific Value	[MJ/kg]	28.30	18.20	14.90	15.90	14.60
C	[kg/kg]	0.729	0.431	0.403	0.359	0.437
H	[kg/kg]	0.039	0.062	0.053	0.053	0.080
O	[kg/kg]	0.056	0.304	0.390	0.285	0.253
S	[kg/kg]	0.014	0.004	0.000	0.012	0.016
N	[kg/kg]	0.017	0.007	0.041	0.006	0.018
Ash	[kg/kg]	0.136	0.121	0.071	0.167	0.000
Moisture	[kg/kg]	0.010	0.071	0.042	0.118	0.198
Temperature drop in reference to coal	[°C]	-	24	28	22	95

Larger scale pilot tests have also been carried out for certain blends of fuels for boiler and energy operations. Ye, et al. [55] applied pilot-scale experimental and numerical investigations to study the co-combustion of propane with pulverized coal, pine shells, and textile waste using a laboratory furnace fired by an industrial-type swirl burner. Their findings showed that the co-firing of propane with pine shells and textile wastes yielded higher particle burnout than the propane-coal flame although they were larger in particle size. This was attributed to the high volatile content of the pine shells and textile waste.

The importance of volatile content and particle size has also been studied with similar conclusions for coal-biomass blends [13] and coal-plastics blends [66]. Others, including Rotatori, et al. [29] have reported field scale effects of fuel changes in fuel blends on cement kiln emissions using field monitoring equipment.

Findings of authors such as Hoekstra, et al. [59] and Wagner [67] show that given the proper conditions and context, smaller scale experiments could be used for comparative analysis which could be extrapolated for industrial scale applications. A review of the literature revealed that the choice of the scale of investigation largely depended on availability, bias and capabilities of the researchers and equipment. In the present work, the ultimate analysis of selected WDF has been used to discuss observations in bench-scale experiments, and both the ultimate analysis and bench-scale results have subsequently been used as preliminary basis to suggest expected effects of WDF in full-scale kiln applications.

3.2.3 Choice of experimental set-up

Table 8 shows some apparatus reported in the literature with their operating ranges for studying the thermal degradation of solid fuels. To obtain a reasonable simulation of the process requiring thermal evaluation, different types of equipment have been used by researchers. Thermogravimetric analysers, heated wire mesh (HWM) [68] also referred to as wire mesh reactor (WMR) [69] or heated grid reactor (HGR) [60] or heated foil reactor [56], and the tube furnace reactors are most often used [70].

Table 8. Typical operational conditions in different combustion study apparatus [70]

	Particle size (mm)	Heating rate (°C/s)	Final Temperature (°C)	Residence time (s)
Pulverised coal boiler	< 0.1	10^3 – 10^6	1300–1700	≈ 1
Thermogravimetric analysis	≤ 2	< 1.67	1500	≈ 3600
Heated wire mesh	≤ 2	10^3	800–1400	1–5
Curie-point apparatus	< 0.1	10^2 – 10^4	600–800	> 0.1
PF combustion reactor	< 0.5	10^4	< 1500	2-3

The devices used in various studies, their merits, demerits and suitability differ from study to study. It holds, however, that the thermal analysis apparatus regulate temperature, heating and cooling rate, or atmosphere used as operational variables for characterization experiments.

TGA involves recording the weight loss over a heating period of a powdered sample in a controlled atmosphere. TGA measurements can be conducted for fuel proximate analysis, determination of mixture composition, and to extract slow heating rate kinetic data. TGA curves are used as fingerprints of single fuels for analyzing the general composition of an unknown fuel mixture. The ignition temperature of a material can also be ascertained. For a combustion experiment, this temperature will be the point at which TG curves deviate from the pyrolysis TG curves [71]. TGA has been used to study the decomposition and ignition temperature of bagasse and its blends with coal in Brazil. Though TGA is most commonly reported in the literature, the slow heating rates used for the analysis do not adequately represent many practical, industrial thermal processes [60]. Models developed from kinetic data obtained from TGA may not predict expected conversion in fast heating applications, but because of their usefulness, TGA experiments comparing char reactivity, pyrolysis behaviour and elemental composition of fuel samples are integrated into most of the studies conducted with other specialized apparatus.

In order to evaluate combustion performance, Ciambelli, et al. [72] presented a comparison of operating conditions for two apparatus used in fast pyrolysis studies namely drop tube furnaces or EFR and WMR as shown in Table 9. Several researchers have used the HGR or WMR to study various aspects of the pyrolysis and combustion of solid fuels.

Table 9. Operating limits and conditions for EFR and WMR as fast pyrolysis characterization techniques after Ciambelli, et al. [72]

Entrained Flow Reactor	Wire Mesh Reactor
Calculated heating rate and peak operating temperatures are within the higher orders expected for industrial scale	Heating rates are $\leq 10^4$ K/s. However, heating rate has very little consequence on char beyond 1000 K/s.
Char properties are subject to secondary changes and it is difficult to measure pyrolysis yields compared to WMR	Sample size of approximately 5 mg per test and the use of sweep gases reduces secondary reactions, enhancing the accurate measurement of yields

Fuertes, et al. [73], directly measured ignition temperatures of different pulverized coal samples using the HGR. Fast pyrolysis tests using a novel WMR on pine wood and other model compounds has been documented by Hoekstra, et al. [59]. Depending on what the objective of a particular study was, suitable analytical equipment was attached to the HGR set-up. For example, in obtaining instantaneous measurements of emissions, laser induced fluorescence (LIF) was used to visualize carbon monoxide and formaldehyde produced from the pyrolysis of biomass in a HGR [60]. In other works, the volatile matter yields of pulverized coal samples have been collected and estimated in a HGR attached to a nitrogen-cooled tar trap [68]. Gibbins, et al. [57] described modifications made to the earlier designs of HGR for various pyrolysis experiments. They introduced (1) flow of sweep gas to enable product removal, (2) water cooling to prevent excessive temperature rise in parts of the reactor, and (3) a computerized temperature feedback. In their experiments, the thermocouple was usually placed in contact with the grid for temperature readings as was the case for [68] and [60]. Prins, et al. [61] also quantified heat losses due to the thermocouple and suggested the use of a foil instead of a mesh in cases where uniform heat distribution through the sample mass is of utmost concern. The HGR has been used extensively in fuel characterization since its invention.

Some works have used both the HGR and TGA to study the behaviour of char formed under fast heating conditions. An investigation into the influence of the rate of devolatilization on the reactivity of coal, biomass and their blends by Ciambelli, et al. [72]2003) is one example. Comparisons made in their work between the fast heating HGR and the slow heating TGA showed that the heating rate applied influenced the quantity of volatiles released by a solid fuel. Others, such as Heikkinen [5] applied three different fuel characterization methods—TGA, HGR, and a bench-scale pulverized fuel combustor— to study specific behaviours of different solid fuels under different conditions. The reactor for their experiment was fitted with optical devices that observed the shrinkage of single fuel samples while TGA was used to determine the volatile matter content of the fuel samples. Heated grid reactors have also been used to detect the formation of compounds such as formaldehyde and carbon monoxide via laser fluorescence [68]. In a different approach, using a selection of different characterization techniques, Pipatmanomai, et al. [58] modified a HGR to determine volatile content under simulated industrial conditions. They then resorted to TGA for a reactivity study of the char obtained from the HGR. The flexibility of the HGR to be used in conjunction with other characterization techniques is further highlighted in experimental work on the gasification of coal conducted by Wagner [67]. Thermogravimetric analysis was used to study reaction rates, the HGR was used to quantify product yields and an entrained flow gasifier was employed to sample gases for analysis.

A review of these experiments and designs suggests that HGR experiments can be conducted alone or combined with other characterization methods. It is also important to discuss the

results obtained from these types of experiments with reference to the heating rate and maximum end temperature used. This is because the thermal behaviour of materials may vary significantly under slightly different heating conditions.

3.2.4 Properties characterized

Researchers focus on different aspects of fuel characterization when employing the use of thermo-analytical tools. These include kinetic properties, combustion mechanisms, product yields, gas compositions and char properties (reactivity, conversion and morphology).

Gas compositions and product yields can be obtained directly from thermal and emission analysis experiments. Kinetics and reactivity of char are derived from further mathematical analysis of experimental data. Cai, et al. [68] determined coal char morphology and reactivity for different temperatures, heating rates and pressures to discuss the pyrolysis of coals for gasification processes. Among other findings, they reported that reactivity of coal char reduced with increasing temperature for temperatures below 700°C. This is because devolatilization dominated the thermal degradation process at these temperatures. When measured against increasing heating rate, it was found that the reactivity of combustion related char increased and leveled off at heating rates of 10^3 K/s because rapid release of volatiles led to higher porosity of chars, making them more reactive. Beyond heating rates of 10^3 K/s, there was no distinct influence of heating rate on char reactivity. Literature on characterizations based on kinetic parameters, product yields and gas compositions are most prevalent.

The influence of temperature and heating rate on yield continues to be studied as interest in the production of more homogenous intermediate fuels from the pyrolysis or gasification of solid waste grows. Whereas the work done by Hoekstra, et al. [59] concentrated on the composition and yield of pyrolysis products from the fast pyrolysis of biomass such as pinewood,

works like that of Guizani, et al. [74] discussed a range of characteristics including reaction rate, gas yields and char properties. Similarly, Anastasakis, et al. [56] used collected data on kinetics, product yields and gas compositions to study fast and slow devolatilization behaviors of woody and herbaceous biomass for application in gasification processes. In the literature, yields have been analyzed using a rich selection of devices such as gas chromatography (GC), Fourier transform infra-red spectroscopy (FTIR) and laser induced fluorescence (LIF).

Ptiček Siročić, et al. [75] have worked on extracting kinetics-related data for the degradation of LDPE nano-composites in oxidative and non-oxidative environments and discussed the effect of the ambient gas on the mechanisms of degradation using modified equations pertaining to polymers. The work of Bockhorn, et al. [76] also presented kinetic parameters reporting activation energies for the thermal degradation of polyethylene and polypropylene.

3.3 KINETICS OF THERMAL DEGRADATION

The activation energy (E) and pre-exponential factor (A) for the determination of reaction constants from the Arrhenius equation can be deduced from various thermal analytical studies by applying assumptions and mathematical tools to data acquired from weight loss and product yield experiments. Kinetic parameters could be obtained from (1) isothermal or (2) pre-determined heating rate or non-isothermal experiments. For isothermal experiments, weight loss characteristics are measured for a sample at a constant temperature. Experiments may run for hours to achieve a required degree of conversion. In addition, several experiments at different temperatures need to be carried out for extraction of kinetic parameters to be possible. Experiments run at pre-determined heating rates, involve heating samples at a constant heating rate and recording weight loss vs. time and temperature. This non-isothermal ap-

proach allows reaction rates to be determined in a single run of thermal degradation experiments. The nature of the full-scale application usually influences the choice to use a given set of kinetic data obtained under specific conditions to predict conversion in a thermal process. Saddawi, et al. [77] indicate, for example, that for residence times of approximately 1 s, heating rates of 10^3 K/s and a final temperature of 500°C typical of flash pyrolysis, when high E and A values were used in predictive models for sample conversion, the results matched actual experimental values better than when low E and A values were used. They also mention that E and A values obtained from fast pyrolysis experiments predict conversions better than most of the values obtained from TGA heating rates. For CFD modelling of shorter and steadier flames, higher E values are preferred because flame position and length are largely influenced by devolatilization time. Where flame structure is of less importance such as in coal gasification, the choice of kinetic parameters has been shown to be less critical. Low E values usually means that decomposition occurs at lower temperatures, so for coal decomposition between 500°C and 1000°C under fast pyrolysis, a high E value will predict decomposition behaviour better. However, where there are key temperature range overlaps for different heating rates the value of E becomes less critical [77].

3.3.1 Factors influencing estimated kinetic data

1. Heating rate and the type of sample

Saddawi, et al. [77] compared the kinetics of coal to biomass and pointed out that throughout the literature, variations observed in the kinetic data are attributed to different techniques, heating rates and transport limitations. However, when Kissinger [63] compared data obtained by isothermal experiments to data from non-isothermal experiments on kaolin, he observed that within certain ranges, differential thermal analysis (DTA), which uses constant heating

rates, generated E and A values comparable to isothermal experiments for undiluted kaolin-ites. This suggests that existing differences in kinetic data based on the heating approach may not apply to all materials. In the case of reed biomass, kinetic parameters extracted from fast pyrolysis were significantly lower than those obtained from TGA which is a slow heating experiment. These findings are similar to those from studies on coal, where lower E and A values have been extracted for similar slow heating rates based on the presence of secondary and cross linking reactions [77]. There is also the general observation that using purer components for thermal analysis generates higher activation energies.

2. Thermal lag and holding time

Zabaniotou and Theofilou [15] mention that thermal lag effects could also play a role in the prediction of kinetics using analytical devices. Thermal equilibrium may not be reached for short holding times. Short holding times reduce amount of secondary reactions, and primary cracking reactions become dominant so high values of E predict conversion better.

3.3.2 Mathematical extraction of kinetic data

Detailed reviews of the mathematics of extracting kinetic data are available in the literature [77, 78].

The Arrhenius equation for the rate constant k :

$$k = A \exp\left(\frac{-E}{RT}\right) \quad (3a)$$

or in logarithmic form

$$\ln k = \ln A - \frac{E}{RT} \quad (3b)$$

Assuming the rate of devolatilization and char combustion are considered to be first order kinetics,

$$\frac{d\alpha}{dt} = k(1 - \alpha) \quad (4)$$

Where $\alpha = 1 - \frac{m(t)}{m_0}$ and α is the reaction progress variable taking $0 \leq \alpha \leq 1$, $m(t)$ and m_0 are the current and original weights of the sample respectively. The sample could be the fresh solid fuel or the char in the case of char reactivity calculations.

Combining Eq. (3a) and (4) yields

$$\frac{d\alpha}{dt} = A(1 - \alpha)\exp\left(\frac{-E}{RT}\right) \quad (5)$$

Under isothermal conditions, integrating Eq. (4) with $\alpha = 0$ and $t = 0$ yields,

$$-\ln(1 - \alpha) = kt \quad (6)$$

Hence the slope of plot $-\ln(1 - \alpha)$ versus t gives k . E and A can then be estimated from Eq. (3b) by plotting $\ln k$ versus $1/T$ with intercept $\ln A$ and a slope $-E/R$.

In non-isothermal experiments a sample is heated at a pre-determined rate $B=dT/dt$,

Therefore

$$\frac{d\alpha}{dt} = \frac{dT}{dt} \frac{d\alpha}{dT} = B \frac{d\alpha}{dT} \quad (7)$$

Substituting into Eq. (5) yields:

$$\frac{d\alpha}{dT} = \frac{A}{B}(1 - \alpha)\exp\left(\frac{-E}{RT}\right) \quad (8)$$

Integrating with initial conditions: $\alpha = 0$ at $T = T_0$

$$-\ln(1 - \alpha) = \frac{A}{B} \int_{T_0}^T \exp\left(\frac{-E}{RT}\right) dT \quad (9)$$

Introducing $x=E/RT$ and substituting for the limits of integration yields:

$$-\ln(1 - \alpha) = \frac{AE}{BR} \int_x^\infty \frac{e^{-\zeta}}{\zeta^2} \left(\frac{-E}{RT}\right) d\zeta = \frac{AE}{BR} p(x) \quad (10)$$

where ζ is a dummy variable.

Various approximations exist for the term $p(x)$. Most commonly used approximations are:

1. Murray and White from [77] which can be solved by linear approximation using:

$$p(x) \cong \frac{\exp(-x)}{x^2}$$

Substituting into Eq. (10) and taking logarithms gives:

$$\ln \left[\frac{-\ln(1 - \alpha)}{T^2} \right] = \ln \frac{AR}{BE} - \frac{E}{RT} \quad (11)$$

2. For Coats and Redfern non-linear approach from [77]:

$$p(x) \cong \frac{\exp(-x)}{x^2} \left(1 - \frac{2}{x}\right)$$

Substituting into 10 gives

$$-\ln(1 - \alpha) = \frac{AR}{BE} T^2 - \exp\left(\frac{-E}{RT}\right) \left(1 - \frac{2RT}{E}\right) \quad (12)$$

3. The Senum and Yang [79] approximation uses:

$$p(x) \cong \frac{\exp(-x)}{x^2} \frac{x^4 + 18x^3 + 86x^2 + 96x}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (13)$$

Which can also be substituted into Eq. (8) and solved with non-linear regression to obtain values for E and A . Saddawi, et al. [77] indicate that the values associated with these approximations from first order kinetics usually hold for predictions in slow heating rate applications.

In the present work, the behaviour of a 1:1 fuel blend of coal and petroleum coke, referred to as coal-coke, is studied. The char from fast heating combustion experiments on coal-coke is studied under slow heating conditions in an inert environment for weight loss data. Since no further combustion is expected under inert conditions, all char weight loss can be considered a result of pyrolysis or devolatilization. Estimates of E were obtained for the TGA weight loss data for coal-coke char using the Murray and White linear approximation. The Murray and White approximation was chosen because it is rather simple, straightforward and useful as a quick tool for extracting preliminary estimates from limited data in non-isothermal experiments.

4.1 PRELIMINARY ASSESSMENT OF AVAILABLE WASTE-DERIVED FUELS IN NOVA SCOTIA.**4.1.1 The local cement kiln**

LafargeHolcim Canada Inc., Brookfield, until recently known as Lafarge Cement Canada, Brookfield, is part of the Lafarge North America network of cement manufacturing plants. Being the only cement plant present within the maritime region of Canada, it enjoys a ready market for its products. It has, in recent years, been operating one of two dry process rotary kilns and produces 200,000–300,000 tonnes of clinker annually. Based on these production estimates, the cement plant consumes approximately 1.35 PJ of thermal energy annually– the equivalent of 45,000 tonnes of coal. Limestone is supplied from a quarry situated near the plant. Its location gives the plant less flexibility in substituting raw materials than in substituting fuels. The plant has pursued the use of waste oils, crude glycerol, waste roofing shingles and more recently plastics as alternative fuels to reduce the cost of production. It has also partnered with the Resource Recovery Fund Board (RRFB) now called DivertNS, a not-for-profit body which administers the Province’s waste diversion programs, to increase the diversion of potential alternative fuels from landfills. The target for the Province has been to reduce landfill disposal to 300 kg/person/year. An increased use of WDF in the cement kiln pushes the Province closer to this target. The 50-year old cement plant is also a major employer within the community and continues to provide valuable support to its constituents. Presently, the cement plant operates a long dry cement kiln equipped with an ESP.

4.1.2 Locally available waste-derived fuel

A selection of materials with potential for diversion into cement kilns for energy recovery within Nova Scotia were studied case-by-case and examined for the challenges facing their diversion into kilns. Three general, but related challenges were identified locally: (1) policy and public perception, (2) kiln delivery and (3) potential for harmful emissions.

The available alternative fuel sources were described and evaluated for their potential emissions. The results were compared to that of a coal-coke fuel blend. Scrap tires for TDF, waste shingles for WARS and unrecyclable plastic materials for PDF were the fuels selected for study in this work. Table 10 shows the results of analysis conducted at the EXOVA laboratory, Quebec, Canada for the waste-to-fuel resources collected from recycling facilities, landfills and from the cement plant. Coal and petroleum coke samples used for comparison were oven dried at 50°C for 10 hours before being size-reduced to (80% < 200 mesh) in a roll mill and mixed to a 1:1 ratio. Construction and Demolition (C&D) mixed plastics were used in the analysis shown in Table 10 as a representative sample for unrecyclable plastics. They were collected from a C&D landfill and shredded to 3–5 mm particle sizes. They were composed of a randomized mix of rigid plastic chippings and light plastic fluff. Waste shingles were collected from the cement plant, as received, and stored over the period of this research to be used when required. Given the length of time of storage of the shingles (over 2 years), it is possible that the effect of long-term storage and different batch-processing conditions could result in variations in results obtained for different loads of waste shingles. The batch used for the ultimate analysis in Table 10 was air-dried and size-reduced to 1.5–3 mm in a hammer mill. Lump-sized scrap tires were collected, shredded to 10–30 cm and then used for the ultimate analysis. The calorific values reported are the lower heating value (LHV)

obtained using the ASTM D-240 standard test. ASTM D5291 and ASTM D-482 standard test procedures were used to analyze carbon and ash content respectively. ‘Dry %’ refers to percent composition obtained on dry mass basis while ‘%’ is used for compositions determined on as-received mass basis without the removal of moisture.

Table 10. Analysis for Scrap tires, C&D plastics, waste shingles and 50-50 coal-coke conducted by EXOVA Laboratory showing elemental analysis, moisture, ash and energy content.

Component measured	Unit	Scrap tires	C&D plastics	Waste shingles	Coal-coke
Chlorine	mg/kg	752	160	220	183
Fluorine	mg/kg	15.1	67.7	58.3	85.2
Carbon	dry %	87.79	65.48	46.22	69.67
Hydrogen	dry %	6.52	10.63	5.08	3.18
Oxygen	dry %	1.8	1.88	10.11	7.11
Nitrogen	dry %	< 0.5	0.5	0.5	1.68
Sulphur	%	1.34	0.1	1.226	3.52
Moisture	%	0.88	0.13	7.70	0.37
Ash at 900°C	%	2	7.66	41.18	13.43
Calorific Value	MJ/kg	38.45	42.15	16.46	29.63

4.1.3 The case of waste plastics

Plastics are almost completely derived from petrochemicals produced from fossil oil and gas. Around 4% of annual petroleum production is converted directly into plastics from petrochemical feedstock [80]. Besides crude oil, natural gas and coal, plastics can be derived from wood, vegetable oils, sugar and starch as biopolymers or bioplastics. *PlasticsEurope* [81] estimates that worldwide polymer production was 260 million tonnes per annum in the year 2007 for all polymers including thermoplastics, thermoset plastics, adhesives and coatings, but not synthetic fibres.

The major plastic types that stand out in terms of their market share and their identification codes are:

- Type 1.** Polyethylene terephthalate (PET)
- Type 2.** Polyethylene – high density (HDPE)
- Type 3.** Polyethylene – low density (LDPE), linear low density (LLDPE)
- Type 4.** Polyvinyl chloride (PVC)
- Type 5.** Polypropylene (PP)
- Type 6.** Polystyrene solid (PS), expanded (EPS)
- Type 7.** Others such as polyurethane (PUR)

Using ASTM D3176-84 standard test procedures, Islam, et al. [82] also conducted proximate and ultimate analyses on some mixed plastics. The results are presented in Table 11. Their results show that volatile content was 96.88 wt% of the sample. The amount of carbon reported was 83.93 wt% dry-ash-free (daf), which is greater than the carbon content calculated for the C&D plastic analysed in Table 10 (71 wt% daf); however, the mass-based C/H value of 6.2 obtained from Table 10 compares well with the value for plastics in Table 11 (6.53).

Table 11. Proximate and ultimate analysis of waste plastics from Islam, et al. [82].

Proximate Analysis (wt%)		Ultimate Analysis (wt%) Ash free basis	
Moisture Content	0.41	Carbon (C)	83.93
Volatile Matter	96.88	Hydrogen (H)	12.84
Fixed Carbon	0.28	Nitrogen (N)	-
Ash Content	2.43	Oxygen (O)	0.8
		Sulfur (S)	-
		C/H	6.53

4.1.3.1 Disposal of waste plastics

Approximately 2.8 million tonnes of plastic waste are disposed of annually in Canada of which 719,000 tonnes are from residential sources and 2 million tonnes are from non-residential sources including industrial, commercial and institutional (IC&I) sector such as grocery stores and goods manufacturing plants. Of the total disposed, an estimated 1.9 million tonnes are packaging waste. [83]. According to the Clean Foundation [84], 490 million plastic bags are used in Atlantic Canada alone each year. At 5 g per bag, this represents an estimate of 101 PJ/year using reported calorific values for plastic film shown in Table 12. Since most of these plastics are unrecyclable, they usually end up in landfills.

Table 12. Analysis results obtained from EXOVA Laboratory for size-reduced containers, carpet, clothing, plastic film, C&D plastics and expanded polystyrene.

	Containers	Carpet	Textile	Plastic film	C&D plastics	EPS
Chlorine (mg/kg)	3687	714	502	257	160	83.6
Fluorine (mg/kg)	15.7	54.0	<15.0	78.0	67.7	68.7
Carbon (% dry)	80.4	50.78	60.99	80.14	65.48	91.57
Hydrogen (% dry)	12.7	7.29	4.49	13.05	10.63	7.64
Oxygen (% dry)	1.91	17.65	32.87	3.46	1.88	<0.5
Nitrogen (% dry)	< 0.5	4.82	<0.5	< 0.5	0.5	< 0.5
Sulphur (%)	0.046	0.088	0.031	0.025	0.1	0.0135
Moisture (%)	0.32	0.59	0.36	0.38	0.13	0.19
Ash (%)	5.16	17.72	7.44	3.22	7.66	0.16
Calorific value (MJ/kg)	41.57	22.73	22.33	41.41	42.15	41.50

The plastic-based waste materials shown in Table 12, which were assessed for their suitability as kiln fuels, were collected from various sources throughout Nova Scotia: (1) plastic waste comprising a randomized mix of rigid and flexible plastics resulting from C&D projects and recovered from a C&D landfill; (2) Plastic film which were made of LDPE and LLDPE film collected from curbside collection programs at a Material Recovery Facility (MRF); (3) mixed plastics (4-7), excluding PVC, were mostly plastic containers collected from MRF's; (4) polypropylene (PP)-based carpet backing collected from carpet recyclers; (5) textiles and fabric from used-clothing not-for-profit collectors; (6) expanded polystyrene (EPS) cups and packaging material collected from disposal bins at Dalhousie University and the Halifax Infirmary Hospital.

4.1.3.2 Co-processing waste plastics

Thermogravimetric analysis of waste plastics reported in the literature [82], indicates that inherent moisture loss in plastics at about 110°C and is less than 4% of the total sample weight. At a heating rate of 10°C/min, devolatilization of solid plastic was initiated at approximately 250°C. At a temperature of 550°C devolatilization of all volatile components in the sample is achieved [82]. Waste plastics have been identified as a promising resource because they have high energy content and low inherent moisture content. The results from the ultimate analysis conducted on the waste plastics for this work agree with this assertion. Direct waste-to-energy recovery has been studied and applied in industry, as a preferred way of disposing of unrecycled waste including plastics. Such PDFs have been fired with coal for power generation [20, 85] and in cement kilns [86]. Aranda Usón, et al. [87] conducted environmental monitoring of a cement plant utilizing alternative fuels, including MSW plastics. Some of the lessons learnt from their tests were that the heterogeneity of MSW presents a difficulty in predicting

its effects in the cement kiln. It was shown however that with basic plastic selection and high-temperature combustion, elimination of PCDD/F was achieved. In agreement with their work, it is easy to see, from the wide range of calorific values reported for the plastic-based waste in Table 12, why the improper selection of plastics for PDF could result in significant deviation from the expectations for PDF performance.

4.1.3.3 Emissions impact of plastic-derived fuel

The gaseous products expected to be formed from combustion (CO_2 , H_2O and SO_2 and NO_x) were quantified and compared to coal-coke. Figure 3 is a chart showing percentage changes in gaseous emissions expected when equivalent heat content of the six different plastic-based waste materials is combusted completely in place of coal-coke. These were obtained using Eq. (1). For example, at 100% conversion, the 50 MJ of plastic containers will generate 509 kg, which is 18% less than is expected for coal-coke with an equivalent heat content. From the bar chart, plastic-based materials are likely to increase the emission of H_2O by 185%, 199%, 88%, 194% and 136% for containers, carpet, clothing, plastic film, and C&D plastics respectively. The least H_2O is expected for EPS (72%). This corresponds with the relative increase in H composition for these materials. The presence of high amounts of carbon per kg of dry fuel for plastic film, size-reduced containers, EPS and C&D plastics compared to coal-coke will not result in increased CO_2 predictions. This is mainly because of the reduction in the quantity of fuel required on an equivalent heat basis.

Figure 3 also shows a reduction of 18% in potential CO_2 emissions for both size-reduced containers and plastic film, and approximately 34% for C&D plastics. There is an estimated 6% reduction for EPS. These can therefore be classified as Low Carbon WDF's.

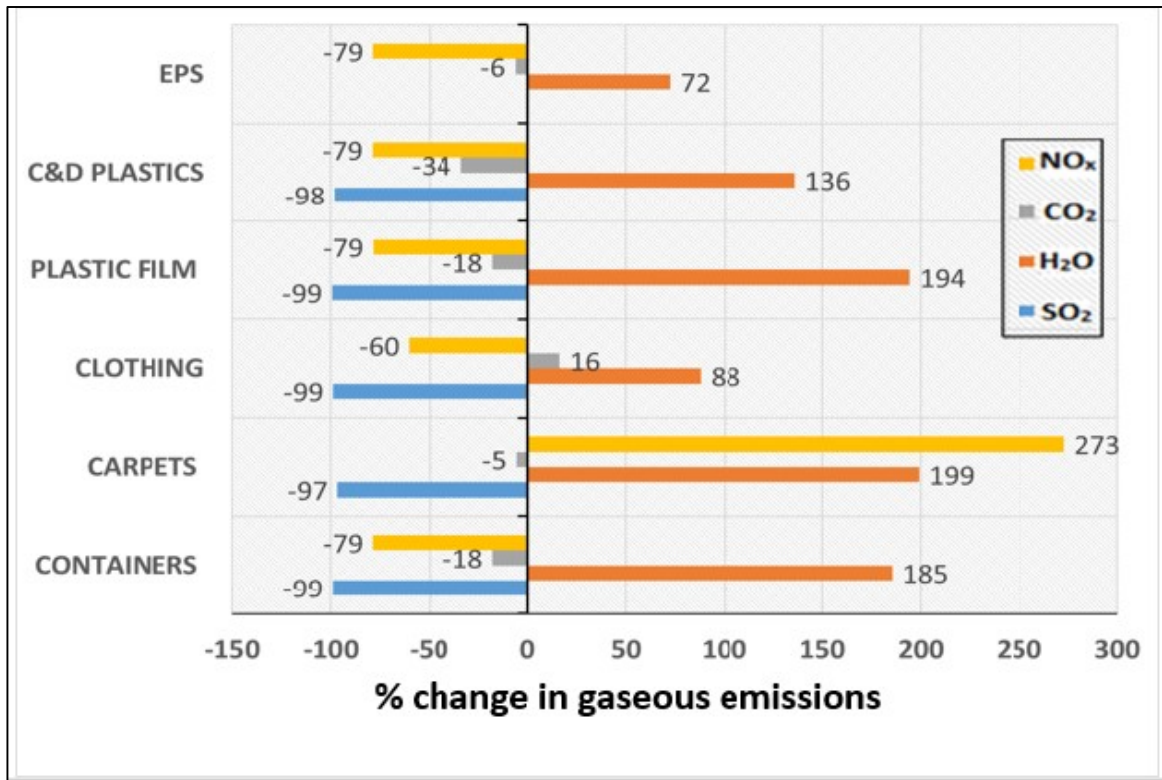


Figure 3. Theoretically expected changes in gaseous emissions from the combustion of plastic-based waste materials based on reported elemental analysis.

All potential plastic fuel samples are expected to generate between 97 to 99% less SO₂ than a 50/50 coal-coke fuel mix after complete combustion. This is attributed to the presence of relatively low levels of sulphur in the tested materials in comparison with the quantities available in a coal-coke fuel mix. Although this reduction is remarkable, the oxidation of sulphur, which is present in raw materials used for clinker production may counter the reductions gained in SO₂ emissions by fuel substitution.

Fuel related NO_x, which is produced from nitrogen compounds found in the fuel, will potentially reduce in all cases of plastic-based waste except for carpet. From estimations the combustion of carpet may result in approximately 300% increase in fuel NO_x emissions. The high nitrogen content of carpets can be attributed to the use of adhesives and additives in manu-

facturing. The formation of NO_x at elevated temperatures in the presence of ambient air usually masks the contribution of fuel NO_x in full-scale cement kiln application. Fuel related NO_x accounts for less than 20% of total NO_x emissions from the kiln stack.

The work of Ariyaratne, et al. [25] mentioned earlier in section 3.2.2, indicates, among other things, that higher calorific values translate to a reduction in fuel mass. This reduction will decrease the total kiln flue gas and could lead to higher kiln temperatures. It can therefore be said that waste plastics which have relatively higher moisture content and lower calorific value such as clothing and carpets will lead to an increase in kiln flue gases which may lower the thermal efficiency at the burner. This has been further examined in bench-scale experiments.

4.1.3.4 Status of plastic-derived fuel in Nova Scotia

The effect of waste plastics as WDF on the stack emissions of a cement kiln draws the most concern from policy makers and the community. The other concern tied to emissions expectation is the heterogeneous nature of waste plastic sources and the variability that may exist in their supply. Plastic-derived fuel, though available for the local cement kiln, is still in preliminary stages of permit approvals. In the absence of full-scale trials an effort has therefore been made in this research to study PDF's using bench-scale methods.

4.1.4 The case of waste asphalt shingles

Asphalt shingles are usually manufactured for use as roofing material. The composition may vary depending on whether the shingle base is organic or fibreglass. According to the Asphalt shingle waste management for North East America fact sheet, the following is the compositional break down of shingles: Fibreglass or cellulose backing (2–15%); asphalt cement (19–

22%) on a fiberglass-mat base or a cellulose-felt base made with paper (30–36%). It also contains sand-sized, ceramic-coated natural rock called aggregate (20–38%); and mineral filler or stabilizer that includes limestone, dolomite and silica (8–40%) [1, 88, 89]. The asphalt used in making shingles is a product of the partial refinement of petroleum. Figure 4 is an illustration showing the composition of asphalt roofing shingles.

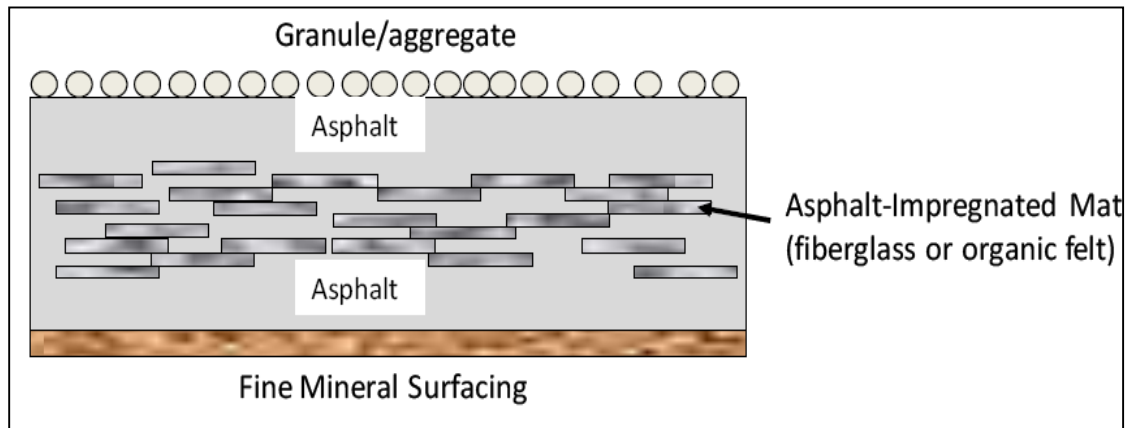


Figure 4. Composition of an asphalt shingle illustrated by the Construction Material Recycling Association [89].

4.1.4.1 Disposal of waste asphalt shingles

Overall, an estimated 1.5 million tonnes of asphalt related roofing waste is generated in Canada, with aggregate, asphalt and mostly organic felts representing 57%, 35% and 9% by mass, respectively [1]. Owens Corning, a roofing shingle producing company, describes several possible applications of waste shingles in energy recovery projects, including use in cement kilns and circulating fluidized beds [88]. The use of waste shingles in hot mix asphalt (HMA) for road and pavement construction is a viable consumer of the aggregate component of waste shingles [90]. In Nova Scotia, after removing the aggregate component (asphalt grit) of the

waste shingles to be used in HMA, the cellulosic portions (asphalt flakes) are shredded to be used as fuel for cement kilns. Great care is taken in making sure asbestos is not present in waste shingles since it poses a respiratory hazard to humans [1, 90]. According to the RRFB, about 20% of the 200,000 tonnes of C&D debris disposed of annually is waste asphalt shingles. Considering that approximately 30–35% of the waste roofing shingle which is asphalt flake could be used as WARS fuel, disposal of waste roofing shingles in landfills in Nova Scotia amounts to an energy loss of approximately 240 PJ per annum.

4.1.4.2 Co-processing waste asphalt shingles

The petroleum content of shingles plus the cellulosic components provide it with sufficient energy to support high temperature combustion. One major concern is the presence of a large quantity of non-combustible material which may affect the overall combustible property of roofing shingles [90]. For this reason, a pre-processing stage is adopted to rid asphalt shingles of the aggregate and to significantly reduce its size for easy handling. This constitutes part of the fuel handling challenge associated with waste shingles. A proximate analysis of shingles received onsite at the cement plant in Brookfield after pre-processing was conducted by Certispec Services and is presented in Table 13. The energy content of shingles indicated is the higher heating value (HHV) whereas the values reported in Table 10 are lower heating values (LHV). Differences in results reported in Table 10 and Table 13 could be attributed to differences in the sources and pre-processing of different batches of shingles used for testing. The batch for the analysis shown in Table 13 were shingles as received. The two analyses in Table 10 and Table 13 were conducted almost 6 years apart with Table 10 being the more recent. Waste shingles have a heating value that fits the energy requirement of a fuel to be used as a supplement to coal (> 15 GJ/tonne) [2].

Table 13. Compositional and heating value analysis of waste shingles prepared by Certispec services.

COMPOSITION			AS RECEIVED	DRY BASIS
Total moisture	%		9.48	--
Ash	%		15.69	17.33
Volatile matter	%		65.82	72.71
Fixed Carbon	%		9.01	9.96
Sulphur	%		1.75	1.93
Gross value	Calorific	MJ/kg	23.90	26.82

4.1.4.3 Emissions impact of waste asphalt roofing shingles

Based on theoretical calculations, at 20 MJ/kg of WARS, Figure 5 shows there is potential for a 9% reduction of CO₂ emissions, a 55% decrease in fuel based SO₂ emissions. There is a potential 60% decrease in Fuel NO_x and H₂O may see an increase of up to 120% respectively. The theoretical potential of reduced CO₂ emissions qualifies WARS as a Low Carbon WDF.

4.1.4.4 Status of waste asphalt roofing shingles in Nova Scotia

Waste asphalt shingles have been used to boost clinker production at the local cement kiln since 2007. Preliminary field trials showed that the size of the shingle particles as received (about 2 cm) were too large to burn properly and therefore limited the quantity that could be combusted for ideal kiln performance. Larger sized particles have less surface area in contact with the direct flame and therefore have longer burning times which results in localized reducing conditions in the product as burning continues on the surface. Attempts to further reduce the size of shingles using equipment on site proved difficult because solid petroleum asphalt softened and led to lump formation at elevated milling temperatures. The general concern was to improve burning time and increase the consumption of WARS. Fuel handling and

fuel delivery into the cement kiln constitutes a major setback for WARS application. Furthermore, studying the characteristic thermal behavior of WARS on a bench-scale will provide data to aid operators and researchers to improve the application of WARS.

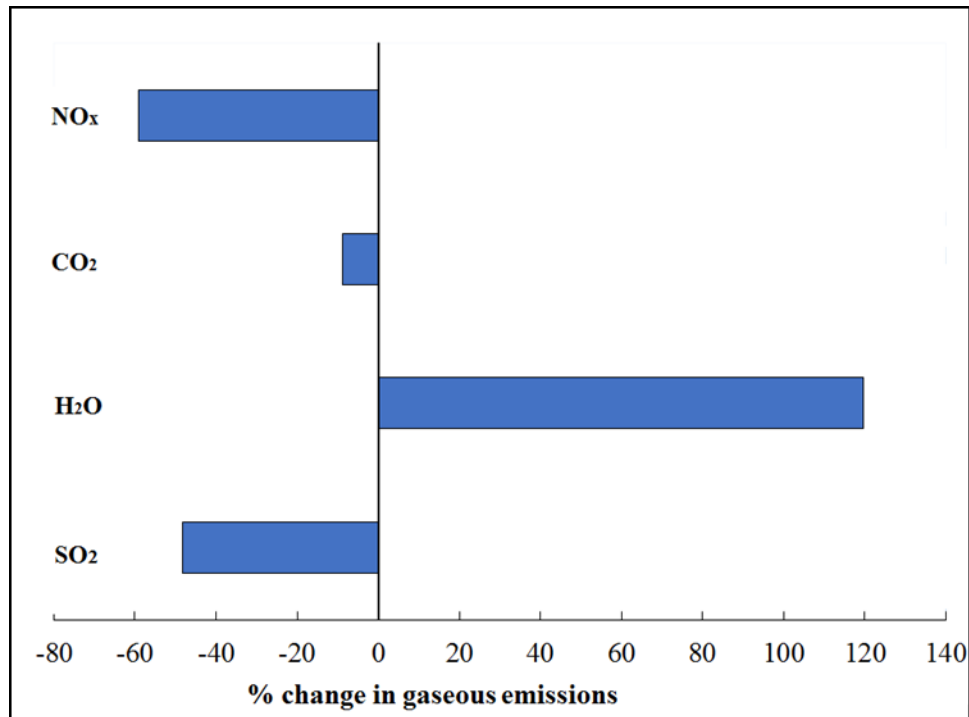


Figure 5. Theoretically expected changes in gaseous emissions from the combustion of WARS based on reported elemental analysis

4.1.5 The case of scrap tires

Tires are composed generally of vulcanized rubber, reinforcing fillers and fibres; and petroleum oils which improve low temperature flexibility of vulcanized rubber [91]. 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. The rubber compounding components of tires SBR and carbon black make up approximately 90%, extender oils, ZnO and S 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 [51] reports the composition of tires by weight as shown in Table 14.

Table 14. Composition of tires by weight from Rubber Manufacturers Association [51].

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 12 kg, Scrap 9 kg.	New 55 kg Scrap 45 kg

4.1.5.1 Disposal of scrap tires

Approximately 1.4 billion tires are produced worldwide annually. One billion tires are disposed of yearly and it is estimated that 4 billion waste tires are currently in stockpiles and landfills [92]. 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 [93]. RRFB reports that an estimated 1 million tires (approximately 75% of tires disposed) are shredded to 5–30 cm pieces called tire-derived aggregate (TDA) and used for the construction of roads as base and fill [94]. Other non-fuel applications of scrap tires include retreading used tires, using shredded tires in civil engineering applications and incorporating tire rubber into new products.

While solely shredding tires is more cost effective than the production of crumb rubber, tire crumbs have more uses including making sports surfaces, vehicle products, molded products, and asphalt additives. About 50–60% of one standard vehicle tire can be produced as crumb rubber. To be defined as a tire crumb, the particles must be 1 cm or less [95]. Scrap tires can also be used to produce devulcanized rubber, which 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 [96]. The de-vulcanization process involves rubber crumbs being exposed to strong shearing and compressive forces, a mechano-chemical process, to alter the structure [97].

4.1.5.2 Co-processing scrap tires

The effect of particle size, heating rates and temperature on the thermal decomposition mechanism of tires during combustion and pyrolysis has been discussed extensively in the literature [98-102]. In their pyrolysis study of tire conversion for tire particles 2 mm and lower, Aylón, et al. [99] indicated 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 [101] who concluded that heating rate played a more influential role for process and kinetic parameters than did particle size. The mechanism of 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 [101]. The devolatilization characteristics of larger particles of tire were studied using a macro-thermogravimetric analytic reactor by

Larsen, et al. [100], who showed that for tire particle 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 reported a more significant effect of surrounding temperature on devolatilization rates. In another study, Nielsen, et al. [102] discussed the effect of mixing larger fuel particles in a pilot-scale rotary kiln. They found that large fuel particles placed on the top of the bed of kiln material were 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. The combustion mechanism, ignition and burnout characteristics of blends of waste tires with high ash coal were studied by Li, et al. [103] using thermogravimetric analysis. They noted that the blending of waste tires with high-ash coal improved combustion characteristics of the 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. Pegg, et al. [104] completed a report on the use of TDF which contains a thorough review of these benefits and the potential changes expected with the use of TDF.

4.1.5.3 Emissions impact of tire-derived fuel

Results from calculations to quantify potential changes in gaseous emissions expected for the displacement of coal-coke with TDF are shown in Figure 6–Figure 7. The calculations are based on Eq. (1) using ultimate analysis data obtained for scrap tires.

In Figure 7, the gaseous emissions of a hypothetical kiln substituting 30% of the thermal energy requirement with TDF scenario using production capacity is compared to a 100% coal-coke cement plant with the same production capacity.

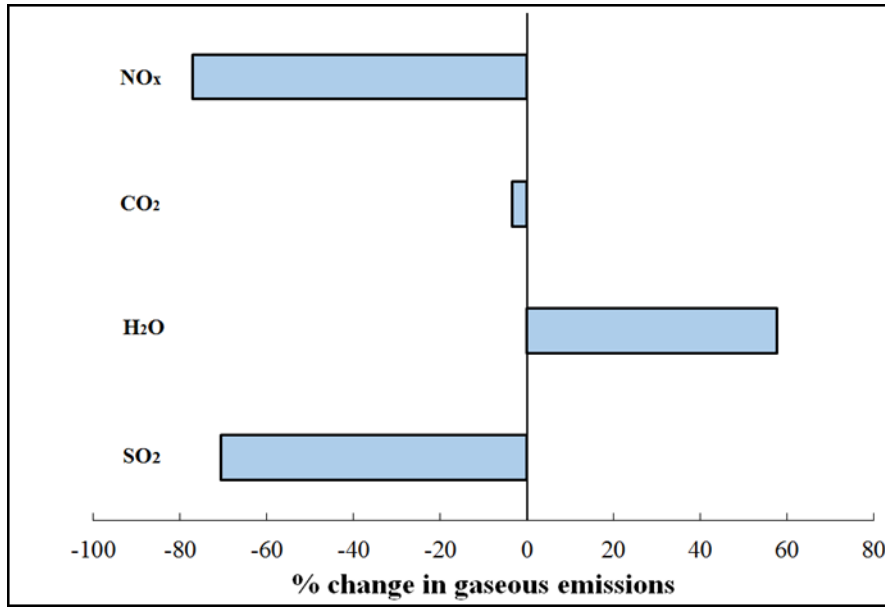


Figure 6. Theoretically expected changes in gaseous emissions from the combustion of TDF based on reported elemental analysis

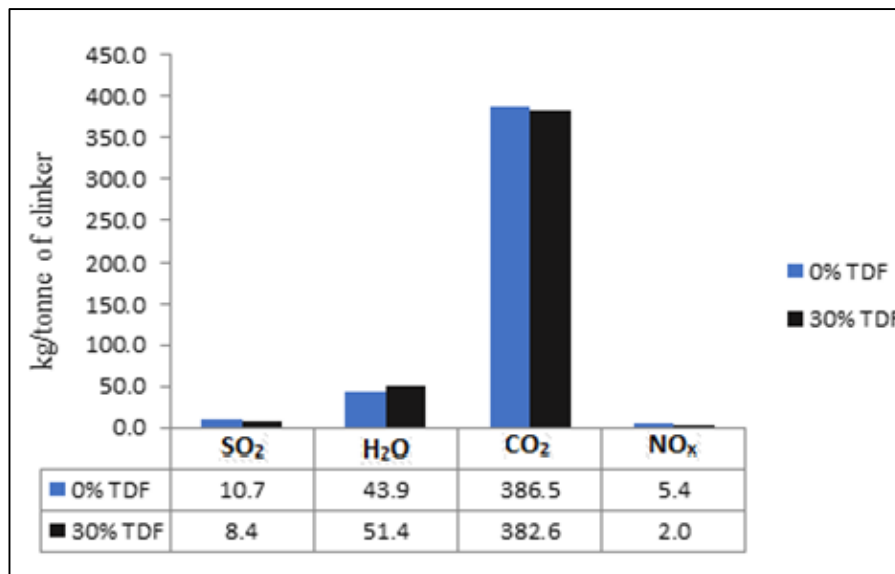


Figure 7. Predicted gaseous emissions from the complete combustion of hypothetical 30:70 blend of tire-derived fuel: coal-coke.

The elemental composition of used tires in Table 10 was used for the calculations on TDF. On an equivalent heat basis, there is an expected 71% reduction in fuel-related SO₂; 77% reduction in fuel-based NO_x emissions; 3% reduction in CO₂ and a 58% increase in H₂O when coal-coke is replaced with scrap tire. Scrap tire or TDF therefore qualifies to be called a Low Carbon Fuel because of the reduction in carbon dioxide intensity. In the case of a fuel blend made up of coal-coke and 30% heat-equivalent TDF, overall fuel SO₂ emissions are expected to reduce by approximately 21%, CO₂ by 1% and NO_x by an estimated 23% with a 17% increase in H₂O as can be seen in Figure 7. 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 this fuel blend due to an expected increase in H₂O emission. Table 15 shows a summary of predicted changes in gaseous emissions for coal-coke-TDF blends.

Table 15. Summary of changes expected in gaseous emissions for two coal-coke displacement with tire-derived fuel scenarios.

Gaseous product	Per 50 MJ	30:70 TDF: coal-coke for 4.5 GJ
SO ₂	decrease	decrease
H ₂ O	increase	increase
NO _x	decrease	decrease
CO ₂	decrease	decrease
Total gaseous emission	No significant change	No significant change

4.1.5.4 Status of tire-derived fuel in Nova Scotia

The major challenges associated with diverting scrap tires to cement kilns as TDF in Nova Scotia are: (1) competing end of life uses of scrap tire and (2) the perception of more harmful emissions. Other alternative uses of scrap tire such as retreading and TDA do not provide enough consumption for the vast numbers of used tires produced annually [104]. As a cost-effective, in-province and sustainable method of tire disposal, and given the current state of

used tire disposal in Nova Scotia, there is potential to use TDF to displace non-renewable coal and coke. Permits have not yet been acquired for full-scale application, and given the extensive review of TDF available in the literature; it has not been studied further in the experimental work.

A report titled: 'Use of scrap tires as an alternative fuel source at the Lafarge cement kiln, Brookfield, Nova Scotia, Canada [105] which was completed and submitted to stakeholders in the course of this research provides a further look at the status of TDF within the province. Table 16 shows a summary of the status of WDF for co-processing in Nova Scotia, which were assessed for this research, and the questions associated with each.

4.2 DESCRIPTION OF EXPERIMENTAL APPARATUS

1. Bench Scale Electric Tube furnace

A Lindberg electric tube furnace, model number 59544, shown in Figure 8 was used for combustion tests. It is 190 cm long and has a 5 cm internal diameter. Temperatures within the furnace reach a maximum set temperature of ~1400 °C. The ends of the hot metal tube are cooled with water flowing through copper tubes. The sample holder is fitted on a long probe fitted with a K-type thermocouple which doubled as a handle for adjusting samples into place in the furnace. Exhaust gas from the sample combustion is swept by air into a metal gas sampling chamber cooled with argon. The end of the tube furnace through which the thermocouple probe runs is clamped shut with an open connection to a dry air supply. The opposite, exhaust-gas end is attached to the primary sampling chamber with a clamp which is unlocked for the introduction of samples.

Table 16. Summary of the Status of potential waste-derived fuel in cement kilns in Nova Scotia, Canada

QUESTION	TDF	PDF	WARS
Is it available in sustainable quantity?	YES	YES	YES
Is there sufficient literature on the characterization of the resource as a fuel?	YES	YES	NO
Is there competition from other end-uses?	YES	NO	NO
Can the fuel be classified a Low Carbon Fuel?	YES	YES	YES
Based on ultimate analysis, are there any concerns on gaseous emissions?	NO	NO	NO
Are there concerns on fuel heterogeneity?	NO	YES	NO
Are there fuel handling and kiln delivery concerns?	N/A	N/A	YES
Phase of implementation	Pending consultation	Preliminary trial permit granted	Full-scale application on-going



Figure 8. Lindberg electric tube furnace for bench-scale emission experiments.

2. Heated grid reactor

A heated grid reactor was designed and built in-house. The hardware comprises a reactor core, the stand, and the sampling chamber. The core is made up of stainless steel blocks placed 3 cm apart and mounted on a laminated fiberglass platform. The platform is fastened to a circular stainless steel base with stands. There is a 1 mm-diameter circular opening at the center of the platform through which the thermocouple is positioned during measurements., K-type bare wire thermocouples of 0.13 mm diameter were positioned through the 1mm opening and centered to be in contact with the mesh during experiments. The electrode leads were designed such that there was a slot allowance in which the mesh could be placed before fastening the screws. Power was delivered to the electrode leads, via 12-AWG, electrical wire connected to a receiving terminal attached to the circular base. The receiving terminals are connected to the main power supply by 8-AWG insulated electrical wire.

A stainless steel ANSI 304 wire cloth which could withstand temperatures up to 1000°C was used as sample holder and resistance heater. The mesh was woven to an aperture of 0.07 mm. For each experiment, a 15 mm × 30 mm mesh was cut, wrapped around a sample and was slotted in between the electrode and the stainless steel blocks where it was screwed in place. The power supply is a Delta Elektronika S6-40 capable of delivering maximum voltage and current of 6 V and 40 A respectively. The stand, a circular stainless steel base, served as support for both the reactor core which is securely fastened to it, and the sampling chamber which can be removed and replaced with ease. The platform also houses channels and connections for power and thermocouple wiring. The sample chamber is made of stainless steel with ports for fitting detection devices. The connecting ports on the sample chamber were fitted with glass wool to protect sensitive detection devices from excessive contamination. The stand, reactor core and sample chamber are shown in Figure 9.

The computer feedback and temperature control shown in Figure 10 ran on LabVIEW using hardware interface data acquisition devices (DAQ). K-type thermocouples provided fast temperature response within the operating temperature range and enabled adequate temperature control. NI-9213, a 16-channel, analog data input module was used to input temperature data obtained from the high response 0.13 mm-diameter, K-type thermocouple in contact with the grid. The LabVIEW Virtual Instrument built included a set-point profile ramp for PID controllers. This made it possible to increase the temperature set-points by a pre-determined ramp rate, which could also include hold times. The power output was controlled by a NI-9263 4-channel, analog output module. Heating rates of 10³ K/s were reached using this set-up and experiments were conducted at atmospheric pressure.

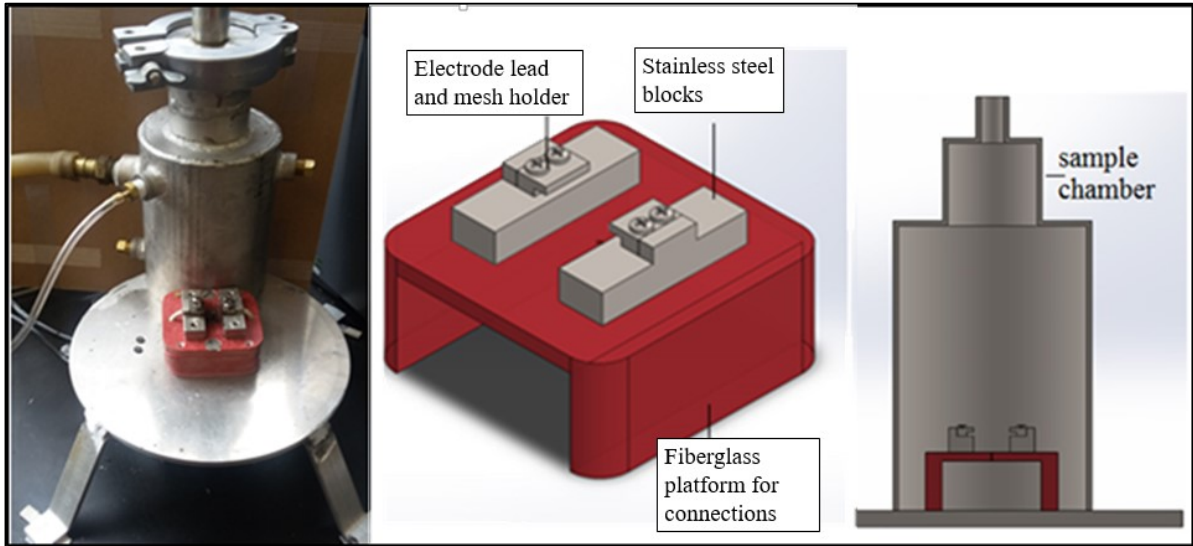


Figure 9. View of the heated grid reactor main block, and the reactor-sample chamber assembly.

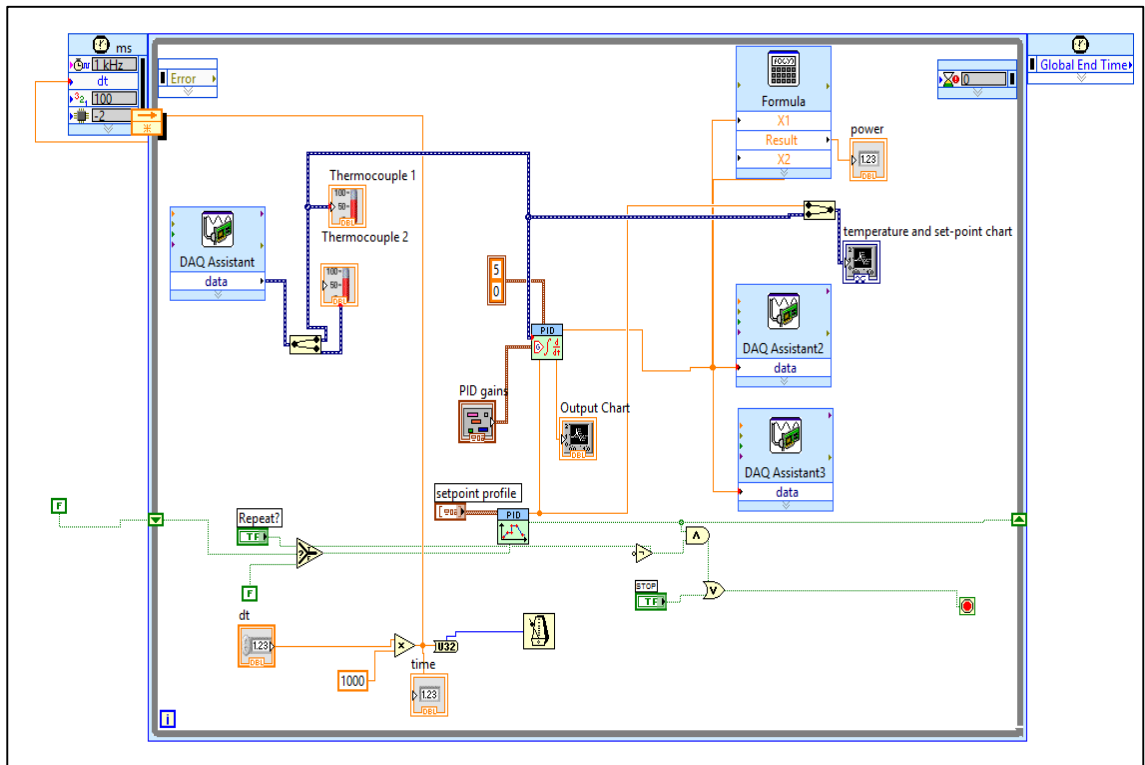


Figure 10. Snapshot of heated grid reactor LabVIEW block diagram showing connections for the feedback and control system.

3. Thermogravimetric analysis apparatus

A Netzsch STA 449 F1 which performs simultaneous differential scanning calorimetric- thermogravimetric (DSC-TG) analysis was used to conduct weight loss experiments on char samples after the combustion tests. All TG experiments were performed at atmospheric pressure using alumina crucibles. The enthalpy and temperature of the DSC were calibrated using samples of pure metals In, Sn, Zn, Al, Ag and Au. The standard uncertainty, u , of the temperature is the larger of $1.5\text{ }^{\circ}\text{C}$ or $u(T) = 0.0025 \times T$. The STA 449 has a TG resolution of $0.025\text{ }\mu\text{g}$.

4. Dylos DC1700 air quality monitor (Dylos)

The Dylos DC1700 air quality monitor is a laser particle counter. It employs the use of a laser to count the number of PM/cm^3 of gas. It measures PM sizes between $0.5\text{--}2.5\text{ }\mu\text{m}$, which are considered in this work as small particles and PM with sizes $> 2.5\text{ }\mu\text{m}$, called large particles. The Dylos has a logging interval of one minute and can store 10,000 data points.

5. Thermal desorption tubes (TDT)

Stainless steel, 9cm-length and 6.35 mm-diameter thermal desorption sorbent tubes (TDTs) were used to collect various VOC's during each sample run. The TDT were packed with Tenax TA, which is a polymer resin suitable for trapping non-polar VOC's between n-C-7 to C-26 in air [43]. A Markes international unity-2 thermal desorption unit, coupled to a Thermo Trace 1300 gas chromatograph that was coupled to a Thermo ELITE ISQ EI mass spectrometer, was used to identify and quantify the VOC's sampled by the TDT.

6. Photron FASTCAM Mini UX100 camera

The Photron FASTCAM Mini UX100 camera provides high speed imaging performance in a small and lightweight camera design. It is able to provide 1.3 Megapixel image resolution (1280 × 1024 pixels) at frame rates up to 4,000 frames per second (fps) and 1 Megapixel resolution (1280 × 800 pixels) at 6,250 fps.

7. Hammer mill

The hammer mill crusher shown in Figure 11, has a capacity of 450 kg of coal per hour using a 4.8 mm-diameter perforated screen plate; 226 kg using a 1.6 mm-screen. The covered feed hopper has a capacity of about 11,000 cm³ (9 kg) and a manual-feed control gate. The rotor-swing hammers for crushing are heat-treated and hardened and the rotor speed is about 3450 rpm. The container is sealed to the discharge spout during milling.



Figure 11. Hammer mill crusher used at Dalhousie University.

4.3 TUBE FURNACE EMISSIONS EXPERIMENTS ON WASTE PLASTIC MATERIALS

This section includes extracts from a full report completed and submitted to Lafarge cement and the Canadian Plastic Industry Association (CPIA) in the course of the research work [106]. A comparative study of different plastic based fuels and blends with coal, petroleum coke were conducted and discussed based on variations in residual VOC, and PM in combustion products collected using the TDT, and the Dylos respectively. Subsequent GC-MS was then conducted on the TDT to determine the abundance of detected VOC's.

4.3.1 Experimental procedure

The heat equivalent of 2 g of coal-coke was weighed for all containers, plastic film, clothing and carpet. The plastic-based materials used for these experiments were from the same batch that was collected and prepared for ultimate analysis in Table 12 . Figure 12 shows a selection of some of the materials before and after preparation. The weighed samples shown in Table 17 were introduced into the pre-heated furnace via the probe-basket assembly to be combusted in the set-up illustrated in Figure 13. The furnace was held at a maximum temperature of 1100°C for the combustion of the samples for a residence time of 3 minutes. Dry air supply at ambient temperature was kept at 10 L/min to sweep combustion products to the exhaust. The exhaust gases were swept by the air into a primary distribution chamber that also serves to cool the exhaust gases. The combustion product samples were collected by devices attached to sample ports 1,2,3 and 4. Argon gas was introduced into the primary chamber at 4 L/min to keep the exhaust gas at temperatures of 50°C and below. This was done to mitigate secondary reactions and also to bring products to temperatures suitable for the particle counter. The exhaust gases then flow into a 6 L secondary plastic chamber where they are drawn into

the particle counter at 1.7 L/min. The secondary chamber was to ensure that concentrations were within the safe limit of the detection for the attached devices. The VOC sample collected at 10 ml/min into the TDT attached to the primary chamber. The other sample ports on the primary and secondary chambers were shut off when not in use.

Table 17. Weights of 2 g, coal-coke heat equivalent for all containers, plastic film, clothing, carpet and C&D plastics used in tube furnace experiments.

Sample	Weight (g)
EPS	1.43
Plastic film	1.43
Containers	1.43
Carpet	2.61
Clothing	2.65
C&D Plastics	1.41



Figure 12. A selection of received plastic based waste (plastic film and plastic containers) before and after size reduction.

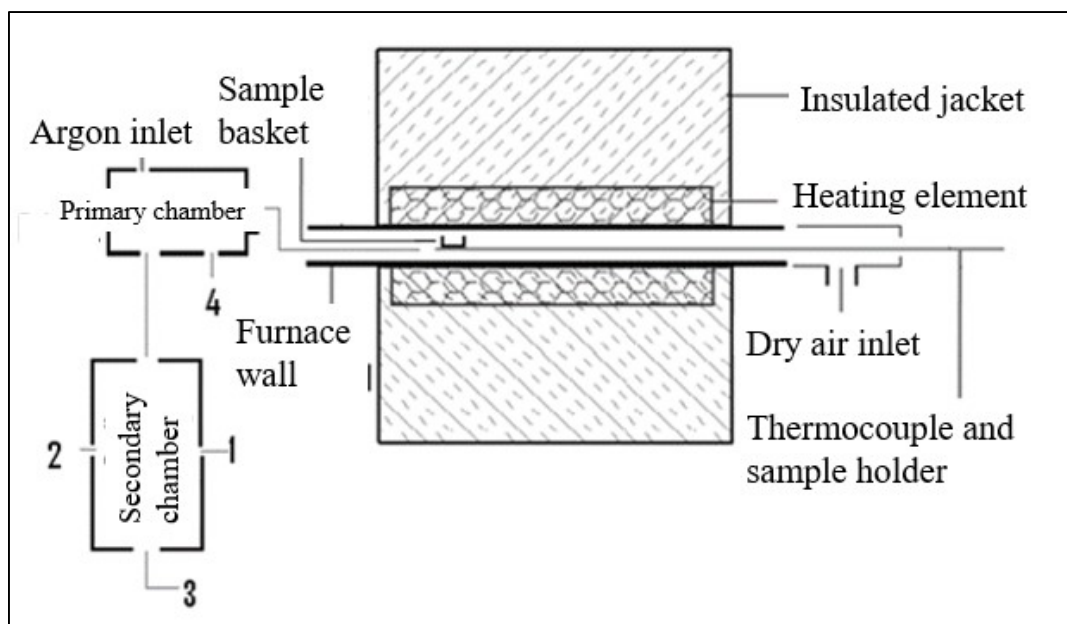


Figure 13. Schematic cross-section of tube furnace and attached sampling chambers used for combustion tests.

4.3.2 Results

Analysis conducted on samples from combustion in the tube furnace obtained using the TDT are shown from Figure 14–Figure 19. The abundance of 27 different VOC species in the exhaust collected in desorption tubes was measured using GC-MS. The number of VOC species detected followed in decreasing order: carpet (21), clothing (16), containers (13), plastic film (4) and EPS (1) as shown in Figure 14–Figure 19. These VOC species would degrade with increasing temperature and gas residence time. They are therefore unlikely to persist in the actual kiln environments. However, the quantity of VOC detected from the combustion of a material under these sub-kiln conditions gives an indication of the extent of the combustion, which is a measure of combustion efficiency. This efficiency can be compared to that of other materials under similar conditions. Carpets recorded the largest quantity (mg-VOC/ kg of sample tested) and EPS recorded the least.

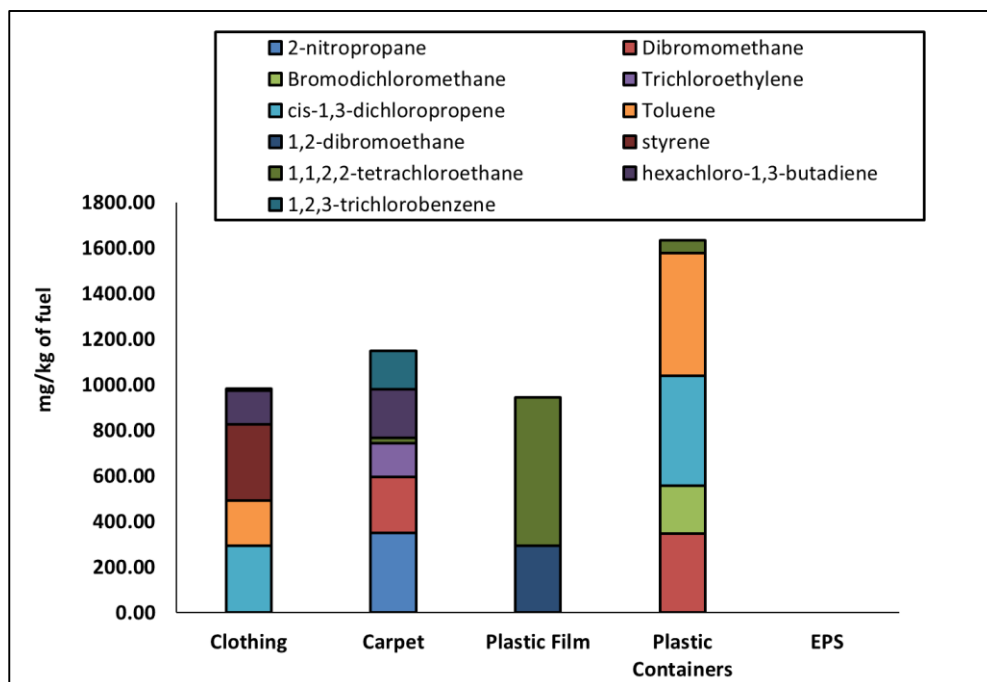


Figure 14. Volatile Organic species detected and measured using gas chromatography-mass spectrometry on the collected exhaust from the combustion of each plastic-based fuel in tube furnace (1 of 3).

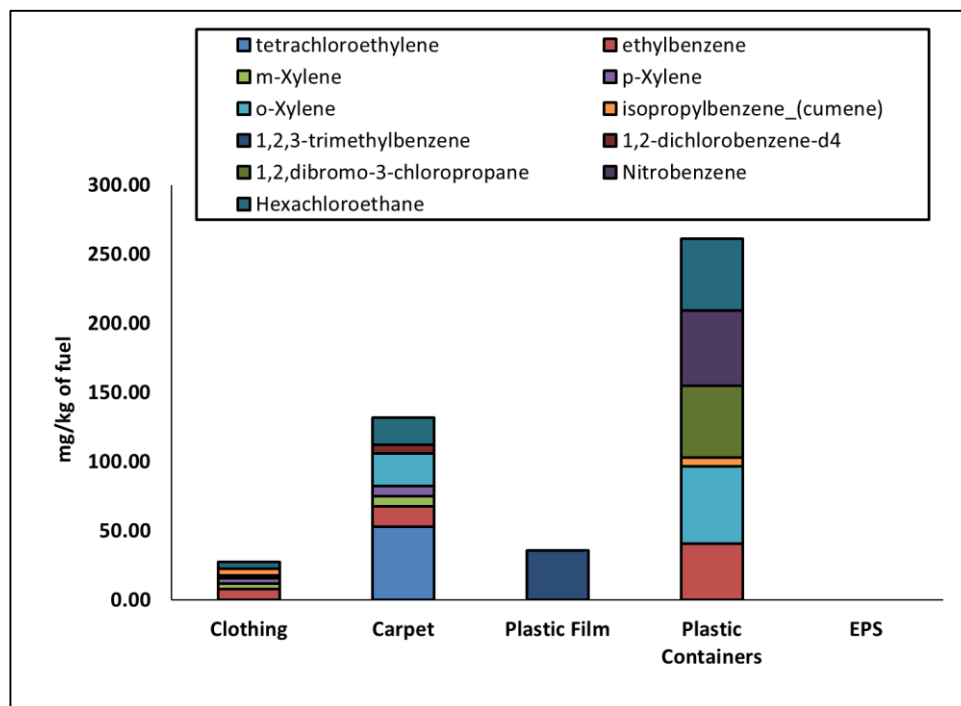


Figure 15. Volatile Organic species detected and measured using gas chromatography-mass spectrometry on the collected exhaust from the combustion of each plastic-based fuel in tube furnace (2 of 3).

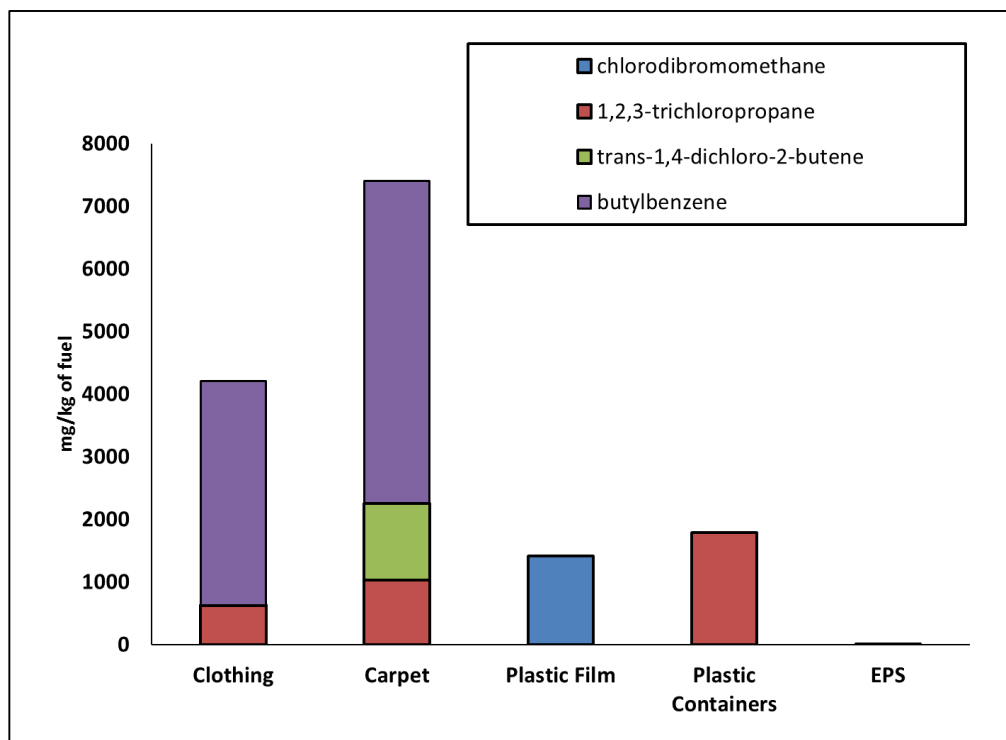


Figure 16. Volatile Organic species detected and measured using gas chromatography-mass spectrometry on the collected exhaust from the combustion of each plastic-based fuel in tube furnace (3 of 3).

Figure 17– Figure 19 are combined plots showing trends of selected characteristic properties of the plastics tested and the quantity of VOC measured. Figure 17 shows trends in VOC emission and energy content of the tested sample. Figure 18 shows trends in VOC emission and moisture content. Figure 19 shows trends in VOC emission and the ash content. The values of the VOC's are reported in mg/kg of sample evaluated in the GC-MS. The calorific value, moisture content and ash content are from ultimate analysis data shown in Table 12.

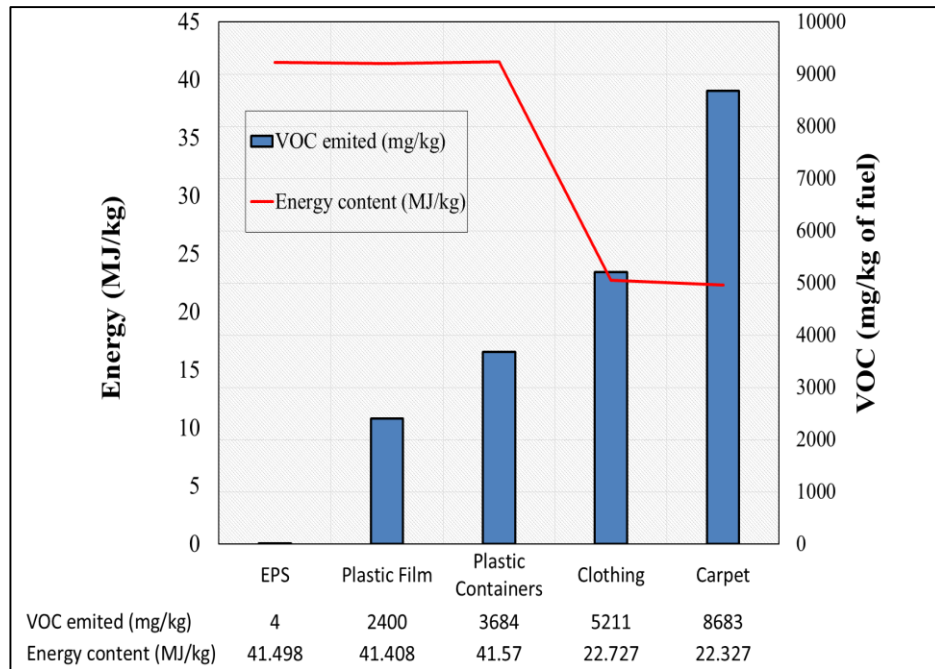


Figure 17. Combined graph of energy content and the total VOC detected for plastic-based material samples tested in tube furnace experiment.

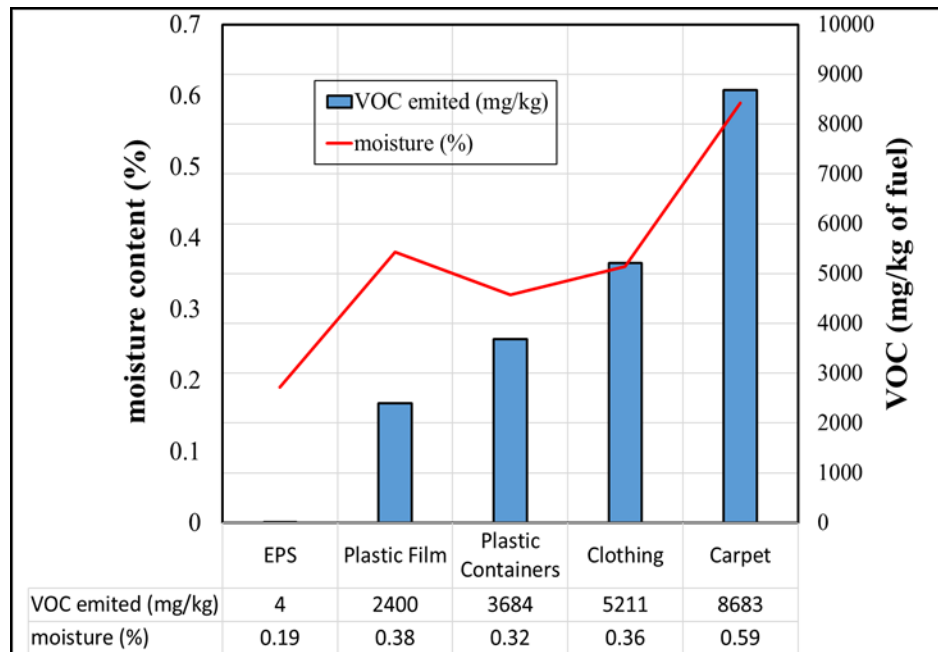


Figure 18. Combined graph of moisture content and the total VOC detected for plastic-based material samples tested in tube furnace experiment.

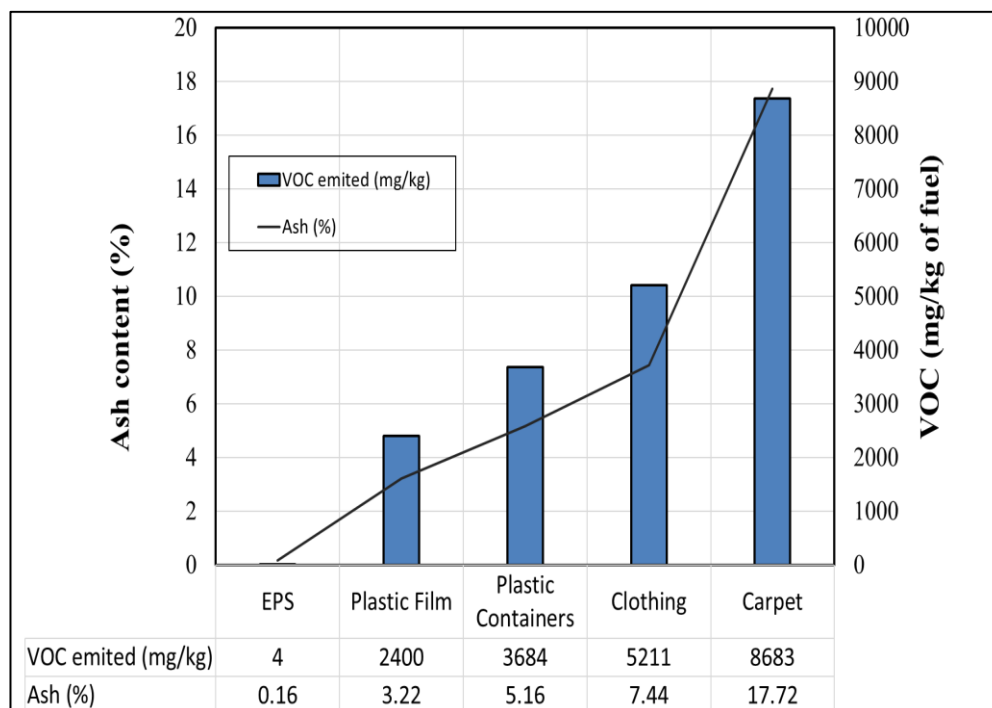


Figure 19. Combined graph of ash content and the total VOC detected for plastic-based material samples tested in tube furnace experiment.

Figure 20–Figure 21 show the count of small (0.5–2.5 μm) and large (> 2.5 μm) airborne PM in the exhaust of the tube furnace during the combustion of the fuel samples. The figures show the number of particulates detected by measuring devices after tube furnace combustion over a 3-minute resident time.

Table 18. Result of the small particles counted in the exhaust from the tube furnace.

Sample	Median	(Min: Max)	Ash (%)
EPS	6,852	(510: 22,599)	0.16
C&D plastics	6,884	(434: 17,589)	7.66
Containers	9,862	(747: 12,372)	5.16
Clothing	10,648	(1375: 10,886)	7.44
Carpet	10,700	(1,918: 15720)	17.72
Plastic film	10,838	(5,978: 17,637)	3.22

The particulate matter was compared on the basis of the median of the data associated with it. The horizontal lines across the box plots represent the median; the box extent represents the 25th and 75th percentile respectively; whiskers represent the 10th and 90th percentiles. Outliers are shown by circles above or below whiskers. For the number of small particulates shown in Figure 20 the particulate counts in the form median (min: max) per cm³ for plastic based fuel samples arranged in ascending order of the median can be seen in Table 18. For large particulates, seen in Figure 21, the count measured is expressed in similar fashion as the small particulate count and written in ascending order of the median (min-max) per cm³ and shown in Table 19.

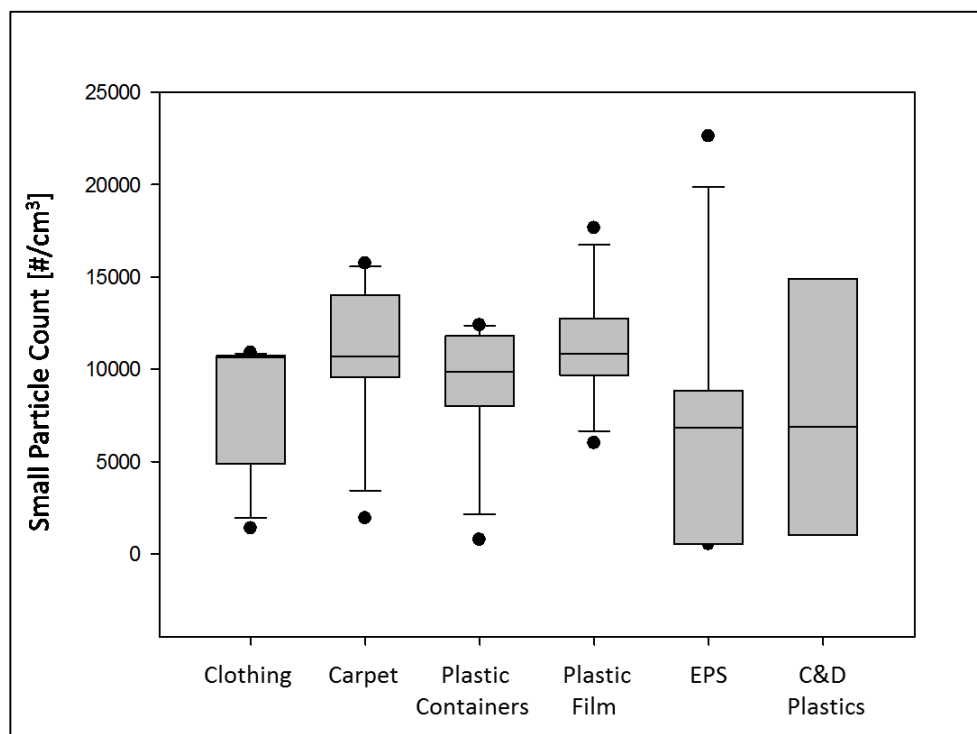


Figure 20. Small particle count #/cm³ of exhaust collected from the combustion of plastic based fuels in tube furnace over a 3-minute residence time.

Table 19. Result of the large particles counted in the exhaust from the tube furnace.

Sample	Median	Min: Max	Ash (%)
C&D plastics:	519	(41: 14,671)	7.66
EPS	2,231	(62: 14,054)	0.16
Containers	4,741	(188: 11,859)	5.16
Plastic film	5,665	(938: 14,013)	3.22
Carpet	7,772	(66: 10,033)	17.72
Clothing	9404	(298: 20,080)	7.44

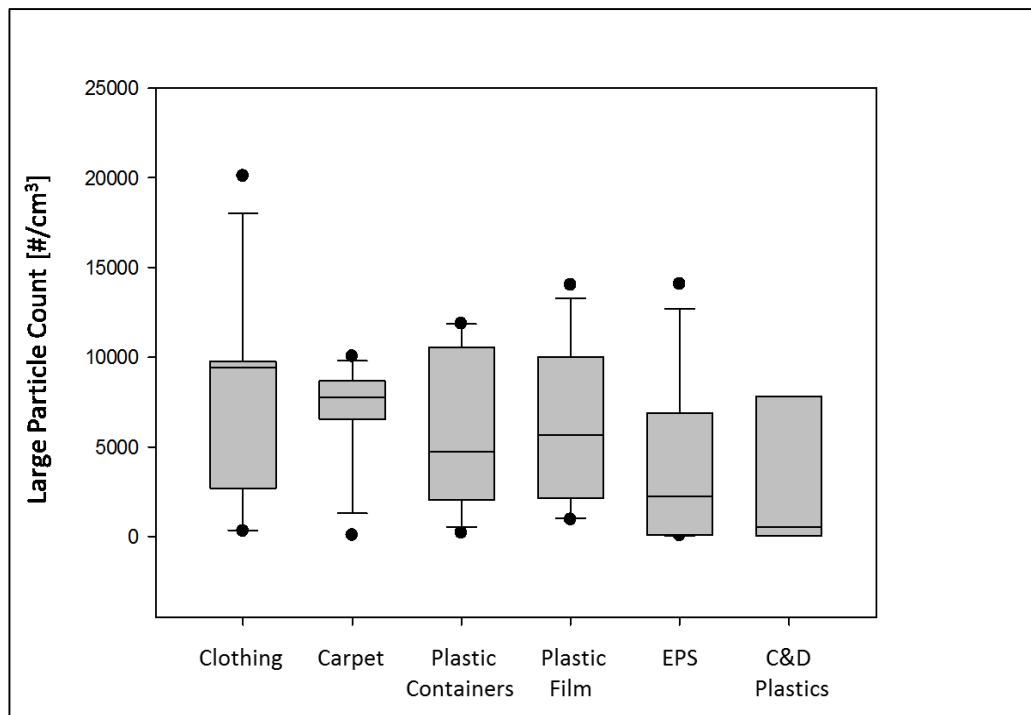


Figure 21. Large particle count $\#/cm^3$ of exhaust collected from the combustion of plastic based fuels in tube furnace over a 3-minute residence time.

4.3.3 Discussion

4.3.3.1 Volatile organic compounds

Compared to coal-coke, most plastic fuels are generally more reactive as a result of their higher volatile matter content. The presence of VOC's in exhaust is influenced by the combined effect of the initial volatile matter content, the rate of devolatilization, and the extent of combustion. These factors depend physically on the temperatures of operation, quantity, size and structure of fuel particles and residence time among others. Though it is difficult to quantify the effect of all these factors from the tube furnace experiments, general trends in VOC emission provide insight into the behavior of waste plastic-based materials under similar conditions for a given residence time. Figure 17–Figure 19 highlight the effects of energy content, moisture content and ash content on the VOC emission trend. Figure 17 shows that the total VOC's detected in the exhaust was less for the samples with energy content above 40 MJ/kg than for samples with energy content below 30 MJ/kg. This could be explained by the fact that higher energy density results in a reduction of the fuel mass required which reduces the potential VOC emissions expected.

As seen from Figure 18, increased moisture content generally resulted in more residual VOC emission. The presence of moisture reduces the thermal efficiency of the fuel by the loss of heat to vaporization. This also means that within a given residence time, the period of moisture loss is extended for the materials with high moisture content, thereby reducing the time and energy available for the oxidation of volatiles after they are released. The reduced thermal efficiency and the loss in oxidation time could explain the relation between increased moisture content and increased residual VOC.

Figure 19 shows VOC emission increasing with increasing ash content. High ash content reduces the thermal efficiency because it represents a fraction of the fuel that does not generate energy and consumes sensible heat. The lowered thermal efficiency then results in the incomplete oxidation of the volatiles with the set conditions. These trends in residual VOC emission match well with the observations made by Ariyaratne, et al. [25] and Ariyaratne, et al. [65] who used simulation and full-scale tests to determine the effect of fuel substitution on kiln gas temperatures and clinker production rate. For the fuels they studied, increased fuel requirement, high moisture content and low ash content generally resulted in increased kiln flue gas, lower kiln gas temperatures and reduced clinker output. The molar H/C had a less direct effect on the trends of fuel performance in the kiln. The agreement of the trends in bench-scale experimental results and trends observed in the full-scale studies discussed in the literature on kiln thermal performance show that the tube-furnace test provides a bench-scale means to develop comparative estimations of expected changes in the full-scale thermal performance with the introduction of a selected PDF.

Among the plastics with energy content > 40 MJ/kg (EPS, plastic film and containers), the physical properties of the fuel seemed to affect the level of VOC emissions. EPS, with a light and aerated structure, recorded very little residual VOC's. Its low structural density allows for better diffusion of heat and oxygen into the particle. The structure also enhances the removal of volatile matter from the core of the particles for oxidation. Volatiles are therefore consumed more effectively within the given residence time. Similar explanations could be given for plastic films, which were less dense compared to the chips of the rigid containers. The presence of inerts and fire-retardant additives used in the production of clothing and carpet are primary reasons why they were less combustible as received.

The results on VOC show that in addition to moisture content, calorific value and the relative abundance of H and C, the physical structure (size, homogeneity and density of the plastic based fuel samples) may also affect the extent of combustion within a given residence time. These results, compared to work by others show that trends in bench-scale analysis of combustion properties such as VOC emission match expectations from elemental analysis and can therefore be used as a screening method for PDF and for that matter selection of other WDF. Tested materials which report more residual VOC in tube furnace tests are likely to reduce thermal performance of the kiln. They can however be blended with other waste materials with efficiency-enhancing properties to compensate for the losses.

4.3.3.2 Particulate matter

The box plots shown in Figure 20–Figure 21 indicate, first, that the particulate emissions recorded in these experiments are not significantly different for the tested plastic samples. A Mann-Whitney non-parametric test on any two data sets confirms this. However, using the median particulate count, some general deductions can be made. Plastics with higher energy content, (EPS, C&D plastics, plastic containers and plastic film) generated smaller amounts of particulates $> 2.5 \mu\text{m}$, compared to carpets and clothing. A higher extent of thermal decomposition and low ash content could have resulted in the diminished presence of large particles during the duration of the test. The effect of increased quantities of shredded carpet backing and used clothing required per equivalent heat was also a main contributing factor. In terms of predictability, even though no very clear trends can be seen, counts of larger particulates generally increase with decreasing energy content and increasing ash content. In the case of smaller particulates, it was observed that the range of the median values are much

closer compared to the range of the median values for large particulates suggesting that the emissions of smaller particulates are more similar for the plastic-based fuels than are the large particulates. PM formation depends on secondary events such as coagulation and condensation; hence they may differ more randomly from sample to sample. The tube furnace data does not provide a clear trend into expected PM emissions behavior from waste plastics. The data however shows that PM emissions do not differ significantly among the samples. This is also expected for WDF in full-scale kilns. Bench-scale observations on PM emissions may therefore, not be an effective screening guide for the selection of suitable WDF.

4.4 HEATED GRID REACTOR COMBUSTION EXPERIMENTS ON COAL-COKE, PLASTIC AND SHINGLE BLENDS

The heated grid reactor was set-up as illustrated in Figure 22, and was used in conjunction with other devices for fast heating experiments. This section describes and discusses these experiments. Mixed plastics, waste asphalt shingles, coal-coke and their blends were tested in this set of experiments.

4.4.1 Experiment on ignition behavior of fuel blends

Samples of coal-coke, waste plastics, shingles and blends of coal-coke with waste plastics and shingles were prepared to a 10-mg coal-coke equivalent heat content. For the blends 30% of the thermal energy required was supplied by either plastics or shingles. The samples and their weights are shown in Table 20. Table 20 contains the mass composition of all samples used in all the HGR experiments. The HGR was mounted in line with the high speed camera as seen in Figure 23. A 5-second heating cycle, including a hold time at 1000°C, was used for these set of experiments. The Photron FASTCAM Mini UX100 high speed camera was used

to record each event at 500 fps. The video playback of the individual runs was synchronized at a speed of 30 fps, and analyzed for the time to ignition.

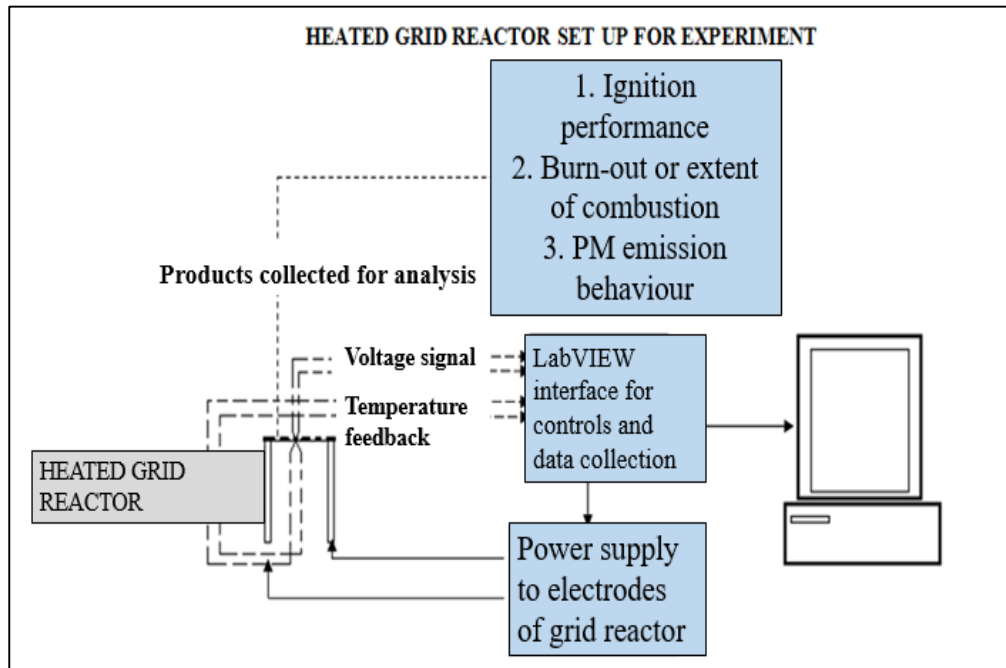


Figure 22. Schematic of Heated Grid Reactor set-up with controls and sample collection devices used in experiments.



Figure 23. Camera-Heated Grid Reactor set-up for fuel blend ignition study.

4.4.1.1 Results

In a test conducted for the single fuels, ignition of shingles after devolatilization occurred 0.960 seconds after heating had commenced, followed by waste plastics with an explosive ignition inside the mesh at 1.358 seconds. Waste plastics however formed a steadier flame than the shingles. Coal-coke ignition occurred last, after 1.472 seconds igniting in a floating plume above the mesh before forming a full flame. The steady flame regime for waste plastic lasted for 3.056 seconds while the flame regime for coal-coke ended 2.968 seconds after heating began. The flame for shingles engulfed the entire mesh due to the downward release of volatiles during the early stages of heating. This could be attributed to softened asphalt seeping through the mesh before and during devolatilization. This was not as noticeable with waste plastics though present to an extent. From Figure 24C, coal-coke char combustion became very prominent between 4.304 seconds and 4.768 seconds after heating began. Minimal combustion activity occurred after the end of flame regime for waste plastics. Some evidence of glowing char or ash was noticed for shingles at this point.

In the experiment with coal-coke-waste plastics blend and coal-coke-shingles blend, a calm primary ignition occurred for the coal-coke-shingle at 1.080 seconds with a more vigorous secondary ignition occurring at 1.318 seconds. A similar primary ignition occurred for coal-coke-waste plastic at 1.270 seconds with a vigorous secondary ignition occurring at 1.280 seconds, a hundredth of a second later. Given that coal-coke only ignited after 1.472 seconds under the same heating conditions, the TTI for the blend is an improvement on that for coal-coke only. As seen in Figure 25B, the flames for the blends and the single coal-coke samples at 1.936 seconds are all steady. They are however larger for the blended fuels than for coal-coke only. Whereas char combustion for the single coal-coke intensified from 4.304 seconds

through 4.768 seconds, char combustion for the coal-coke-waste plastic blend began earlier, at 3.000 seconds, and ended 0.584 seconds later. Char combustion in the coal-coke-shingles blend intensified between 4.094 and 4.582 seconds after heating commenced.

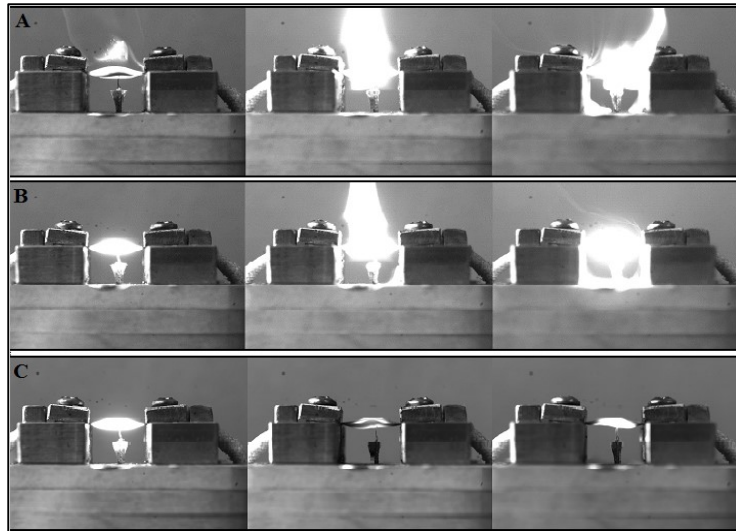


Figure 24. Snapshot from Photron FASTCAM Mini UX100 recording at 500 fps, various stages of combustion for single fuel samples heated at 10^3 K/s to 1000°C for 5 seconds. From left: coal-coke, waste plastics and shingles at A. 1.472 s, B. 2.968 s and C. 4.768 s.

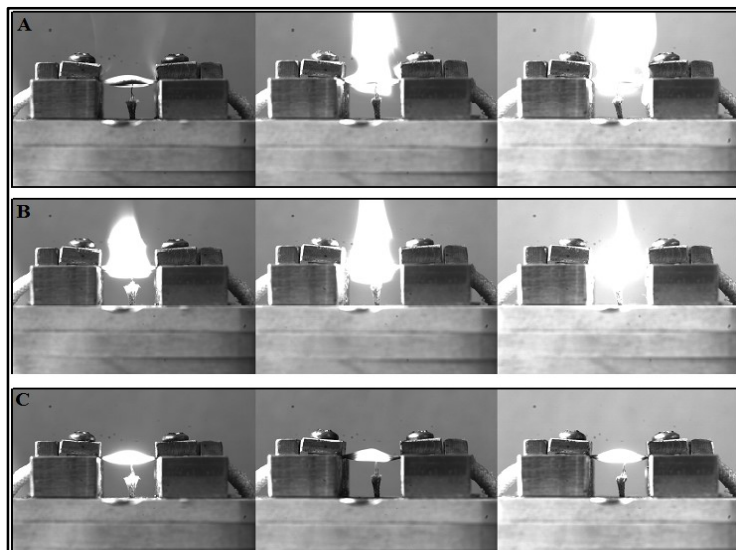


Figure 25. Snapshot from Photron FASTCAM Mini UX100 recording at 500 fps, various stages of combustion for fuel blends heated at 10^3 K/s to 1000°C for 5 seconds. From left: coal-coke, coal-coke-waste plastics and coal-coke-shingles at A. 1.318 s B. 1.936 s and C. 4.768 s.

4.4.2 Experiments on particulate emission behavior of fuels and blends

Three samples of single component fuels and blends prepared to an equivalent heat of 10 mg of coal-coke, with 30% energy contribution from mixed waste plastics and waste shingles as with previous experiments, were combusted in the HGR. A 10-second heating cycle to a maximum temperature of 1000°C followed immediately by a 5 second cool down was applied. The sample chamber was connected to the Dyllos PM counter. Small (0.5–2.5 μm) and large ($> 2.5 \mu\text{m}$) PM count per cm^3 was recorded over a 5-minute period starting at the same time as the heating cycle. The data were averaged for each experiment and used to discuss the PM impact of blending with WDF in the following sections. Figure 26 and Figure 27 are interval plots showing the variability of the PM data collected by the particle counter over 3 sets of experiments for each sample ($n = 3$). The medians for each interval are displayed on the plot.

4.4.2.1 Results

From the interval plots shown for the PM counted, it can be said with 95% confidence that for the given sample size, the behaviour of small particles and large particles from the combustion of coal-coke only does not differ significantly from that of plastics only, shingles only, or their blends with coal coke. There are however comparative inferences which are further highlighted in the discussion section.

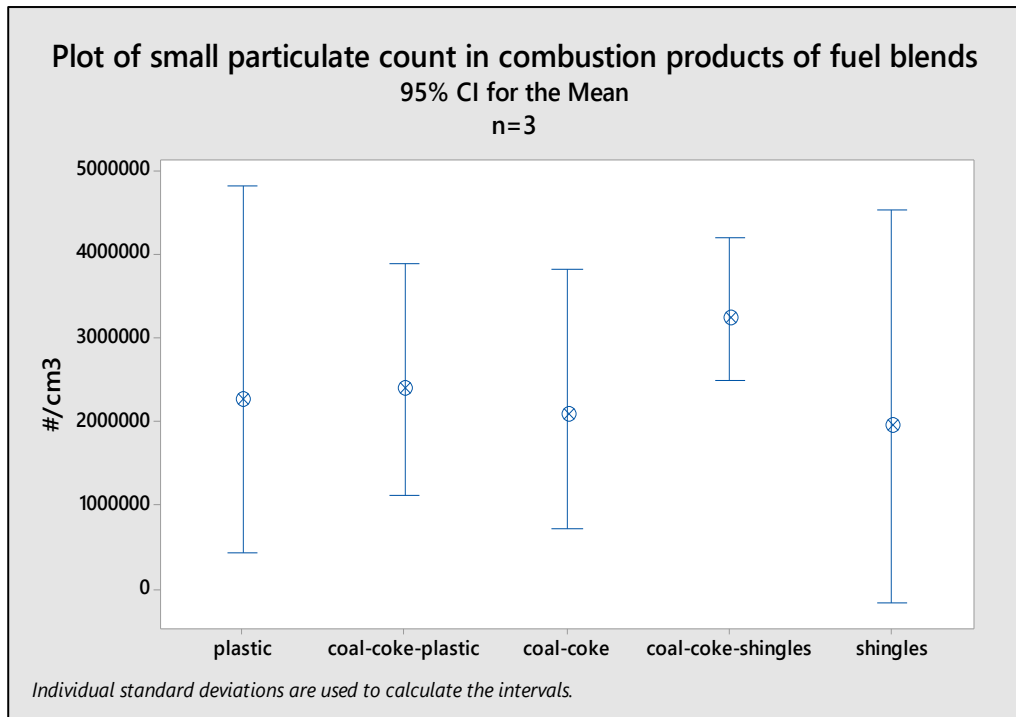


Figure 26. Count of small particles present per cubic centimeter of combustion products of tested coal-coke fuel and blend samples.

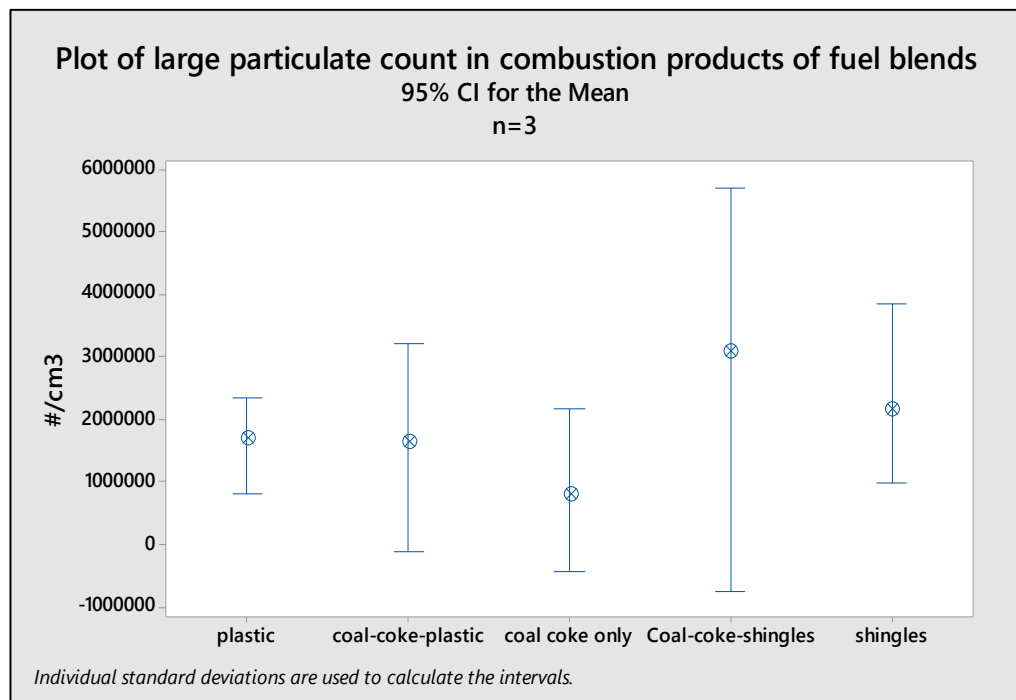


Figure 27. Count of large particles present per cubic centimeter of combustion products of tested coal-coke fuel and blend samples.

4.4.3 Burnout experiments on residual char.

The residual char from the fast heating experiments was collected, weighed and placed in an alumina crucible for TG experiments. The TGA was evacuated to $\sim 10^{-2}$ mbar and refilled with inert gas (99.99 % pure helium) ahead of heating. Samples with a mass between 5–15 mg were heated to 1000 °C at 20 K/min and cooled down with no holding time. The flow rate of helium was maintained at 70 mL/min for the duration of the experiment. The samples were the residual char collected from the fast combustion of fuel blends in the HGR. The samples combusted in the HGR were prepared to a 10%, 30% and 50% energy contribution of the alternative fuel. Shredded LDPE, approximately 2 mm long and 1 mm thick, which was obtained from virgin or parent LDPE plastic, was introduced in this set of experiments. This was to investigate the effect, if any, of downstream processing and the use of plastic products on the combustion efficiency of the waste plastics. The sample composition before HGR combustion and weight of residual char for TGA tests are shown in Table 20. The mass loss vs. time and temperature were corrected to match the calibration of the apparatus and reported in Figure 28–Figure 31. Variations were made in the percentage of the WDF component and the overall mass of the fuel blend combusted, to evaluate their effects on the char behavior in the TGA. The efficiency of the combustion was measured by the burnout attained during the combustion of the fuel blends. The char burnout was quantified by the magnitude of the weight loss experienced by the char in the TGA. Given that TGA experiments were conducted in an inert atmosphere, the loss in weight can be solely attributed to pyrolysis or loss of volatiles. The smaller the weight loss, the more effective is the pyrolysis stage of the fuel blend during the HGR combustion. A larger weight loss in the TGA means a lower char burnout

during combustion, and indicates lower combustion efficiency for the tested blend. An attempt was also made to then estimate the activation energy for the weight loss process observed in the coal-coke char TGA experiment.

Table 20. Weights of samples prepared for the Heated Grid Reactor and TGA experiments with TGA weight loss results.

Sample tested	Weight for HGR (mg)	Weight of char used for TGA (mg)	Weight loss %
Coal-coke only	10	12.37	10.96
Mixed plastics only	7	-	-
Waste Asphalt shingles only	14	10.79	3.40
Coal-coke + 10% energy plastics (LDPE)	9 + 0.7	10.95	2.22
Coal-coke + 30% energy from plastics (LDPE)	10 + 3	10.43	2.61
Coal-coke + 30% energy from plastics (LDPE/mixed)	7 + 2.2	9.14 (LDPE) n/a (mixed plastics)	2.10
Coal-coke + 50% energy from plastics (LDPE/mixed)	6 + 3.6	7.85(LDPE) 5.70 (mixed plastics)	2.90 (LDPE) 4.05 (mixed plastics)
Coal-coke + 30% energy from shingles	7 + 4.5	11.33	3.87

4.4.3.1 Results

The weight losses of the different thermal fractions of virgin LDPE in 10 mg coal-coke blends are shown in Figure 28. The weight loss plot is steeper (10.96% weight loss) for the char of the single fuel than for the char of the blends. The weight loss characteristics of the char collected from the blends did not vary greatly with the change in composition. The 30% LDPE

fuel blend showed the least weight loss (2.10%) over the heating period. 50% LDPE (2.90% weight loss) and 10% LDPE showed 2.22% weight loss. It can be seen that the presence of LDPE at the tested compositions in the blend at all times influenced the combustion of the blends by enhancing the pyrolysis of the coal-coke component and speeding up devolatilization.

Figure 29 shows the comparative weight losses for two chars obtained from the combustion of different masses of 30% coal-coke-LDPE blends. The char obtained from the combustion of 13 mg-blends showed a weight loss of 2.61% which is slightly larger than the weight loss for char obtained from 10 mg-blend combustion experiments.

The weight losses for the char from the combustion of 50% coal-coke-LDPE and 50% coal-coke-mixed waste plastics are compared in Figure 30. The char from the blend made with waste plastics showed a weight loss of 4.05%, while that of the blend made with virgin LDPE recorded 2.90% weight loss. The reduction in the influence that mixed waste plastics had on coal-coke burnout compared with the parent or virgin LDPE, indicates some effect of production additives and everyday use on the thermal efficiency of discarded plastics. Figure 31 shows the weight loss characteristics of char from 100% shingles (3.40%) and coal-coke-shingle blend with 30% shingles on energy basis (3.87%). Both are greater than the weight loss seen for char from only coal-coke. Because the pyrolysis events occur on unburned coal-coke in the residual char whose initial weight is difficult to ascertain from the experiment, the kinetics likely to be obtained for the weight loss of the residual char using any of the non-isothermal approximation techniques presented earlier will not be representative of the kinetics for the pyrolysis fresh coal or petroleum coke samples.

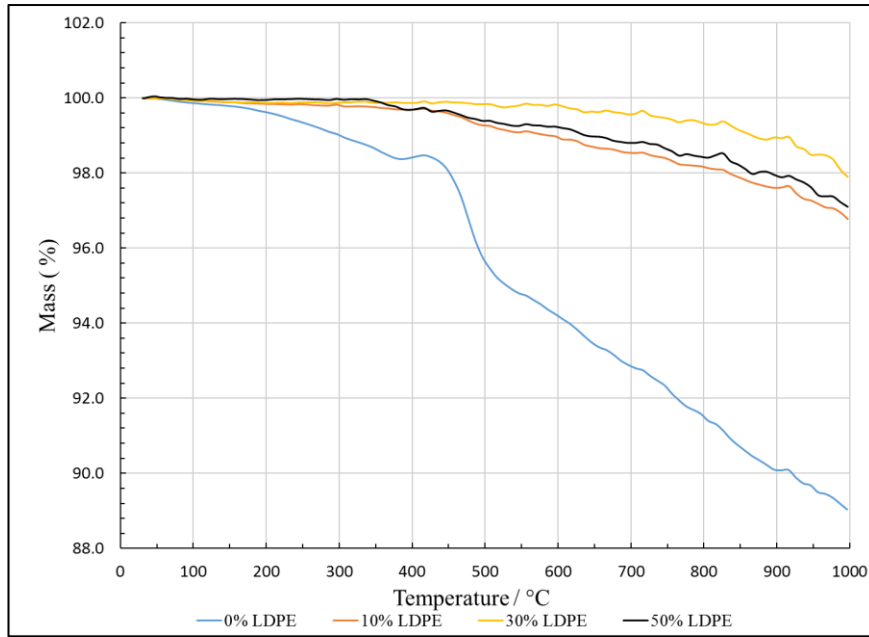


Figure 28. Thermogravimetric plot for the char of coal-coke fuel blended with 0% LDPE, 10% LDPE, 30% LDPE and 50% LDPE after combustion in heated grid reactor.

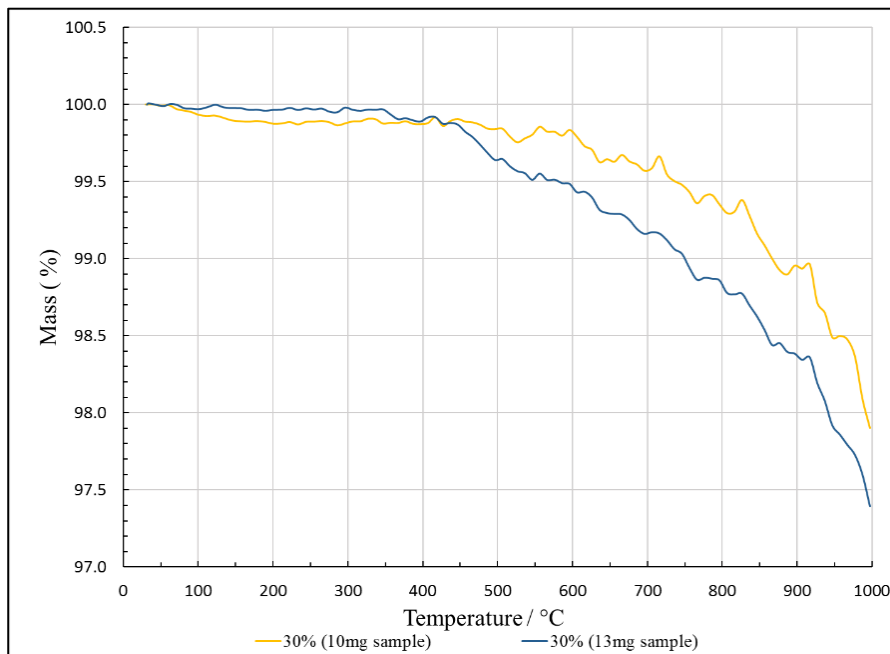


Figure 29. Thermogravimetric plot for the char from the combustion of 10 mg and 13 mg samples of coal-coke fuel blended with 30% LDPE in the heated grid reactor.

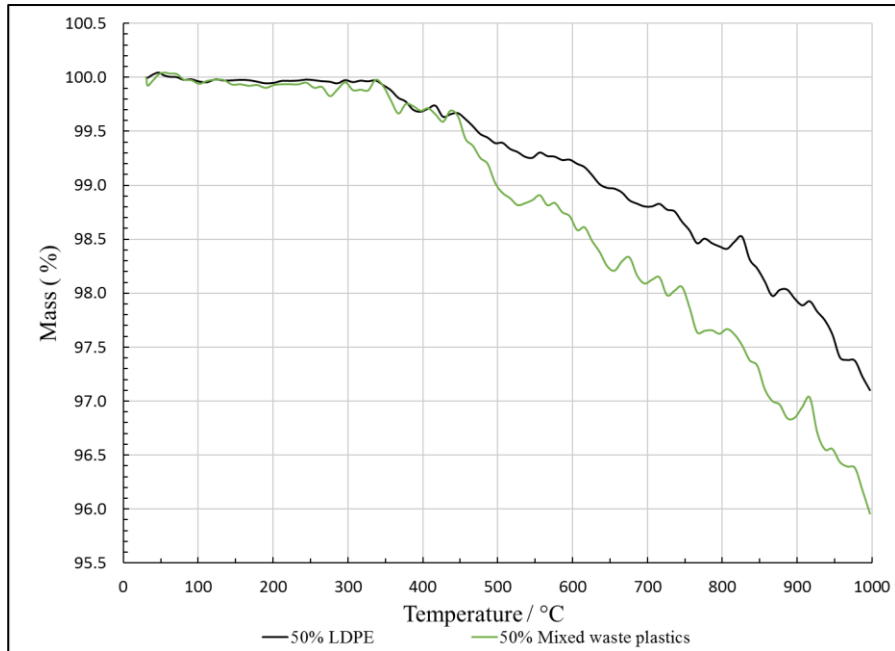


Figure 30. Thermogravimetric plot for char of coal-coke fuel blended with 50% virgin LDPE and 50% mixed waste plastics from combustion in the heated grid reactor.

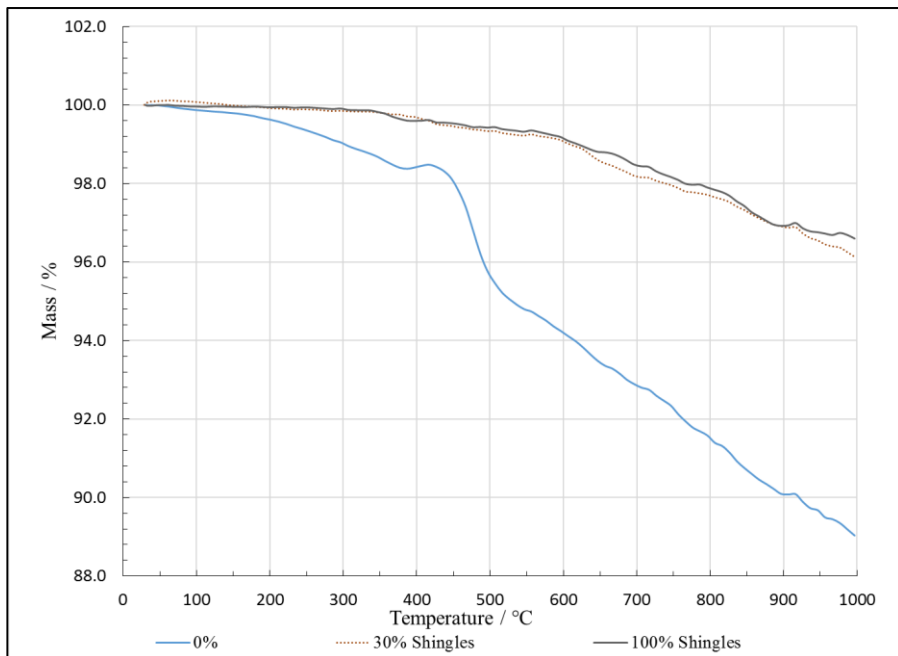


Figure 31. Thermogravimetric plot for the char from the combustion of samples of coal-coke fuel blended with 0%, 30% waste shingles and char from 100% shingles in the heated grid reactor.

4.4.4 Discussion on heated grid reactor combustion experiments

4.4.4.1 Effect of waste plastics and shingles on ignition of coal-coke fuel blends

Time to ignition (TTI) for the coal-coke blends with waste plastics and shingles was approximately 150 to 400 ms less than that of the single coal-coke fuel. Time to ignition values either remained similar or reduced slightly for the single WDF compared to its coal-coke blend, as is seen for coal-coke-plastic blends. For both blends tested, primary and vigorous secondary ignitions occurred. The explosive nature of these ignitions is a result of the increased quantities and rate of volatile release which lead to the formation of very reactive air-fuel mixtures. Improvement on the TTI under fast heating conditions implies that in actual flame conditions, where early devolatilization aids in keeping a steadier flame, fuel blending with WARS and PDF may become beneficial. On the other hand, the explosive nature of the ignitions could present flashback concerns. This can be mitigated by proper design of the fuel delivery system for fuel blends to be delivered in a controlled continuous fashion. A case of flashback was reported in the full-scale trials for waste shingles described later in section 4.5.3. Observations from the bench-scale HGR study therefore, provide information transferrable to full-scale designs for WDF handling in cement kilns.

4.4.4.2 Effect of plastic and shingles on particulate emissions behavior

From the plots generated for PM data in Figure 26 and Figure 27, a review of the median counts for the single fuels and blends shows a mix of additive and synergistic effects of blending. The coal-coke-plastic blend records a median small particle count within a similar range as its single component fuels but shows a reduced spread over the interval, suggesting a synergistic effect. For the large particles of this blend, a similar effect can be seen for the median

values, but with an increased variability in the data. The coal-coke-shingle blend on the other hand, shows a more pronounced increase in the median of small and large particle counts, suggesting an additive effect for the blended fuel. This increase in PM within the measured range could be attributed to more ash residue and the increased mass requirement due to a lower energy density. The effect of PM emissions on health and environment have been discussed in earlier review sections of the thesis. The control and mitigation of such emissions in the case of full-scale cement kilns has also been reviewed.

Given the results obtained on a bench-scale for PM emissions in the HGR, it can be said that, though the variability of fuel related PM emissions might increase with the addition of WDF's, the overall behaviour of PM emissions will not differ significantly from that of coal-coke. This agrees with bench-scale tube furnace observations on PM emissions from different waste plastics. This means under full-scale conditions that no additional PM emission control devices will need to be installed for the use of coal-coke blended with the selected WDF. A proper functioning ESP, as is available at the local cement plant, should handle the PM variability satisfactorily well.

4.4.4.3 Effect of plastic and shingles on char burnout of coal-coke

The joint HGR-TGA experiments were useful in showing the effect of WDF's in the fuel blend as the weight loss for the chars with increased plastic or shingles content was less than for the coal-coke only. The experiments with different proportions of plastics suggest that there may exist a limit to the proportion of WDF used in coal-coke fuel blends for which a substantial gain in burnout will be expected. These limits, if they exist, seem unrelated to the mass of the fuel combusted. Indeed, the weight loss gains made by smaller samples in the

HGR could be attributed more to better heat transfer between the mesh and the fuel particles than to any other factors. Supplying 30% of the energy content of the fuel blend with shingles or plastics enhances the pyrolysis rate of coal-coke. The benefits are reduced for waste plastics compared to virgin LDPE. The presence of plastics and shingles cause coal-coke to devolatilize more in the blended fuel than as a single fuel within the same period. This occurrence agrees with Sami, et al. [13] who suggest, based on the relation for combustion efficiency shown in Eq. (2), that a blend becomes more efficient if the supplementary fuel is richer in volatile matter. Furthermore, the combustion efficiency is enhanced if, when compared to the conventional fuel, the supplementary fuel achieves greater char burnout under similar conditions. Volatile content of the waste-derived fuel studied in this work ranged between 65% and 90%, which is greater than what is reported for bituminous coal and petroleum coke; hence the observed results.

In the case of plastics, Sushil, et al. [66] mentioned in their work that the presence of plastic contributed to increased burnout because the rapid release of heat by the combustion of plastic volatiles modified the coal char structure, making it more reactive. The high speed images taken during the HGR combustion experiments gives credence to this assertion. Due to the early onset of volatile combustion and the extended flame burning regimes for the WDF's, it is possible that there is increased heat transfer to coal-coke, causing it to thermally degrade faster in the blended fuel.

Tchapda and Pisupati [107] have reviewed the literature on co-conversion of coal and biomass or waste and have discussed chemical interactive mechanisms which explain the possible synergistic behavior observed by several workers on fuel blends during combustion or gasification. They mention that synergistic effects are usually observed in the devolatilization or

pyrolysis step. They further indicate that the working explanation for such effects is the interaction of free radicals and the donation of hydrogen. Sjöström, et al. [108] proposed the following mechanisms for this occurrence after observing the co-gasification of biomass: (1) weaker covalent bonds and the higher content of oxygen lead to early reaction, releasing volatiles which break down and release free radicals or which undergo combustion reactions where oxygen is present in the system. (2) the free radicals react with coal and enhance its decomposition. (3) the gases resulting from cracking of the heavy volatiles and light volatile molecules are rich in hydrogen, which react with coal's free radicals as hydrogen donors, thereby preventing recombination reactions and reducing the amount of less reactive secondary chars. The explanation of free radicals and the donation of hydrogen can be adopted to explain the present results since the WDF (waste plastics and shingles) used in these current experiments contain more oxygen and hydrogen than the coal-coke fuel and also contain large amounts of volatile matter. It is also possible that for shingles and plastics, the softening or melting of the solid in the early stages of heating provides less restriction to the release of the volatiles compared to coal-coke, leading to better devolatilization.

The possibility of beneficial micro-scale synergistic effects of the use of WDF has been shown through bench-scale HGR experiments. The thermogravimetric weight loss of the chars obtained from the combustion of fuel blends with coal-coke and WDF was noticeably less than the weight loss of single coal-coke char samples. The blends were shown to have obtained better burnout for the traditional fuels by improving the pyrolysis rate. This phenomenon has been observed and explained in the literature as the possible result of the increased volatile content, the presence of inherent oxygen to speed up WDF reactions, and the presence of hydrogen which inhibits re-condensation of free radicals. High speed camera observation of

the combustion of mg-samples of single fuels and blends with WDF in the HGR also showed improvements in the TTI of the blends with PDF and WARS, thus confirming the proposition that the WDF is likely to boost combustion efficiency when introduced into cement kilns. Observations made on emissions suggest that fuel-related PM emissions will not significantly differ if the WDF's studied were used to displace 30% of the thermal energy required in a kiln.

4.5 FULL-SCALE KILN DELIVERY TRIALS FOR INCREASED USE OF WASTE SHINGLES.

A major challenge facing the increased use of WDF's, which have been shown to be beneficial in fuel blends, is the efficient and safe delivery into the cement kiln. Field-scale trials on an operating cement kiln were conducted at the Brookfield cement plant over a cumulative one-year period covering two internships (April 2011–March 2012). A full report was completed and submitted to RRFB in the course of this research work as Asamany [109]. Information on parameters of cement production and their response to the changes made in shingles delivery were observed during the trials. After a careful discussion of the results, useful recommendations are made for processes and equipment that will make an increase in the use of shingles technically feasible. Short-term and long-term innovations based on the results of field trials are then discussed.

As seen in Figure 32, pulverized coal (PC) is transported from the PC bins to the Pfister feeder that volumetrically controls the supply of ground coal based on oxygen level in the furnace. A supply of air through a manifold transports the coal to the burner pipe where it is introduced under pressure into the kiln via the burner pipe. Fuel handling and delivery methods that could practically lead to an increase in the quantity of asphalt shingles introduced into the kiln were

tested. Three main types of trials were conducted with variations based on their short-term and long-term applicability:

1. Size reduction of WARS for improved kiln deliverability with existing burners.
2. Modification of burner arrangement to increase consumption of larger WARS particles.
3. Combination of size reduction and burner modification techniques.

An estimate of the potential increase in waste shingle use was obtained and used in ranking preferable fuel delivery approaches. Figure 33 is a simplified diagram showing locations selected for delivery tests and Figure 34 is a flowchart summary of all the kiln delivery trials based on the strategies proposed.

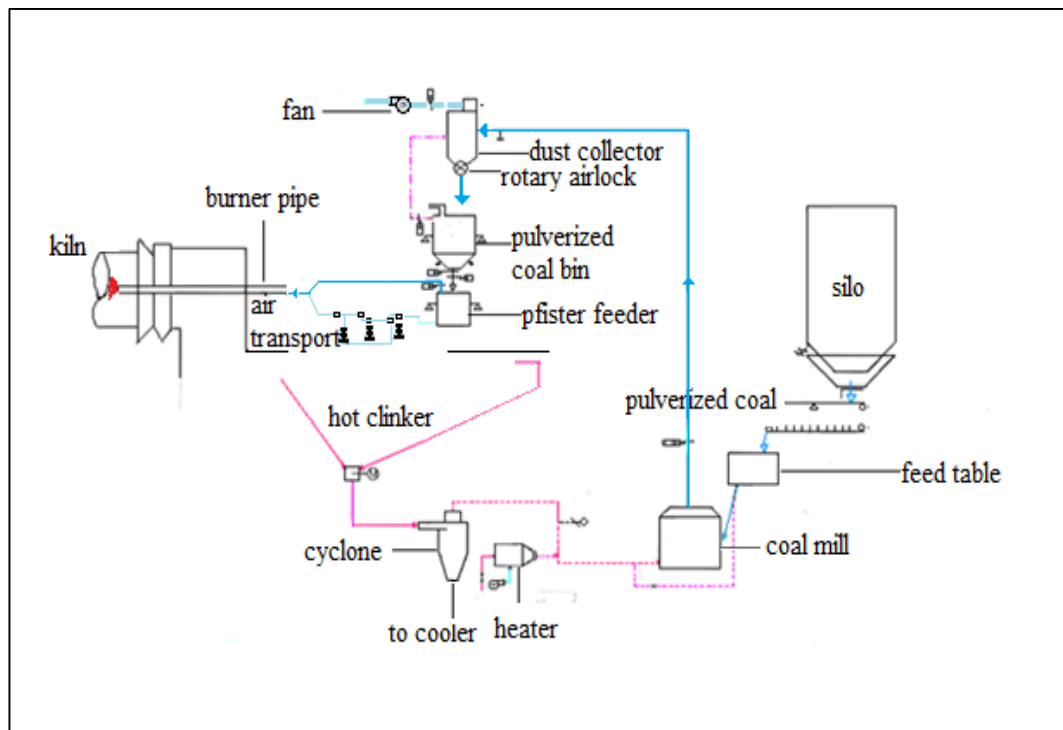


Figure 32. The fuel handling and delivery system for coal and coke as used at the local cement plant.

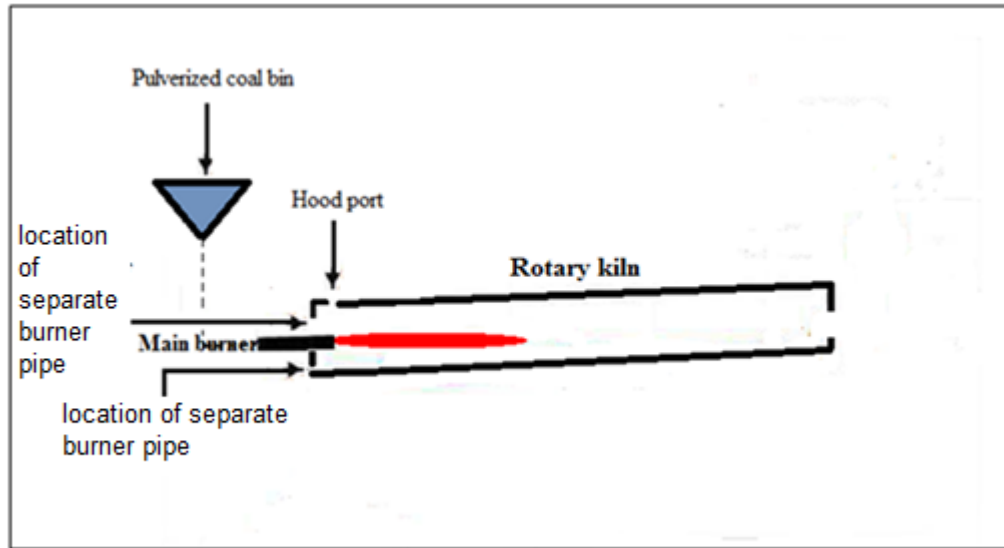


Figure 33. Simplified diagram showing the locations selected for the full-scale tests on the delivery of shingles into cement kiln.

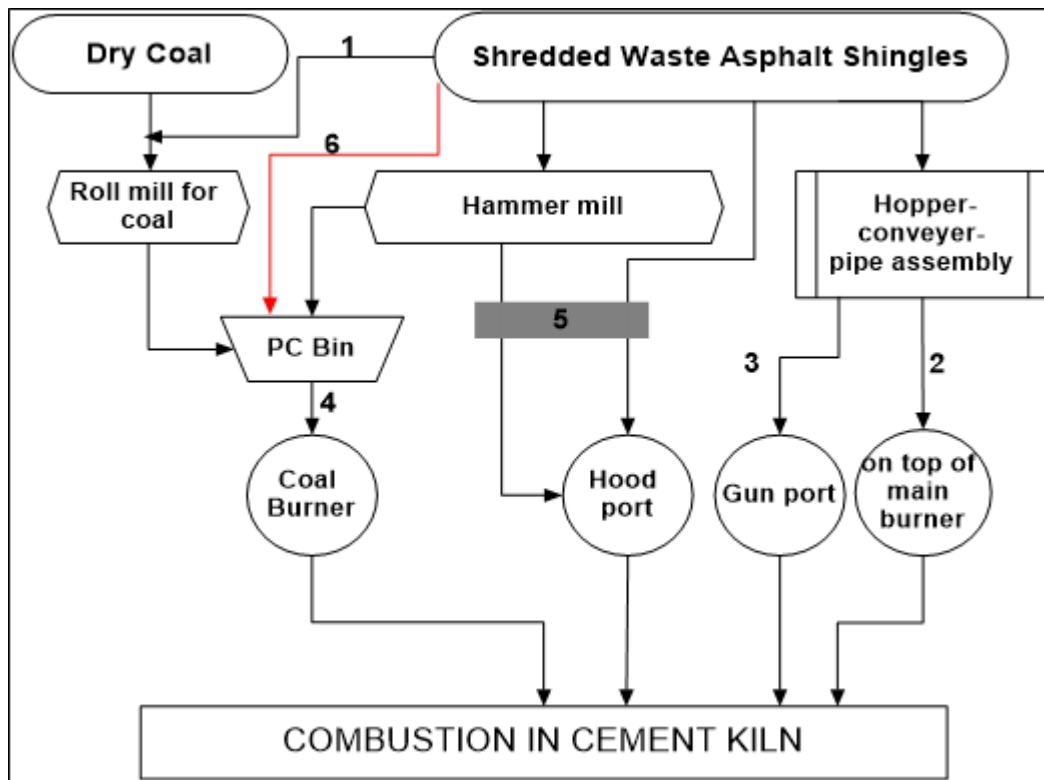


Figure 34: Flowchart summarizing various waste shingle delivery approaches tested: 1. Joint size reduction 2. Separate burner on top of main burner 3. Separate burner through gun port, 4. Mixing size-reduced shingles in PC bin, 5. Delivery through hood port 6. Failed attempt to mix shingles as received in PC bin.

4.5.1 Tests on size reduction

The first test was to introduce a measured quantity of shingles into the coal mill to be size-reduced with dried coal. The second set of size reduction tests on shredded asphalt shingles was undertaken with a separate hammer mill off site. The hammer mill was used to reduce the size of air-dried, shredded shingles obtained from the cement plant. This was to ascertain whether separate milling would yield results significantly different from co-milling.

4.5.2 Tests on burner placement

The shingles used in these tests were as-received (2 cm) with no further milling. An improvised conveyor and delivery system for the WARS which comprised a hopper and conveyer as used for WARS delivery. The conveyer discharged into a venturi feeder which fed the air-solids mixture at pressures adequate to overcome losses going upstream into the kiln. The picture of the conveyor set-up is shown in Figure 35. In one set of trials, the improvised delivery system delivered WARS into the kiln via a separate burner pipe located on top of and aligned with the main burner. This was monitored and evaluated for quantity of WARS used on a monthly basis. The separate pipe, seen in Figure 36, comprised a steel pipe sized and cut to desired length and insulated to withstand the high temperatures.

In a second approach, the improvised delivery system delivered WARS as received by means of a short, separate burner pipe through the gun port of the rotary kiln. This approach was also evaluated for monthly consumption of shingles. The gun port is an access point through which an industrial shotgun may be fired to free clinker build-up at the front of the kiln, or to break-up a large ball of clinker formed in overheated conditions. The gun port is located to the lower left corner of the main burner pipe as shown in Figure 33.



Figure 35. Improved hopper and conveyor assembly for delivering shingles as received.



Figure 36. Separate burner pipe constructed to be used for shingle delivery into kiln.

4.5.3 Combined size reduction and burner placement tests

These tests were conducted on short time scales in the order of 1–2 hours to observe changes in kiln parameters such pressure in the transport air and kiln oxygen levels. Based on experience from previous approaches and a researcher-operator brainstorm session, an approach to deliver coal and shingles together through circuits in the main burner pipe without co-milling was pursued. Two variations of each proposed test were conducted. The first was with shingles as-received and the second was with size-reduced shingles collected from the hammer mill. These variations were conducted to ascertain the necessity or otherwise of size reduction for the particular delivery choice.

The Pulverized Coal (PC) bin was chosen as a convenient mixing station for the first trial. The bin holds about 2.5–3 tonnes of material which empties into the Pfister feeder where a 30 kPa air transport system carries it from the manifold into the burner pipe. A capped opening beneath the PC bin rotary air lock was selected as an entry point into the PC bin. The shingles fell directly under the influence of gravity and suction due to lower pressure into the PC bin. To determine whether there were any size restrictions for the shingles downstream the PC bin a controlled field trial was performed with a rigorous risk assessment, hazards identification and emergency response plan. Trials were conducted using a bucket each of shingles as-received and size reduced.

In the second trial, a bucket each of hammer-milled shingles and shingles as-received and size-reduced were introduced over a short time scale into the kiln via a hood port at the burner end of the kiln. The hood port is on top of the kiln burning zone. This was to see if the shingles as-received would gain better combustion by staying longer in suspension when introduced through this port. The trials required an improvised funnel to allow delivery into the kiln.

4.5.4 Results

4.5.4.1 Size reduction trials

By mixing coal and shingles in proportions before milling it was easier to determine the proportion of shingles in the fuel mix since these ratios were predetermined before crushing. This approach also removed the need for any new equipment. It was conveniently implemented on site. During the implementation of the co-milling approach, however, the bowl mill occasionally got clogged with large lumps of milled product which was a result of the ‘softening’ of asphalt shingles at the slightly elevated temperatures inside the mill— approximately 50°C. Removal of these lumps meant a loss of coal and loss of production time. The mixed milling process was only manageable with about 5% shingles by mass in the fuel mix. Given that the major size reduction impediment observed from co-milling was the large lump formation, the success of the separate milling was evaluated for the percentage throughput and the residence time in the hammer mill for the shingles at ambient temperature.

The results of size reduction trials show that separate milling of the shingles under ambient conditions could eliminate the problem of softening. Results obtained from separate milling experiments displayed in Table 21 show that single run trials using decreasing screen size in the hammer mill increased residence times but did not significantly affect the percentage throughput. The granulometry also shows that single run trials yielded shingles with comparable size distributions to the trials, which involved secondary milling. This was because of clogging which occurred when fine shingles had longer residence times in the hammer mill, thereby reducing the efficiency of the two-stage milling approach. Trial 2 using 1.5 mm screens yielded better size reduction (44% < 1 mm-mesh) than trial 1 using 3 mm screens (37% < 1 mm-mesh) with little loss of time— approximately 5 seconds.

Loss of time was generally a result of screen clogging during milling. Single run milling yielded more satisfactory results than two-stage runs. This is because double runs involved milling smaller sized particles which had greater tendency to clog screen pores at the onset of the milling process.

4.5.4.2 Burner placement trials

When a separate pipe for shingles as received was placed above the main coal burner, there were noticeable fluctuations in stability and flame shape. Differences in the delivery velocities of the venturi feeder and the air transport for the main burner would account for these fluctuations. At its peak, however, this method combined with the co-milling of shingles and coal led to an average coal substitution percentage of approximately 10% by mass over eight months. The monthly maximum was 16.9% as shown in Table 22. The improvised separate pipe was unable to handle the high kiln temperatures over the extended period. The pipe got warped with extensive use due to the continuous expansion and contraction of the stainless steel pipe. The refractory construction for the pipe was inadequate for the prevailing temperatures and was unable to maintain pipe's structural integrity over long periods in the kiln.

The location of the gun port did not provide much time for shingles to burn in suspension so some of them settled on the clinker surface and continued burning. This contributed to unfavourable localized reducing conditions exiting the kiln. Because the gun port location was relatively cooler than the area around the main burner, there was no reported deformation of the burner-pipe.

Using the gun port for the delivery of shingles as received yielded a maximum monthly substitution of 12.2% by mass. Figure 37 shows the clinker production in October 2011 with the use of waste shingles through a separate burner pipe. Production peaked and stabilized at 900 tonnes of clinker/day.

Table 21. Products from four trials of size reduction experiments of shingles in hammer mill.

Parameter for shingle particles	Trial 1 3 mm screen	Trial 2 1.5 mm screen	Trial 3 <1 mm screen	Trial 4 3 mm followed by <1 mm
% throughput	98.66	97.66	84.03	95.05
Retained material	light plastics	plastics and aggregate	Shingles as-received	Clogged fine material
Residence time	14–28 s	20–38 s	120–180 s	Over 5 minutes
% through 1 mm mesh	37.11	43.69	38.10	31.74
% through 3.35 mm mesh	97.70	100	100	99.90

In summary

1. Production was kept at appreciable levels over this period. ~900 tonnes of clinker per day was produced and maintained and emissions did not significantly differ.
2. Generally, the separate shingle system approach recorded higher substitution performance compared to the other trial conducted over long production periods.
3. A more durable separate pipe would be required for a long term application.

Table 22. Summary of results for amount of shingles used and observations made in trials.

Trial and Brief description	Highest % substitution by mass (monthly)	Comments on set backs
Industrial scale tests conducted over long production periods (months)		
1. Co-milling and delivery through coal burner	~5 %	Softening of shingles-coal mixture leading to loss of time and fuel.
2. WARS as received via pipe placed on top of main burner	16.9 %	Incomplete burning of suspended shingles
3. WARS as received via short pipe connected to the kiln gun port	12.2 %	Shingles fall and burn on clinker surface
Tests conducted over short time scale (hours)		
4. Mixing of shingles with pulverized coal in Pulverized Coal (PC) bin		Clogging of channels with shingles as received. Successful with hammer milled shingles
5. Delivery of shingles via kiln hood port		More successful with hammer milled shingles than as received but with some flashback concerns.

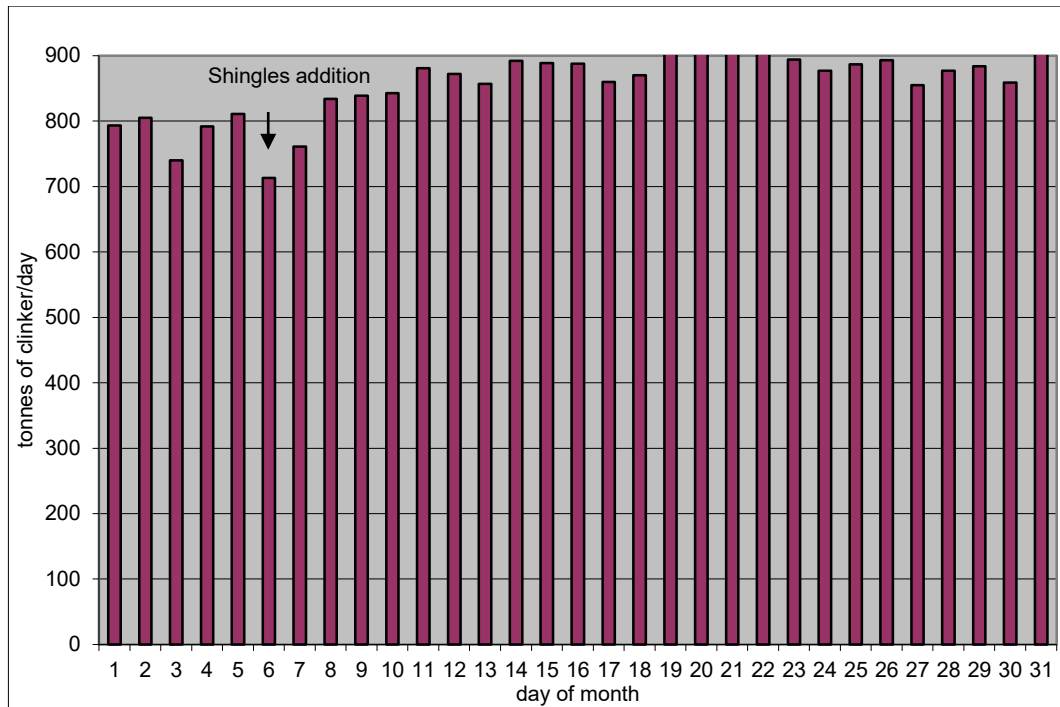


Figure 37. Clinker production in October 2011 with the introduction of waste shingles production peaked and stabilized at 900 tonnes of clinker/day.

4.5.4.3 Combined size reduction and burner placement trials

These trials were conducted over short time scales (1–2) hours because they posed a risk to production losses if they were to fail mid-test. The plant was only available for a short window of time within which these tests were to have been completed. For the trial where shingles as received were delivered through the PC bin and into the main burner pipe, a sharp oxygen spike accompanied with a sudden drop of air pressure indicating fuel cut-off was encountered. The large shingle sizes encountered restrictions in the Pfister feeder and the main burner pipe. Back-up bunker fuel oil was used to maintain production while extensive clean-up of the coal delivery circuit was done. When shingles were size-reduced and delivered the same way, no incident of clogging was encountered.

For similar short time scale trials using the hood port as the delivery point, the observation was that when shingles were delivered as received, they settled directly on the burner pipe and were not effectively transported into the flame as hoped. Due to incomplete burnout during the period the particles were suspended, the shingles continued burning with visible flames all the way into the clinker cooler which was undesirable. Using size-reduced shingles in a similar test increased the rate of burnout. It however resulted in flame flashback as a result of increased ignitability of the shingles and the imbalance between the fuel feed rate and the burning velocity of the flame, thereby posing a danger to operators. There did not seem to be any significant increase in suspension times for the size-reduced shingles. There was however an absence of visible flames on the surface of clinker that was exiting the kiln. The combustion was therefore more extensive for the size-reduced shingles in the burning zone.

4.5.5 Discussion

For the three main approaches conducted over months of production, the highest coal substitution rate was reached using a separate pipe placed on top of the main burner pipe. This approach yielded a high of approximately 17% substitution of coal by mass representing 11% of the thermal energy input. The highest substitution rate attained using the gun port for delivery was approximately 12% by mass (8% of thermal energy input) which are both improvements on the mixed-milling of coal and shingles at 5% by mass or 3% of thermal energy required. During the implementation of the long-term trials, clinker production levels were maintained and no adverse emissions were reported. The maintenance of production levels is a good indication that at the substitution percentages reached with WARS, the thermal efficiency of the kiln remained stable and in some cases could have increased.

This result is in agreement with predictions made from the bench-scale tests on the properties of WARS and its effect on the combustion efficiency of coal-coke-shingles blends.

From the short-term trials also, helpful deductions can be made on future applications of WARS. Since the trials where size-reduced shingles were introduced into the PC bin, gave the better outcome in terms of kiln performance, the approach is preferred to delivery via the hood port. Additionally, in terms of safety and ease of monitoring, delivery via the PC bin outperformed delivery via the hood port. The flashback concerns encountered in the trials with size-reduced shingles via the hood port agree well with the observations of vigorous ignition observed in bench-scale combustion tests. Though the PC bin approach is preferred, applying it successfully comes with additional requirements for size reduction. In this regard, the size reduction tests conducted showed that reducing shingle particles to 1–3 mm diameter without lump formation was possible. An improved long-term strategy is therefore to design a separate milling and delivery system for WARS. The system would deliver size-reduced shingles to the PC bin for combustion in the coal burner. Nevertheless, if WARS is to be used as-received without extra processing costs, the most suitable approach chosen to increase its consumption is to use a separate pipe placed at a height that allows better combustion of shingles in suspension (above the main burner pipe). The pipe refractory and construction must be improved for long-term durability and for continued success in delivering WARS. By using field observations and trials, both interim and long-term strategies for the continuous improvement in fuel handling and delivery of WARS for the purposes of increasing its use were investigated.

This field trial approach, which has been used successfully to address the challenge inhibiting increased WARS application, forms the foundation for a guide to optimize delivery options of other WDF for the local cement kiln. Kiln parameters such as clinker production rate that

are related to thermal performance, were monitored and reported during the full-scale trials of WARS, and they showed an agreement with bench-scale predictions for WARS performance in maintaining clinker production. The trials also highlighted the importance of bench-scale combustion behaviour in anticipating WDF handling hazards such as aggressive flashback and flame instability.

4.6 SUMMARY OF EXPERIMENTAL FINDINGS

In summary, the bench-scale experiments using the tube furnace and HGR provided observations, which matched with ultimate-analysis expectations for the tested WDF's. The results also matched expectations in full-scale applications. They therefore provide a means for screening and studying local WDF on a small scale. The results on TTI, VOC emission, and char burnout agree well with trends observed in both simulation and full-scale studies of kiln gas temperature, flame stability and overall thermal performance. The similarities in the bench-scale residual VOC and full-scale thermal performance suggest that prior to full-scale trials, the tube furnace set-up can be used as a means to comparatively estimate the effect that the fuel composition might have on the kiln's thermal performance. Actual full-scale tests conducted on waste shingles at the local cement plant showed that kiln thermal performance could be maintained or improved by the use of WDF. This was seen in the maintenance of clinker production rates over the period of firing waste shingles. A similar behaviour is expected for blends of coal-coke and waste plastics because compared to most of the waste plastic samples, waste shingles contain less energy, more ash and more moisture per equivalent heat, and because of the effect that these characteristics can have on bench-scale combustion efficiency and full-scale kiln thermal performance, it is defensible to expect that firing equivalent amounts of the tested waste plastics would not reduce clinker production as a result

of lowered fuel combustion efficiency or lowered kiln thermal performance. The fuel handling approaches for the waste plastic fuel stream may however be different due to differences in density and particle size of the fuels as received. There is need for further studies on the comparative behavior of single plastic and waste shingle particles for a better prediction, however, since the key to obtaining actual trial permits is the comparison of new fuels to fuels already in use based on available data, the expectation for waste plastics though not elaborately arrived at, forms an initial argument for acquiring of actual full-scale trial permits.

Concerning PM emissions, both bench-scale tests showed that no significant deviations from the norm were expected if WARS or PDF replaced coal-coke. Both bench-scale and full-scale observations made on PM emissions show that for the most part, changes that are solely attributable to fuel change are not significant when co-processing waste shingles and coal-coke. Given the agreement so far between the bench-scale and full-scale results, it is expected that PM emissions during full-scale application of WDF would not significantly differ from the reference fuel. Field-scale trials have also shown a step-by-step delivery test approach for the improvement of WDF delivery which are applicable to other local WDF once trial permits are obtained.

Based on these results bench-scale observations can be used to preliminarily describe expectations for full-scale performance with an acceptable degree of confidence as has been done for C&D plastics as PDF for example in Table 23.

Table 23. Expected behavior for full-scale application of PDF based on deductions from bench-scale experiments.

	Compared to coal-coke	Bench-scale attributes	Full-scale performance
	<i>Analysed</i>	<i>Observed</i>	<i>Observed</i>
WARS	<u>Positive</u> higher VM high H/C	<u>Positive</u> Better ignitability Better char burnout Possible size reduction No significant difference in PM emission	<u>Positive</u> Clinker production maintained No adverse emission concerns
	<u>Inhibitive</u> higher ash lower energy more moisture larger size	<u>Inhibitive</u> Higher mass requirement Higher air requirement	<u>Inhibitive</u> Flame fluctuation Incomplete combustion in kiln
	<i>Analysed</i>	<i>Observed</i>	<i>Expected</i>
PDF: C&D plastics	<u>Positive</u> higher VM lower ash higher energy less Moisture high H/C	<u>Positive</u> Better ignitability Better char burnout lower mass requirement lower air requirement No significant difference in PM emission	<u>Positive</u> Clinker production will be maintained or improved. No adverse emissions will arise. Complete combustion in kiln (no solid residue).
	<u>Inhibitive</u> larger size more varied	<u>Inhibitive</u> Challenging size reduction	<u>Inhibitive</u> Possible flame fluctuation. Possible reduction in ash for clinker.

5.1 CONCLUDING REMARKS

Experimental work ranging from bench-scale tests to full-scale trials were conducted to investigate the proposal that proper co-processing of available WDF in a cement kiln in Nova Scotia will not only result in macro-scale environmental gains, but could also be predicted, using bench-scale experiments, to improve the efficiency of the combustion process on a micro scale, and that these improvements will not adversely affect particulate emissions significantly. This was achieved by assessing present opportunities for waste diversion from landfills to the local cement kiln in light of the hypothesis. Findings from these experiments have addressed a hierarchy of challenges in the following ways.

1. Technical modifications for fuel handling

An improvised and inexpensive shingle conveyer system to deliver WARS, as received or further size-reduced in a hammer mill, through a separate burner pipe dedicated to WARS was used to increase coal substitution by WARS from 5% to approximately 17% by mass, thus improving WDF use by a fuel delivery modification. Further proposals have been made for long term modifications to the burner and fuel delivery systems based on successes of short term trials conducted during this research.

2. Fuel performance and emission testing

An approach using a tube furnace set-up was used to compare and discuss particulate matter and VOC emission characteristics of plastic based materials with potential to be used as PDF.

This set-up was successful in providing useful insight into the impact of additives, everyday use physical properties and energy content on particulate matter and residual VOC emissions under tube furnace conditions. Based on the variations existing in the emissions of plastic based samples, the potential of construction & demolition plastics and expanded polystyrene for co-combustion ranked higher, compared to plastic containers, used clothing, carpet backing and plastic films, based on their potential to reduce particulate matter and VOC emissions in combustion. The potential for VOC reduction on a bench-scale matched well with the observations made in the literature on full-scale kiln thermal performance parameters related to fuel properties. The set-up can thus be used as a screening method to select appropriate WDF for actual kiln targets. Additionally, the comparative data from bench-scale tests, though not directly applicable to field scale predictions without further scrutiny and tests, present a good resource for operators to obtain preliminary data to acquire fuel trial permits and to inform heterogeneous WDF selection.

3. Competing waste management interests

Elemental analyses and theoretical calculations were used to justify the claim that scrap tires, waste plastics and waste roofing shingles qualify to be used as lower carbon-intensity fuels in the local cement kiln. First, the energy demand of approximately 1.35 PJ required for production at the local cement plant is relatively small compared to the energy available from the quantity of waste disposed of within the maritime region. Additionally, the long-term storage of these materials in landfills can be deduced from the study on ignition behaviour, to pose a considerable fire hazard. Furthermore, the demand on these waste resources for other appli-

cations is inadequate to meet all the resource recovery targets of the Province. The implications of co-processing on the waste management goals of the province are therefore positive and non-detrimental to other waste diversion approaches.

4. Gaps in knowledge due to variations in local content

Bench-scale experiments using the heated grid reactor in conjunction with other devices on blends of coal-coke with locally available WDF with given elemental and energy compositions, have provided evidence to show that expectations of increased combustion efficiency (ignition performance and total coal-coke burnout) without adversely affecting particulate emissions are quite defensible for the selected WDF. The blends were shown to have obtained better burnout by improving the pyrolysis rate of coal-coke. The literature suggests that this phenomenon is the possible result of the increased volatile content, the presence of inherent oxygen to speed up WDF reactions, and the donation of hydrogen. High speed-camera observations of the combustion of small quantities of single fuels and blends with WDF in the heated grid apparatus also show improvements in the time to ignition for the blends with PDF and WARS. The literature on works conducted on the combined HGR-TGA experiments on primary fuels blended with non-biomass, non-hazardous alternative fuels such as PDF and WARS are scarce. The trends observed in this experimental study, which were conducted with an in-house HGR, therefore, contribute to making future discussions on the subject richer. Moreover, since some results from the repeatable and less cumbersome bench-scale experiments can be used as basis for expectations for WDF in terms of full-scale kiln performance, the bench-scale tests have been proposed as screening and study methods for preliminary assessments of WDF's identified for use in full-scale cement kiln applications.

The objectives set out for the research, to test and apply fuel handling strategies that result in the direct increase of alternative WDF in a local cement kiln, to develop a bench-scale preliminary selection approach based on particulate matter and VOC emissions, and to contribute to the body of knowledge on co-combustion by studying the effects of locally available WDF's in fast heating environments were reached successfully.

5.2 RECOMMENDATIONS FOR FURTHER STUDY

1. Due to kiln availability and permit constraints, full scale fuel handling trials of PDF and TDF were not conducted. In future, the strategies applied for the full-scale application of WARS could be used as a guide and applied to study strategies to optimize the delivery of PDF and TDF into the local cement kiln on a full-scale.
2. Future experiments can be conducted with the HGR to study the behaviour of the current selection of WDF in coal-coke-WDF blends, but in non-oxidative fast pyrolysis or gasification environments. The HGR could also be modified to include a balance for comparative weight loss measurement in fast pyrolysis which more adequately represent industrial kiln conditions. The weight loss data could be used to extract useful kinetic parameters for better modelling of WDF combustion.
3. To advance the fundamental understanding of combustion emissions associated with coal-coke-WDF blends from bench-scale and pilot studies, macro-scale observations of emissions from cement kilns utilizing WDF could be used to study actual environmental and health impacts of the emission improvements from cement kilns across Canada and North America. This could be accomplished using tools such as the NASA Tropospheric Emissions Monitoring of Pollution (TEMPO) remote sensing package to buttress bench-scale and full-scale observations.

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