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Characterization of coal and waste plastic combustion products in the Lafarge Cement Kiln, Brookfield

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EXECUTIVE SUMMARY

Waste plastics destined for landfills possess large amounts of untapped energy that could be used to fuel high temperature furnaces such as rotary cement kilns through direct combustion. Redirecting such waste to a local cement kiln presents a dual solution to both cost and environmental concerns. In an effort to reduce fuel costs and reduce environmental emissions, Lafarge Cement Inc., Brookfield, Nova Scotia has explored the use of waste materials substituting for coal and coke as fuel sources at their cement plant. A potential fuel source is mixed waste plastics.

The research objective was to comparatively study and to predict any potential changes in stack emissions in a cement kiln equipped with an Electrostatic precipitator (ESP) if an equivalent amount of heat was shifted from the 50-50 blend of coal/coke to an equivalent heat amount of plastics. An experimental set up at Dalhousie University's, Process Engineering and Applied Science department comprising a tube furnace with an exhaust stream connected to emission detection devices was used in investigations. Existing literature, chemical elemental analysis, and comparative experimental data were employed to predict potential changes in major emissions such as carbon dioxide (CO_2), sulphur dioxide (SO_2), nitrogen oxides (NO_x), airborne particulate matter (PM) and volatile organic compounds (VOCs). All results were discussed with full regard to the limitations that the experimental set up encountered in mimicking actual industrial kiln conditions.

The findings of the study as presented in this report show that based on equivalent heat amounts, 30% less plastic by mass is required to contribute the same energy as the coal/coke blend. There was a considerable potential reduction in CO_2, SO_2, and fuel NO_x emissions by 34%, 98% and 80% respectively. On an equal mass basis, more VOC species were detected during the combustion of plastics than for coal/coke however all VOC species would thermally degrade to CO_2 and H_2O given kiln temperatures in excess of 1100 to 1400°C and considerable kiln residence time. Changes in stack emissions in terms of VOCs are therefore expected to be minimal. Projections based on elemental analysis and experimental data also indicate that the particulate matter contribution from plastics lie within ranges which emission control technology such as electrostatic precipitator (ESP) presently in use at the Brookfield plant is capable of removing from the flue gas stream.

The preliminary results provide sufficient insight into the expected performance of waste plastics compared to coal/coke fuel blend under similar conditions. Proceeding to full scale field trials for plastic combustion in the cement kiln with emissions monitoring apparatus has been recommended. Field trials will provide data that will first of all, confirm experimental predictions or otherwise; and secondly fully quantify the effects of the electrostatic precipitator on the predicted changes in emissions.

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1. INTRODUCTION

1.1 BACKGROUND

Approximately 2.8 million tonnes of plastic waste is disposed in Canada by residential and non-residential sources annually. An estimated 719,000 tonnes are disposed by residential sources and an estimated 2 million tonnes are disposed by non-residential sources from the Industrial Commercial and Institutional IC&I sector which includes grocery stores and goods manufacturing plants [1]. Of the total disposed, an estimated 1.9 million tonnes is packaging waste and the remainder is non-packaging plastics. The Canadian Plastic Industry Association recommends the 4'R's (Reuse, Reduce, Recycle and Recover) as a way to reduce the impact of the plastic industry. The fourth 'R', a recent addition to the widely known 3 'R's represents the waste-to-energy recovery possibilities for waste plastics that are destined for landfill [2].

The fuel and energy requirement for the production of clinker in rotary cement kilns is such that the cement industry relies heavily on coal which increases the cost of production by virtue of its price, and also negatively affects the sustainability rating of the cement production process because it is considered a non-renewable resource. The use of cheap and readily accessible alternative solid fuels in rotary cement kilns without adversely affecting kiln performance is of essential interest to the industry and forms the motivation for this study. Waste plastics destined for landfills possess large amounts of untapped energy that could be used to fuel high temperature furnaces such as rotary cement kilns through direct combustion. Redirecting such waste to a local cement kiln presents a dual solution to both cost and environmental concerns. In an effort to reduce fuel costs and displace the use of imported pulverized coal (PC), Lafarge has explored the use of waste materials as fuel source for co-firing with PC at their Brookfield cement plant. A potential fuel source is mixed waste plastics.

At Lafarge, Brookfield, dry crushed limestone from an onsite mine is introduced into a 90 metre long rotary kiln shown in figure 1, slightly tilted at an angle. The feed moves counter to the flow of hot flue gases generated from combustion processes on the opposite end of the kiln. As the feed progresses along the length of the rotating kiln, chemical reactions are initiated and the resultant effect is the production of clinker which is cooled and crushed and made into cement.

Figure 1: Image of the rotary cement kiln at Lafarge Inc, Brookfield [3]

1.2 OBJECTIVE

This scope of work aims to identify products of combustion from waste plastics available for use at Lafarge, Brookfield by testing various fuel mixes with varying percentage compositions of plastics. The chemistry and particle distribution of the combustion products constitute the main focus of this study. The research case is to empirically answer the question that given the two test fuels and the Lafarge kiln equipped with an Electrostatic precipitator (ESP), what will the change in emissions from the stack be if an equivalent amount of heat was shifted from the 50-50 blend of coal/coke to an equivalent heat amount of plastics?

1.3 METHOD

A combined approach using literature, chemical elemental analysis and comparative experimental data was employed to reach the objective. In the experimental procedure, coal, petroleum coke and plastic samples were combusted in a tube furnace at temperatures between 900-1100°C with excess air. Pure coal, pure plastics and some mixtures of coal, plastics and petroleum coke were tested. Exhaust was swept by air through a metal chamber which acts as a distribution chamber that serves the dual function of cooling the tube furnace exhaust while allowing the sampling of the gaseous and particulate combustion products. Argon gas was used to cool the combustion products to a temperature (<50°C), suitable for sampling.

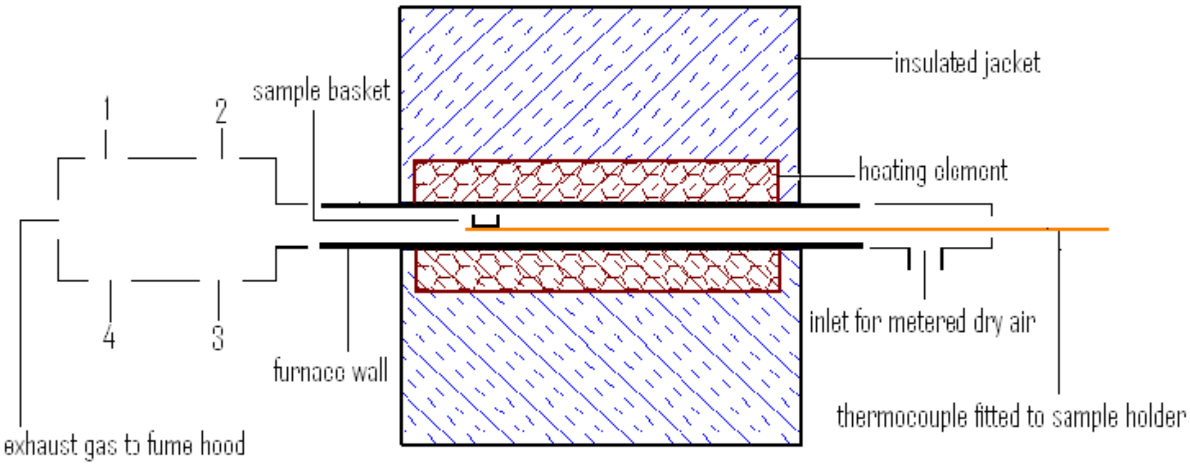


Figure 2: A schematic cross-section of the tube furnace and sample chamber used for combustion studies.

Four sampling ports located on the metal tube allowed the sampling of the following metrics:

Sampling Port 1: Continuous measurement of fine airborne particulate matter with a median aerodynamic diameter ≤ 2.5 microns ($PM_{2.5}$). This measurement was conducted using a TSI DustTrak nephelometer at a flow rate of 1.7 L/min.

Sampling Port 2: Teflon filter sample for additional $PM_{2.5}$ mass concentration determination. The $PM_{2.5}$ filter sample was taken at a flow rate of 10 L/min.

Sampling Port 3: Continuous measurement of fine particle number counts below 2.5 microns (fine#) and coarse particulate number counts between 2.5 and 10 microns (coarse#). These metrics were measured using a Dylos 1100 professional air quality monitor at a flow rate of 1 L/min.

Sampling Port 4 split into two sample streams:

Sample stream 1. Continuous measurement of CO, H_2S, NH_3 and O_2. These metrics were measured using a VRae industrial hygiene monitor at a flow rate of 100 ml/min.

Sample stream 2. Volatile organic compounds species were sampled at a flow rate of 100 ml/min onto ¼” OD x 3½” Tenax TA stainless steel thermal desorption tubes (Perkin-Elmer). The thermal desorption tube samples were analyzed by thermal desorption-gas chromatography-single quadruple mass spectrometry (TD-GC-MS) [4]. The TD was a Markes International, Unity 2 system which was coupled to a Thermo 1300 GC which in turn was coupled to a Thermo ISQ MS.

1.4 LIMITATIONS

The experimental set-up had limitations in mimicking actual cement kiln conditions. These deficiencies and assumptions have to be considered in coming to a good understanding of the changes predicted with the change of fuel. The differences between the industrial set-up and the bench scale set-up are highlighted as follows:

1. *Kiln temperature profile*

The burners in the Lafarge cement kiln are able to generate temperatures in excess of 1400°C which is necessary for the complete clinkerization of the raw feed. Between the feed inlet (flue gas exit) and the main burning zone-a distance of about 90m- temperatures range from 300°C to 1400°C. The components of the flue gases therefore remain at a higher temperature longer than can be replicated by the bench-top tube furnace. In the tube furnace, a maximum of 1100°C is reached and the flue gas only travels a distance of a few centimetres before being exposed to ambient conditions and argon gas which brings it to temperatures below 50°C. It is predicted that toxic chemical species will degrade at temperatures experienced in the kiln and will not be reformed throughout the length of the kiln. In the lab set-up, we sought to identify the species and determine from literature and chemical analysis, if there were any species which will not fully degrade to CO_2 and H_2O.

The presence of the Electrostatic precipitator (ESP)

The ESP works by using electrical charges to ionize and remove impurities from the flue gas stream. It removes solid and liquid droplets from the stream before they exit the kiln stack. Their operation is known to reduce harmful dust and particulates released into the environment. A kiln fitted with a well maintained ESP will greatly reduce the particulate emissions recorded from the stack. The ESP at Lafarge, Brookfield collects and returns about 40 tonnes per hour of total dust to the kiln, the majority of which is raw mix/kiln feed and not coal ash. No facility of the sort was attached to the experimental set-up therefore the large amounts of emissions were expected to be observed at detection points. The lab set-up was designed to evaluate changes in particulate emissions before ESP. The effect of a well functioning ESP on any changes in stack emissions could be evaluated with full scale field trials conducted with continuous emission monitoring.

2. *Fuel delivery and excess air availability*

In our experimental study, a basket was loaded with samples to be tested. This reduced the amount of air available to the middle layers of fuel and may delay their complete combustion over the period. In a rotary cement kiln, fuel is well dispersed by spraying it into the burning zone, giving the fuel particles easier access to air for complete combustion.

2. LITERATURE REVIEW

2.1 PLASTICS

Plastics are currently 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 [5]. Besides crude oil, natural gas and coal, plastics can be derived from wood, vegetable oils, sugar and starch as biopolymers or bioplastics [6]. Worldwide polymer production was estimated to be 260 million metric tonnes per annum in the year 2007 for all polymers including thermoplastics, thermoset plastics, adhesives and coatings, but not synthetic fibres [7].

The major plastic types that stand out in terms of their market share are [7] :

1. polyethylene – including low density (PE-LD), linear low density (PE-LLD) and high density (PE-HD)
2. polypropylene (PP)
3. polyvinyl chloride (PVC)
4. polystyrene solid (PS), expandable (PS-E)
5. polyethylene terephthalate (PET)
6. polyurethane (PUR)

The plastic mix studied in this report was mostly composed of HDPE and LDPE plastics. Using ASTM D3176-84 standard test procedures, Islam et al. [8] conducted analysis on mixed plastics. Their results are presented in Table 1. These compositions will be referred to in this report. The results from the pyrolysis work conducted by Islam et al, shows that volatile content was 96.88 wt% of the sample. The amount of carbon was 83.93wt% of the sample. Given that no sulphur or nitrogen is found in the ultimate analysis, the tendency to form hazardous SO_2 and NO_x gases is greatly reduced. Further elaboration is given to this assertion in this section under emission and pollutant considerations. Thermo-gravimetric plots indicate that inherent moisture loss in plastics at about 110^{o}C, which was less than 4% of the total sample weight. At a heating rate of 10^{o}C/min, devolatilization of solid plastic was initiated at approximately 250^{o}C. At a temperature of 550^{o}C devolatilization of all volatile components in the sample is achieved [8]. These results provide insight into the combustion mechanisms associated with waste plastics.

Table 1: Elemental Composition of some waste plastics from [8]

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)	0.80
		Sulfur	(S)	-
		C/H		6.53

Waste plastics have been identified as a promising resource because they have high combustion temperatures and energy content (typically >17,000 Btu/lb) with low inherent moisture content. Elimination of dioxin and furan can be achieved through basic plastic selection and high-temperature combustion [9].

2.2 FUEL BLENDING FOR COMBUSTION

Combustion refers to the complete oxidation of a solid fuel [10]. It is the most widely used thermal conversion method. When heated, a solid fuel loses moisture and undergoes drying. After drying, heat transfer from the surroundings further increases the particle temperature and releases volatile components which ignite and form the flame. The final stage of combustion is char oxidation. The combustible components of solid fuels are carbon, sulphur and hydrogen and they react with oxygen as follows [11]

$$C + O_2 \rightarrow CO_2$$

$$2H + {}^{1}\!/_{2}\, O_2 \rightarrow H_2O$$

$$S + O_2 \rightarrow SO_2$$

Blending different fuels with coal for economic, environmental and chemical purposes has been discussed to a large extent in literature [9, 12, 13]. The parameters mostly affected and which need to be managed during fuel blending for co-firing include moisture; calorific value; volatility and reactivity; pollution potential; slagging and fouling; and corrosion [9]. The potential for opportunity fuels such as petroleum coke; biomass; municipal waste; and waste plastics depends on their volatile content to positively affect the reactivity of a coal- fuel blend, and to theoretically reduce the formation of harmful emission products. These have been widely discussed in the literature [9, 14, 15]. Evaluating pollution potential of a possible mixed plastic-coal blend is the aim of this report. Other possible effects of introducing plastics into the fuel mix are not investigated in this study.

2.2.1 Emission and pollutant considerations

SO_2 generated during combustion is governed by the sulphur content of the fuel, low sulphur coals have occasionally been blended with traditional coals to reduce emissions. Several major utilities and the U.S Department of Energy have also considered the cofiring of biomass with coal in utility boilers for the same purpose [15]. Results of these studies suggest that given the very low sulphur content in waste plastics ~0 from Table 1, it is likely to reduce sulphur emissions when blended with coal.

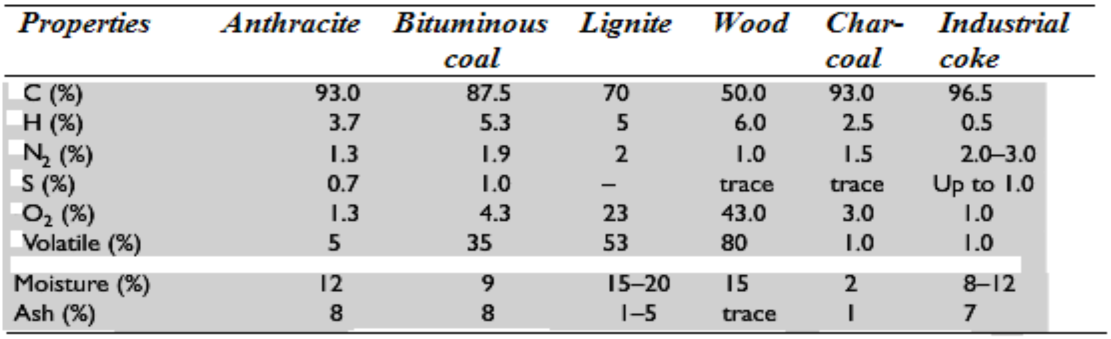
Fuel blending also influences PM emissions, especially PM with a median aerodynamic diameter ≤ 10 µm (PM_{10}) [16]. Total suspended particulates (TSP) are a function of the percentage of ash, or mineral matter, in the fuel, coupled with the unburned carbon resulting from combustion and firing method used [9]. Pulverized coal firing, for example, typically yields 80% solid products of combustion as fly ash compared to 30% from cyclone firing [9]. Fuels such as waste plastics with low ash content can therefore be blended with high-ash coals to reduce TSP. It is also expected that a higher volatile content will reduce unburned carbon in the products of combustion. Gases such as SO_2, NO_x, and VOCs can transform in the atmosphere to form secondary fine PM and ozone (O_3) by a number of chemical reactions [9, 17, 18]. Therefore, the combustion of plastics with low sulphur and nitrogen content coupled with complete combustion of VOCs in the kiln should theoretically produce significantly lower SO_2 and NO_x emissions [19, 20]. This would have the knock on effect of reducing secondary PM and O_3 formation in the emission plume from the Lafarge cement kiln [17, 18, 20]. Wang et al [21] however suggests that the presence of certain elements such as calcium in the fuel's mineral matter or ash, may cause particles to agglomerate leading to lower levels of finer particles than expected.

The treatment of VOC as a combustion product is discussed by Choi and Yi, 2000 [22]. The extent of thermal degradation of produced VOC such as benzene, xylene and toluene is dependent on elevated temperature (> 1000°C) and the retention time within this zone. At these conditions, the mixture of organic vapor and air is oxidized to form CO, CO_2, NO_x and H_2O.

$$C_nH_m + \left(\frac{n}{2}+\frac{m}{4}\right)O_2 \rightarrow nCO + \frac{m}{2}H_2O;\ \text{then}\ CO + \frac{1}{2}\ CO_2 \leftrightarrow CO_2 \quad [22]$$

NO_x formation increases exponentially with temperature because the combustion process requires air which also provides the nitrogen and oxygen that react to form thermal NO_x reaction combustion. However NO_x formed by the oxidation of organonitrogen compounds found in the fuel is dependent on the reactivity of the fuel [3]. Highly reactive fuels promote early release of nitrogen in the fuel mass: the release of nitrogen in the early, fuel rich stages of combustion reduces the formation of NO_x at the later, high-temperature stages of combustion. For a fuel blend to have an effect on reducing NO_x, it must contain less nitrogen and/or constitute a more reactive fuel than was previously the case. Table 2 from [3] gives an elemental analysis of commonly used solid fuels showing the nitrogen contents and more of each. Reactivity of fuels is not directly discussed this report. Other hazardous pollutants such as trace metals and mercury may also be sources of concern if they are present in the fuel mix being used.

Table 2: Proximate and Ultimate analysis of some selected solid fuels [9]



Properties	*Anthracite*	*Bituminous coal*	*Lignite*	*Wood*	*Char-coal*	*Industrial coke*
C (%)	93.0	87.5	70	50.0	93.0	96.5
H (%)	3.7	5.3	5	6.0	2.5	0.5
N_2 (%)	1.3	1.9	2	1.0	1.5	2.0–3.0
S (%)	0.7	1.0	–	trace	trace	Up to 1.0
O_2 (%)	1.3	4.3	23	43.0	3.0	1.0
Volatile (%)	5	35	53	80	1.0	1.0
Moisture (%)	12	9	15–20	15	2	8–12
Ash (%)	8	8	1–5	trace	1	7

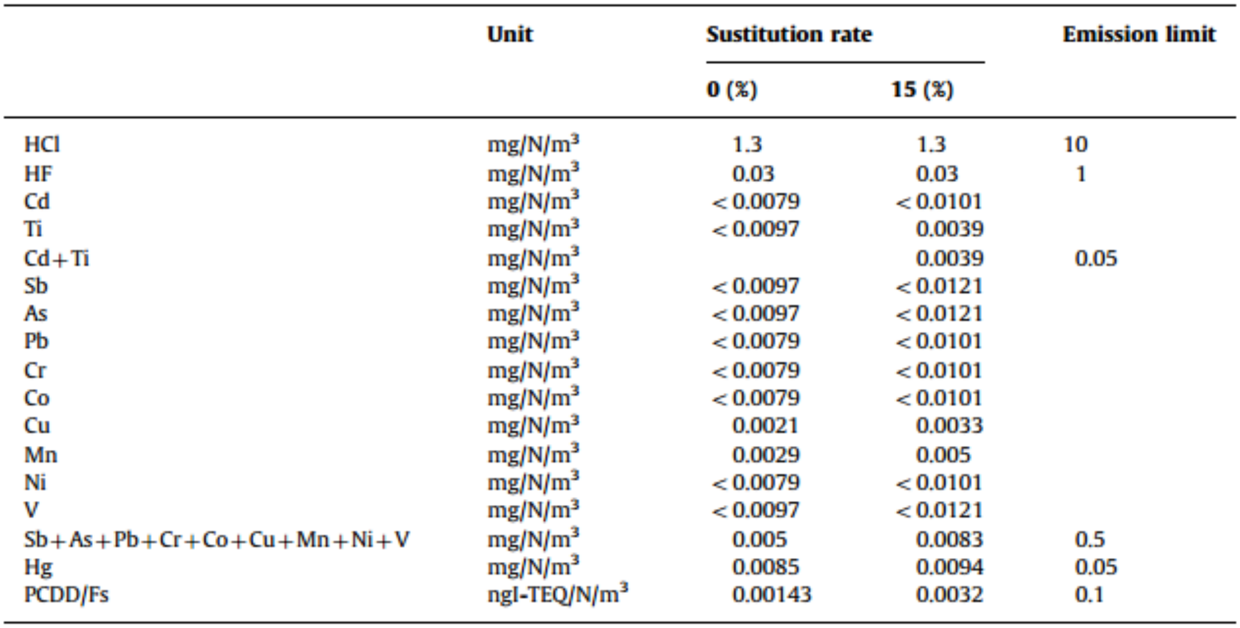
2.3 PLASTICS AS FUEL FOR CEMENT KILNS

The pyrolysis of waste plastics to generate energy rich fuels has been explored by [8]. Using fixed bed pyrolysis the volatile content of waste plastics were collected and studied as fuel. Additional papers have studied the possibilities of derived fuels not only from plastics but other waste materials including tyres [13]. Direct waste-to-energy recovery has also been studied and applied in industry as a preferred way of disposing unrecycled waste including plastics. Plastics-based fuels been fired with coal to for power generation [9] and in cement kilns [23] .

In a study by Rovira et al [24], on a cement plant in Catalonia, Spain, petroleum coke was replaced by up to 20% with refuse-derived fuel (RDF) from (Municipal Solid Waste) MSW. RDF mixture consisted of plastics (35%), paper, and cartons (30%), wood (20%), and textiles (15%). Environmental monitoring was conducted to investigate the effects of the new process. While no significant increases were encountered in PM_{10} emissions and major pollutants, there was a significant decrease in metals; and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in analyzed soil, herbage, and air samples collected around the facility. Table 3 from [25] summarizes a section of results obtained from environmental monitoring. Some lessons learnt are that the heterogeneity of MSW presents a difficulty in studying and predicting its effects in the cement kiln. A more homogenous mix of waste material will eliminate the need to homogenize the waste components via any other thermal degradation methods. A waste stream composed of an all plastic mix provides a more homogenous mixture compared to unsorted MSW [24].

To obtain information on the behaviour of combustion, Jeschar et al., [14] used various plastics in preliminary tests, compared to a bituminous coal as fuel in a calciner of a cement kiln. During testing, it was found that the thermal recovery of plastics as fuel could be quite defensible, from a technical standpoint. Plastics have a positive influence on the emission values for NO_x and CO_2. Jeschar et al also report 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 however, due to limitations of reactor size the results on harmful emission did not agree with theoretical expectations. Their work confirmed that the limitations of size and the challenge of replicating actual kiln conditions may sometimes lead to results that do not conform to theoretical expectations. Results for this report have been discussed in the context of all known experimental limitations.

Table 3: Emission levels of minor pollutants from the stack of cement plant before (0%) and after (15%) partial substitution of fossil fuel [23, 24]



	Unit	**Sustitution rate**		**Emission limit**
		0 (%)	**15 (%)**	
HCl	mg/N/m^3	1.3	1.3	10
HF	mg/N/m^3	0.03	0.03	1
Cd	mg/N/m^3	< 0.0079	< 0.0101	
Ti	mg/N/m^3	< 0.0097	0.0039	
Cd+Ti	mg/N/m^3		0.0039	0.05
Sb	mg/N/m^3	< 0.0097	< 0.0121	
As	mg/N/m^3	< 0.0097	< 0.0121	
Pb	mg/N/m^3	< 0.0079	< 0.0101	
Cr	mg/N/m^3	< 0.0079	< 0.0101	
Co	mg/N/m^3	< 0.0079	< 0.0101	
Cu	mg/N/m^3	0.0021	0.0033	
Mn	mg/N/m^3	0.0029	0.005	
Ni	mg/N/m^3	< 0.0079	< 0.0101	
V	mg/N/m^3	< 0.0097	< 0.0121	
Sb+As+Pb+Cr+Co+Cu+Mn+Ni+V	mg/N/m^3	0.005	0.0083	0.5
Hg	mg/N/m^3	0.0085	0.0094	0.05
PCDD/Fs	ngI-TEQ/N/m^3	0.00143	0.0032	0.1

3. EXPERIMENTAL WORK

3.1 ELEMENTAL ANALYSIS

Elemental analysis was conducted on 1kg of 50-50 Coal/Coke mix; and on 1kg of the mixed plastics. The constituents of interest were those which were most likely to cause considerable adverse changes in the combustion products when plastics are subjected to the same heat conditions that coal and a mixture of coal/coke are subjected to in a kiln. The analyses quantify carbon, sulphur, nitrogen, halogens (chlorine), ash and mineral matter, which directly affect the pollution potential of the combustion products as discussed in the literature review section of this report. An effort is made to theoretically examine the possible changes that waste plastics may present.

3.2 SAMPLE PREPARATION

Coal and petroleum coke were oven dried at 50°C for 10 hours cumulatively before being crushed to specification- (80% ~200 mesh) in a roll mill. Plastics could not be further reduced in size by any available means and were therefore air dried and used as is. The plastic fuel was received as a mix of 'light-weight-fluffy-mm-sized' components and 'granular-mm-sized chips'.

The proportions by weight were pre-determined for the fuel mix to be studied. 5g batches were prepared and labeled for each composition to be studied. These batches were mixed to ensure that a random collection of the batch prepared sufficiently represented the whole. A balance, scoop, and hexagonal Styrofoam containers were used in batch preparation. Table 4-6 show the mix proportions studied. 100% coal, 100% coke, 100% plastics, 50-50 coal-coke were also tested.

Table 4-6: Composition of samples tested in tube furnace

COAL (wt %)	PLASTICS (wt %)
90	10
80	20
70	30
60	40
50	50

50-50COAL-COKE (wt %)	PLASTICS (wt %)
90	10
80	20
70	30
60	40
50	50

COAL (wt %)	COKE (wt %)	PLASTICS (wt %)
80	10	10
60	20	20
50	30	20

3.3 MATERIALS AND METHODS

3.3.1 Lindberg bench scale electric tube furnace:

A tube furnace Type 59544, Serial No. 757121 with rating (Volts 115/230, 35 Watts, and 50/60 Hz) and dimensions: 190 cm length, 5cm ID. It reaches a maximum set temperature ~1400°C. Its ends are cooled with water flowing through copper tubes. The metal tube itself is insulated by a heavily padded jacket. The heating chamber is fitted with a long moveable thermocouple rod attached to the sample basket.

3.3.2 TSI DustTrak Aerosol Monitor 8520

The TSI DustTrak Aerosol Monitor 8520 was used to measure real time $PM_{2.5}$ mass concentration [26]. A pump inside the DustTrak draws air through the $PM_{2.5}$ size selective inlet and past a greased impactor plate at a flow rate of 1.7 Lpm (required flow rate at atmospheric pressure to create a PM aerodynamic median size cut of 2.5 microns and below). Particles with a median aerodynamic diameter greater than 2.5 μm have too much inertia at this flow rate and are collected on the impactor plate. When the $PM_{2.5}$ particles enter the measurement chamber, they scatter light produced by a 90° light scattering laser diode and the laser photometer records the concentration in mg/m^3.

Figure 3: The Electric tube furnace used for combustion studies

The reading is shown digitally on the DustTrak screen. The DustTrak has a sampling range of 0.001 mg/m^3 to 100 mg/m^3 and a resolution of ±0.1%, it can be stored in temperatures ranging from -20ºC to 60ºC, and can operate in temperatures ranging from 0ºC to 50ºC. The logging interval on the DustTrak was set to five seconds with the ability to store 31 000 data points. (TSI, 2010) After sampling, the DustTrak data is downloaded to a PC using TrakPro software.

Figure 4: TSI DustTrak Aerosol Monitor 8520 (Codey Barnett, 2013)

3.3.3 Dylos DC1700 Air Quality Monitor

The Dylos DC1700 Air Quality Monitor, shown in Figure 4, is a true laser particle counter used to measure small (>0.5 µm) and large (>2.5 µm) particle counts. A fan inside the bottom of the Dylos draws air through the inlet at the top. The air passes through a baffle and is illuminated by a light beam. A photo detector opposite the light beam collects the light scattered by the particles. After the air passes through the light beam it is expelled through the exhaust port on the bottom of the Dylos. Based on the light collected, the photo detector displays the particle count on the digital display in units of particle number per 0.01 ft^3 of air. The Dylos has a logging interval of one minute and can store roughly 10 000 data points. (Dylos Corporation, 2013) After sampling, the Dylos data is downloaded to a PC using Dylos Logger software.

Figure 5: Dylos DC1700 Air Quality Monitor. (Codey Barnett, 2013)

3.3.4 VRAE Multiple Gas Monitor

The VRAE Multiple Gas Monitor, shown in Figure 5, is a handheld device used to measure occupational exposure to combustibles and up to four different toxic gases, or three toxic gases and oxygen. The gas levels are displayed digitally on the VRAE screen. The VRAE was configured to measure oxygen levels, lower explosive limit (LEL) of methane, carbon monoxide (CO), hydrogen sulfide (H_2S), and ammonia (NH_3). The oxygen, LEL, CO, H_2S, and NH_3 sensor ranges are 0-30%, 0-100%, 0-1500 ppm, 0-500 ppm, and 0-200 ppm, respectively. The VRAE is typically used in confined spaces, refineries, wastewater treatment plants, landfills, shipyards, and food processing and can operate in environments in the absence of oxygen. A pump draws air, at a flow rate of 0.4 l pm, into the inlet probe of the VRAE and any particles or debris are collected on a filter inside the inlet probe. The gas sample continues past the filter to the sensors.

The VRAE has a catalytic sensor to detect combustible gas, a thermal conductivity sensor for percent volume of combustible gas, and electrochemical sensors for oxygen and toxic gases. The VRAE has the ability to store 16 000 data points. (VRAE, 2013) After sampling, the VRAE data is downloaded to a PC using ProRAE Suite Package software.

Figure 6: VRAE Hand-Held Multiple Gas Monitor. (Codey Barnett, 2013)

3.3.5 THERMAL DESORPTION TUBES (TDT)

Markes International Thermal Desorption Sorbent Tubes (TDTs) were used to collect various gaseous hydrocarbons during each sample run. The samplers were conditioned with Tenax TA, which is a polymer resin used as a column packing material in TDTs for trapping semi-volatile and volatile organic compounds in air or those purged from a liquid or solid [4]. Tenax TA can withstand temperatures up to 350°C, has a low affinity for water, and a density of 0.25 g/cm^3 [3].

A low-flow pump was used to draw air into the tube at 10-15 mL/min for the length of the sample period.

3.3.6 Filters

PALL 37mm Teflon filters were used to collect particles for further $PM_{2.5}$ mass determination (to validate the DustTrak observations). Each filter was loaded into a Zeflon 37mm filter cartridge, which was attached to a pump to draw air through the filter at a flow rate of 2 lpm.

3.4 PROCEDURE

Our experimental set-up measured set parameters for both $PM_{2.5}$ and PM_{10}; and other chemicals including VOC during combustion of plastic-coal blends; and plastic-coke-coal blends under conditions close to that which pertain to a rotary cement kiln. For our investigations the furnace was pre-heated to between 900-1000°C. During the warm-up phase routine checks on temperatures in the sample chamber are made. Sample analysers are cleaned and calibrated before being attached to the ports of the sample holder. At this time air flow is initiated mostly at approximately 6.6 litres per minute which represents over 20% excess air for a 2g sample of theoretical coal resident in the furnace for 3 minutes. Argon supply is also set at 3 litres per minute to the sampling chamber. The basket holder, to which the thermocouple is attached, is pushed out to receive the sample basket. After pulling back the sample to the hot-spot of the furnace, the sample chamber is brought within a fixed distance of the furnace outlet to collect the combustion products. The distance is kept to provide a degree of dilution for the combustion products to avoid overloading detection and measuring instruments. The resident time for each sample was kept within 3 minutes.

4. RESULTS

4.1 RESULTS FROM ELEMENTAL ANALYSIS

Table 7: Composition of coal/coke and waste plastics from elemental analysis conducted by EXOVA laboratory

PARAMETER	Unit	COAL/COKE	PLASTICS
chlorine	mg/kg	183	160
fluorine	mg/kg	85.2	67.7
Carbon	dry %	69.67	65.48
Hydrogen	dry %	3.18	10.63
oxygen	dry %	7.11	1.88
Nitrogen	dry %	1.68	0.5
Sulphur (S)	%	3.52	0.1
Moisture	%	0.37	0.13
Ash at 900°C	%	13.43	7.66
calorific value	KJ/kg	29631	42151
Aluminium oxide	%	17.05	4.11
Calcium oxide	%	2.5	17.3
Iron oxide	%	36.49	17.56
Magnesium oxide	%	1.2	0.92
Phosphorus oxide	%	0.57	0.03
Potassium oxide	%	0.92	0.66
Silica	%	34.32	43.38
Sodium oxide	%	0.07	4.1
Titanium oxide	%	0.059	4.92
SO_3	%	8.8	0.25

From Table 7, sulphur content in waste plastics is lower than in the coal /coke mix: 0.1% to 3.52% on an equal mass basis. Carbon and nitrogen content was also less in plastics compared to the coal/coke mix. There are greater quantities of inorganic components: calcium, titanium, sodium and silicon in plastics indicated by their oxides. The remaining inorganic oxides however show lesser quantities of iron and aluminium in the plastic sample compared to coal/coke. The calorific value of plastics from Table 7 is significantly higher than that of coal/coke. A smaller mass of plastics would be required to supply energy equivalent to that of a given mass of coal/coke therefore a comparison of the test fuels based on equivalent heat content should yield lesser masses of these elements in plastics than in coal/coke.

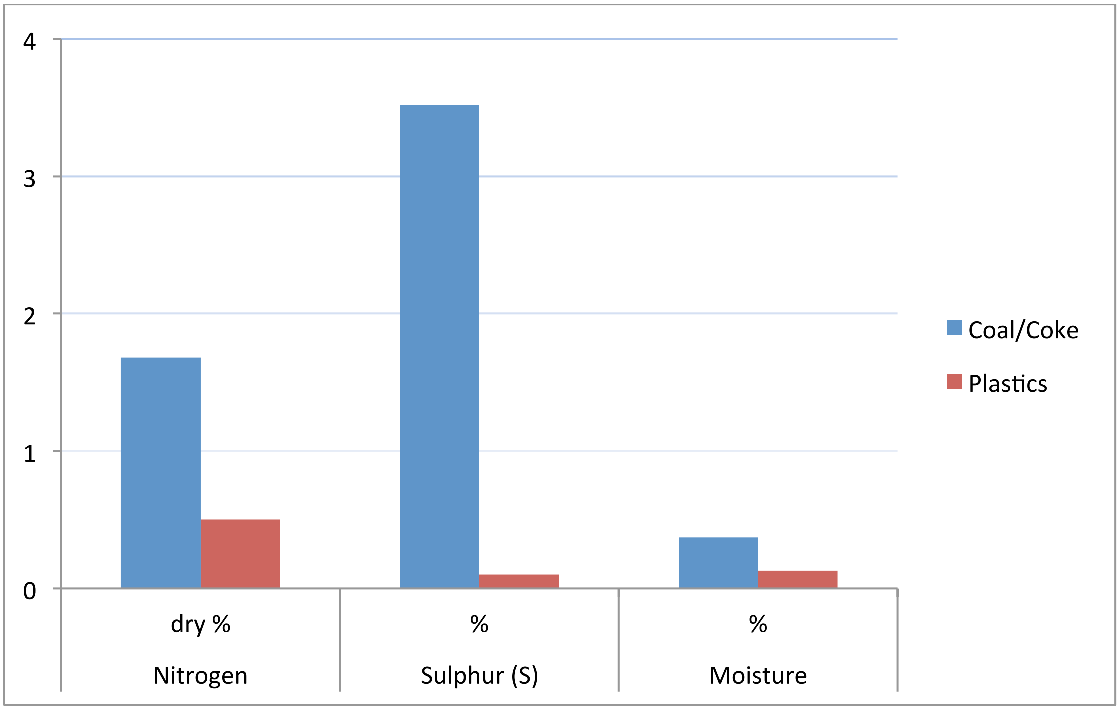


Figure 6: Graph showing the nitrogen, sulphur and moisture contents in equal weights of coal/coke and plastics

From figure 6 it could be theoretically deduced that less SO_2 and NO_x (resulting from the oxidation of nitrogen present in fuel) will be produced is equivalent conditions of combustion are applied to both potential fuels. Plastics contain 79% less nitrogen than coal and coke. This is expected to translate to the reduction of fuel NO_x during combustion. A 79% reduction in the emission of fuel NO_x when equivalent heat amounts of plastic replaces coal/coke under the same kiln conditions. Changes in major combustion products are predicted quantitatively on the basis of equivalent heat are shown in Table 8 of this report.

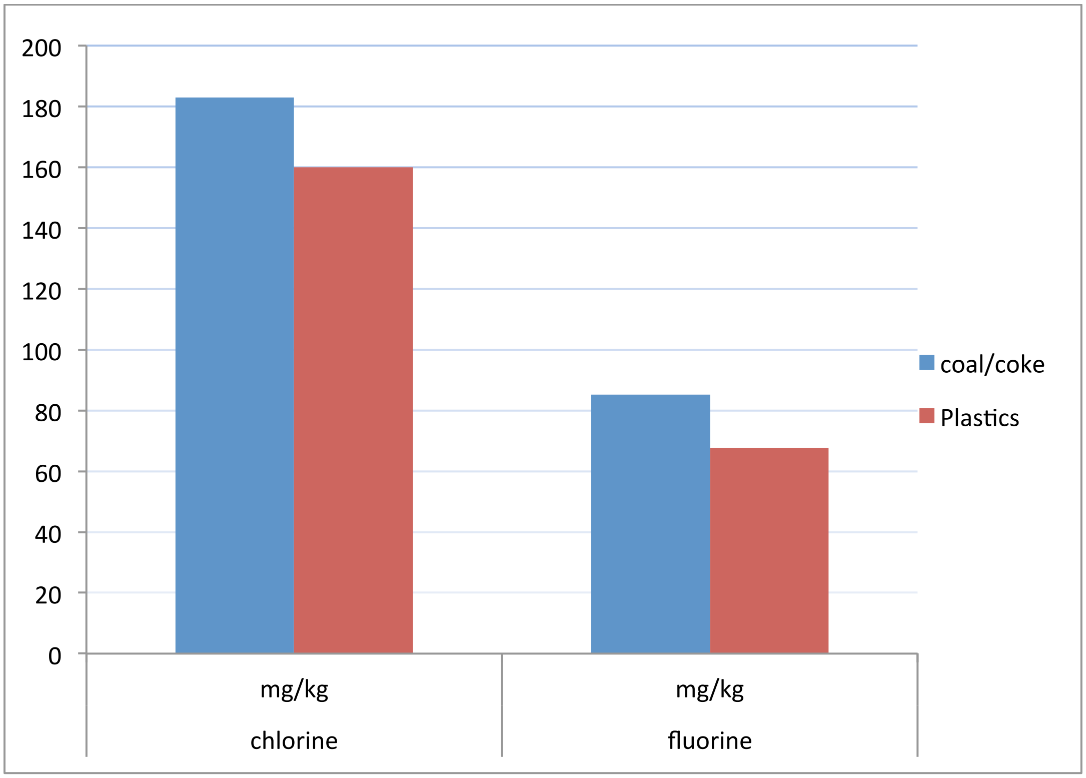


Figure 7: Graph showing the halogen content of equal weights coal/coke and plastics

It can be seen from figure 7 that fluorine and chlorine content in plastics is less compared to the content of the same in coal/coke. The production of halogenated compounds during kiln operation should reduce in cases where plastics replace coal/coke.

From figure 8, equal weights of plastics and coal/coke contained similar amounts of carbon. Plastics contain more hydrogen. The low carbon/hydrogen ratio for plastics suggests more volatile matter will be released during combustion compared to the coal/coke mix. The presence of less inherent oxygen in plastics also suggests that plastics will require more supplied oxygen for combustion compared to the same mass of coal/coke.

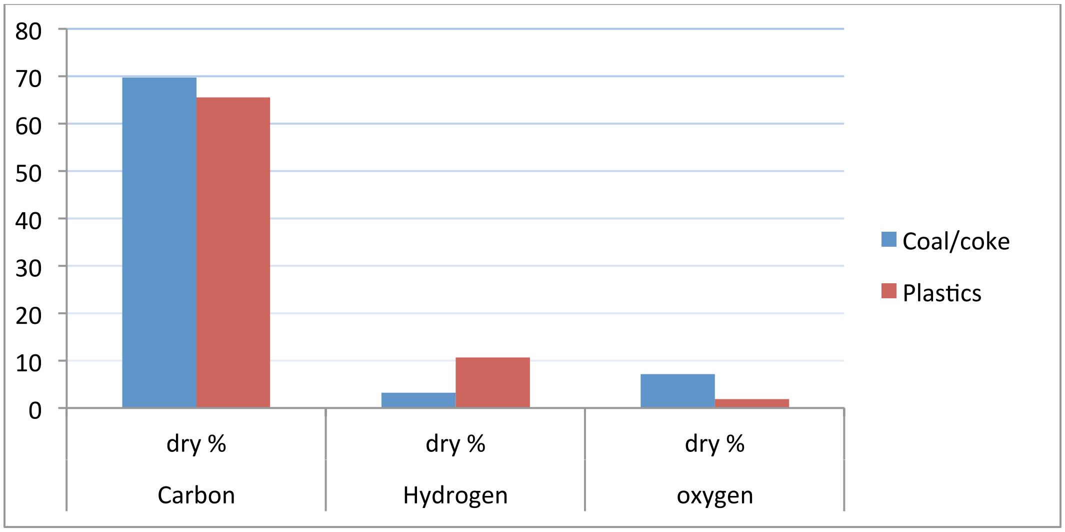


Figure 8: Graph showing percentage composition of carbon, hydrogen and oxygen of dry sample of coal/coke and plastics from elemental analysis

This is theoretically expected for plastics. However, the reduced mass requirement for plastics for a given heat content counteracts the suggestion that extra excess air may be required. A more representative and realistic prediction of the effect of fuel replacement can be obtained on an equivalent energy basis. Quantitative predictions for fuel requirement and products of complete combustion for plastics and coal/coke on the basis of an equivalent heat content of 50,000 KJ was conducted to yield Table 8. The values for the combustion products were obtained using the following generalized equation where *X* is the element being considered and *n* is the Stoichiometric mole ratio of *X* to its oxide:

$$mass\ of\ product\ (g) =$$

$$\frac{50{,}000kJ}{fuel\ calorific\ value\ kJ/kg} \times \frac{\%\ of\ X\ in\ fuel}{molar\ mass\ of\ X} \times \frac{1000g}{1kg} \times molecular\ mass\ of\ oxide\ of\ X \times n$$

Table 8: Expected changes in quantities of combustion products from equivalent heat contents of coal/coke and plastics from elemental analysis.

	50/50 Coal/coke	**plastic**	**% Reduction**
Fuel requirement (g)	1,687	1,186	29.7
CO_2 (g)	4,298	2,845	33.8
SO_2 (g)	119	2	98.0
H_2O (g)	481	1,133	-35.4

The use of plastics could lead to approximately 30% reduction in mass of fuel required. This reduction in mass should translate into savings in transportation and fuel handling costs. The products of complete production with excess air as would be the case in a cement kiln, showed notable reductions in CO_2 and SO_2: a reduction of CO_2 emissions by 34% and a significant reduction of SO_2 by 98%. The table also shows that the emission of H_2O from the combustion of plastics is about 35% more than the amount expected from the combustion of coal/coke. The reduction in emission of CO_2 and the very large reduction of predicted SO_2 emissions resulting from plastics are positive for plastic use in a cement kiln. The ash content of 13.4 % for coal/coke is almost double the ash content of 7.7% for plastics. A realistic projection on the effect of plastics on the stack emissions of a cement kiln will have to consider the fact that 30% less mass is required for plastics to replace a given mass of coal/coke. Consequently, when the plastics ash is multiplied by a factor of 0.7 to compensate for the heat content difference, coal/coke with 13.4% ash will be replaced by a fuel with 5.4% which is less than 50% of the ash content of the coal/coke. It is therefore reasonable to predict that the change in fuel ash or its composition will have minimal impact on the current ESP operation and overall PM emissions.

4.2 TUBE FURNACE RESULTS ON PARTICULTE MATTER

Since the tube furnace as earlier explained, was limited in replicating the exact conditions of temperature and residence time of a cement kiln, one expects to record more particulate matter per unit mass of fuel combusted in the tube furnace compared to an industrial cement kiln due to the release of more condensed combustion products. For the comparative study, equal masses of the test fuels were combusted under the same conditions in the tube furnace; variations in tube conditions for experimental measurement were minimal. An attempt was made to model the impacts on particulate matter emissions coming from the change in fuel. From elemental ash analysis and change in heat content, one would predict that there would be less particulate matter switching to plastics. The test conducted showed that on an equal mass basis there may be an increase in particulate matter. Figure 9 and 10 show plots of $PM_{2.5}$ concentration and number of large particles for equal weights of samples with varying proportions of coal, coke and plastics.

From figure 9 it can be seen that the blank sample basket only produces negligible $PM_{2.5}$ emissions compared to the coal and plastic mixtures. It appears the coal+coke/plastic mixtures burned slower than the coal/plastic mixtures, producing a wider range of $PM_{2.5}$ mass concentration readings and generally lower average readings. Whereas the coal/plastic mixtures seemed to combust quickly, producing a smaller range of $PM_{2.5}$ mass concentration readings and generally greater average readings.

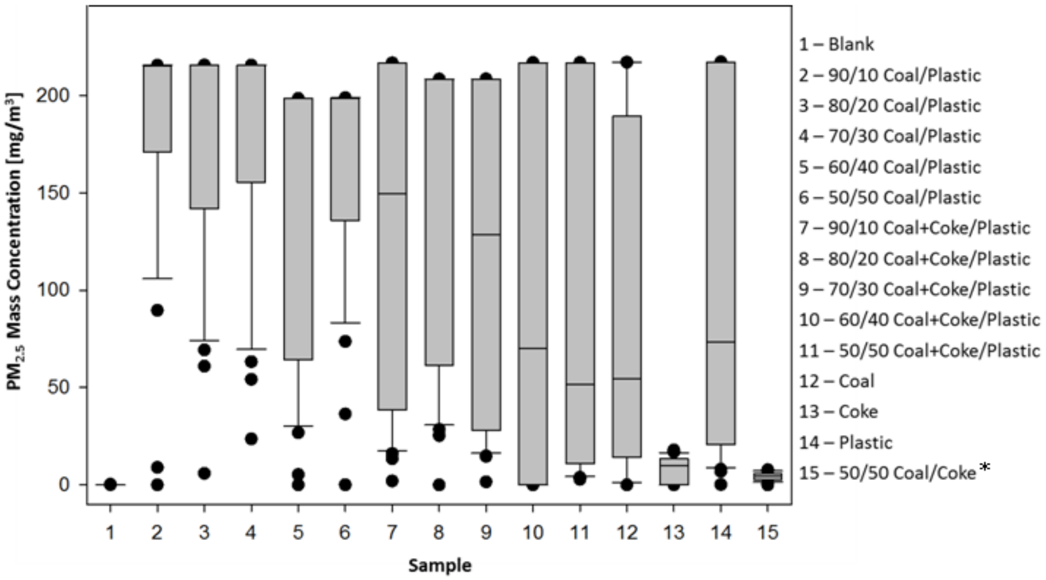


Figure 9: Box plot showing PM$_{2.5}$ concentration in mg/m^3 for samples tested in tube furnace

(Key: the line represents the median, the box extent represents the 25th and 75th percentile respectively, whiskers represent the 10th and 90th percentiles and circles represent outliers)

** Likely experimental error due to equipment failure. Results for this test have been ignored*

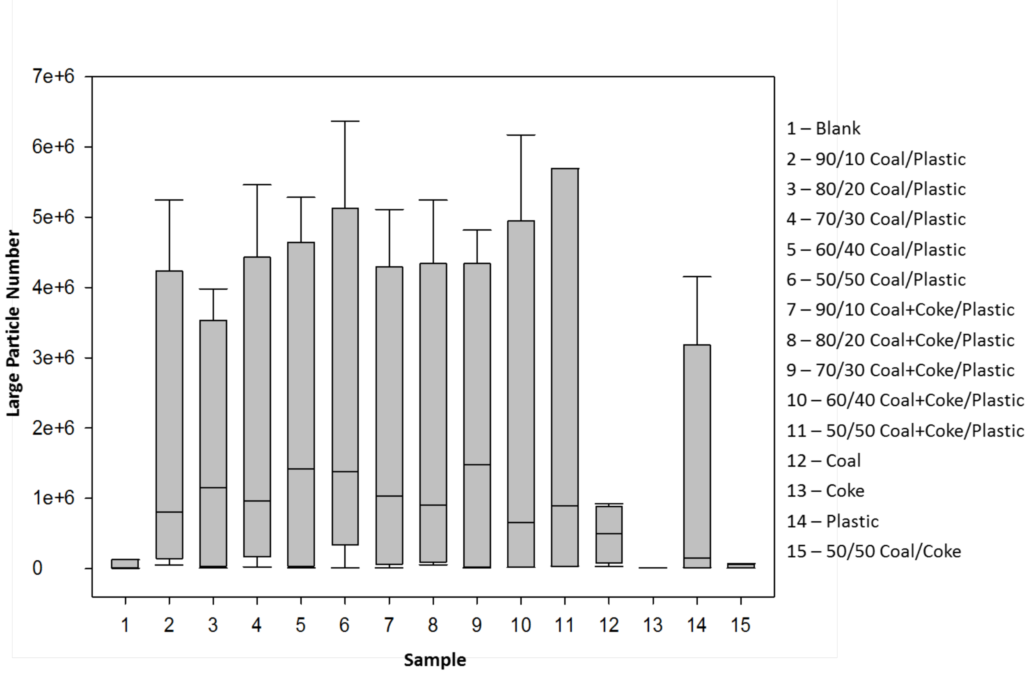


Figure 10: Box plot showing large particle number for samples tested in tube furnace

Discussion

The data on particulate matter suggest that plastics may contribute to an increase in particulate emissions on an equal mass basis. It is necessary to apply the factor of 0.7 to compensate for the difference in heat: the concentration of $PM_{2.5}$ from 100% plastics (line 14 on figure 9) for example, will reduce the maximum concentration from ~200 mg/m^3 to ~140 mg/m^3 which fall well within the range recorded for coal (line 12 on figure 9). From an overall perspective fuel ash represents which around 2% of the total particulate matter collected by the ESP so any effect should be minimal and could be included as an area to focus in the full scale industrial trials.

4.2 TUBE FURNACE RESULTS ON VOLATILE ORGANIC COMPOUNDS (VOCs)

Figures 11 to 14 show VOCs detected during the combustion of equal masses of samples containing 100% coal; coke; coal/coke and plastics. The VOCs were recorded in μg/kg of flue gas emitted. From the graphs, plastics produce the most diverse mix of volatiles as shown in figure 14- ten species. This is as expected because plastics have more volatile content compared to coal and coke. Coke recorded only two volatile organic species; coal generated eight VOC species.

Figures 15 to 20 show VOCs detected when various proportions of coal, coke and plastics were combusted in the tube furnace. A summary of the results from these figures show that for the coal/plastic mix, the VOCs detected consisted mainly of those observed for the two components burnt separately. The following VOCs detected in the coal/plastic samples were also present in the 100% coal sample and included: benzene; carbon tetrachloride; xylene; bromoform; styrene; 1,1,2,2-tetrachloroethane and naphthalene. VOCs detected for some samples of the coal/plastic which were also present in the 100% plastic sample were: naphthalene; toluene; xylene; bromoform; styrene; 1, 1, 2, 2-tetrachloroethane; trans-1, 4-dichloro-2-butene; 1, 4-dichlorobenzene, butylbenzene ; and carbon tetrachloride. All the VOCs detected from the tests with 100% plastic, were also present in the combustion products of the coal/plastic mix samples.

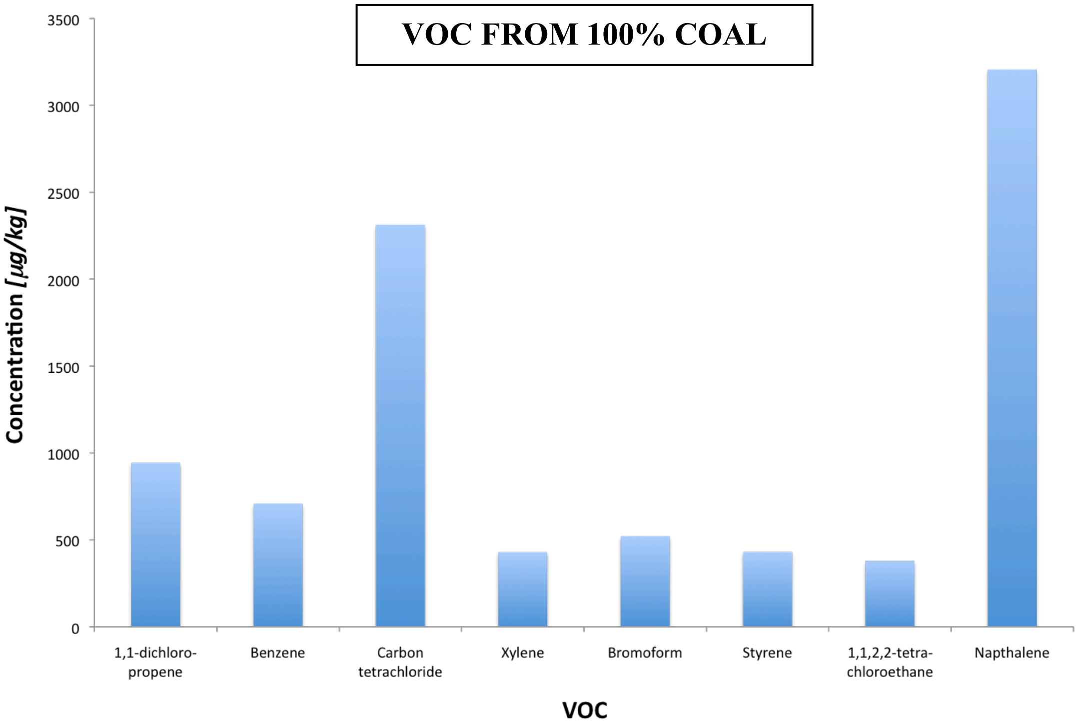


Figure 11: VOC collected in Thermal Desorption Tube (TDT) during the combustion of 100% coal.

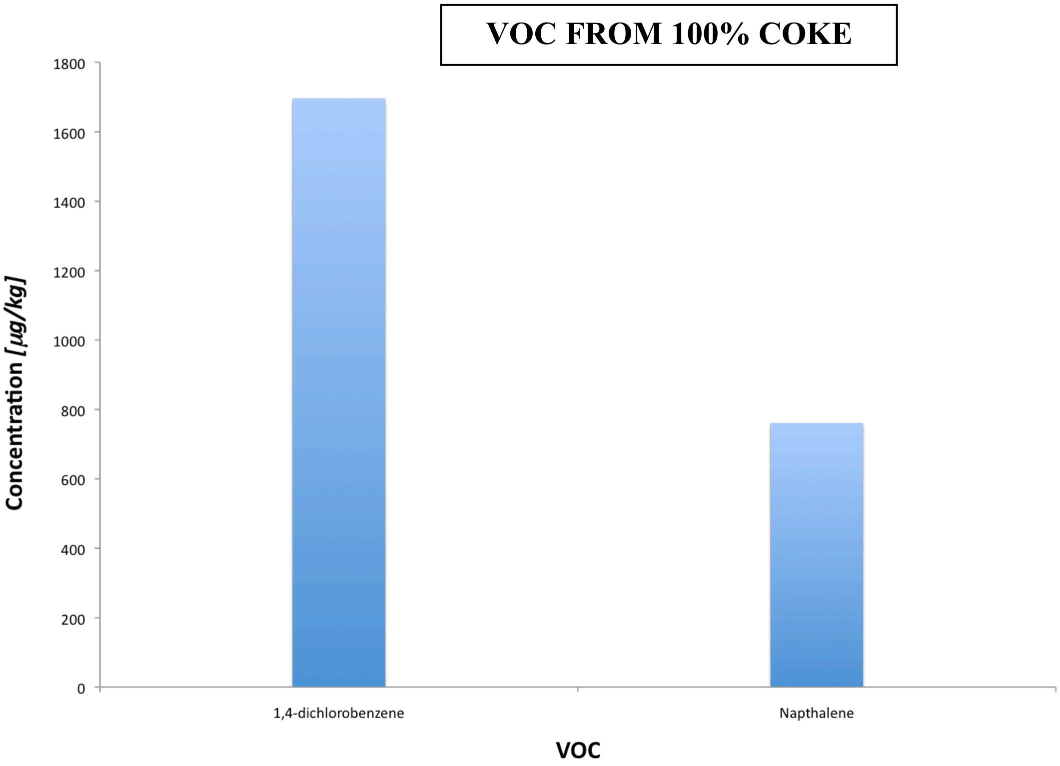


Figure 12: Detected VOC collected in TDT during the combustion of 100% coke in tube furnace

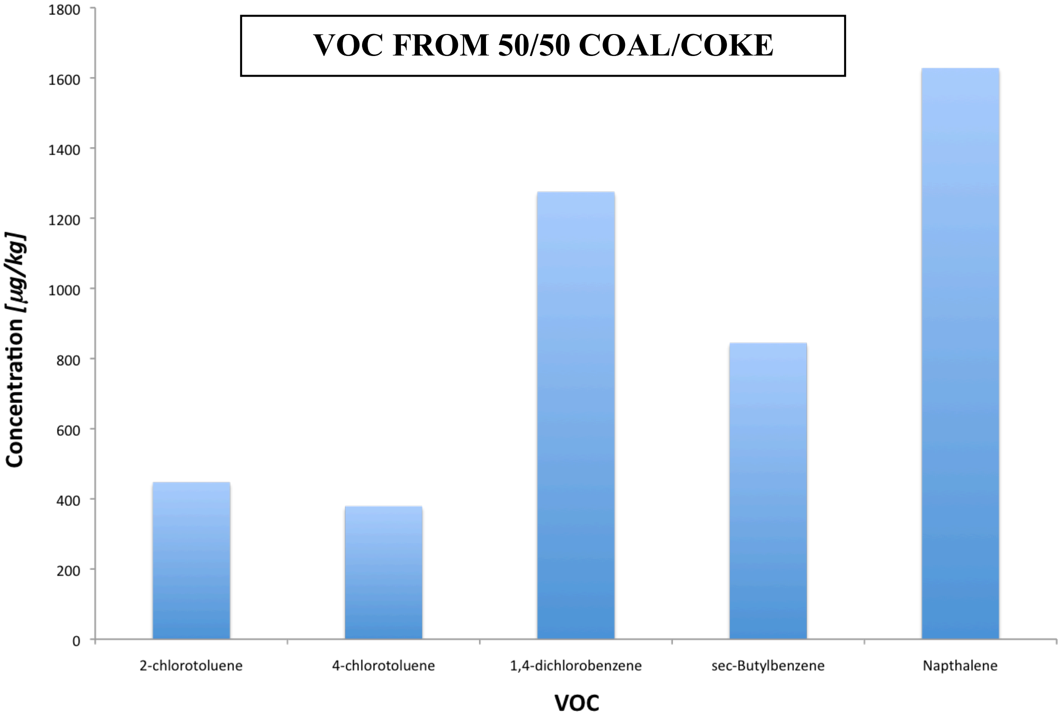


Figure 13: VOC collected in TDT during the combustion of 50/50 Coal/Coke mix in tube furnace

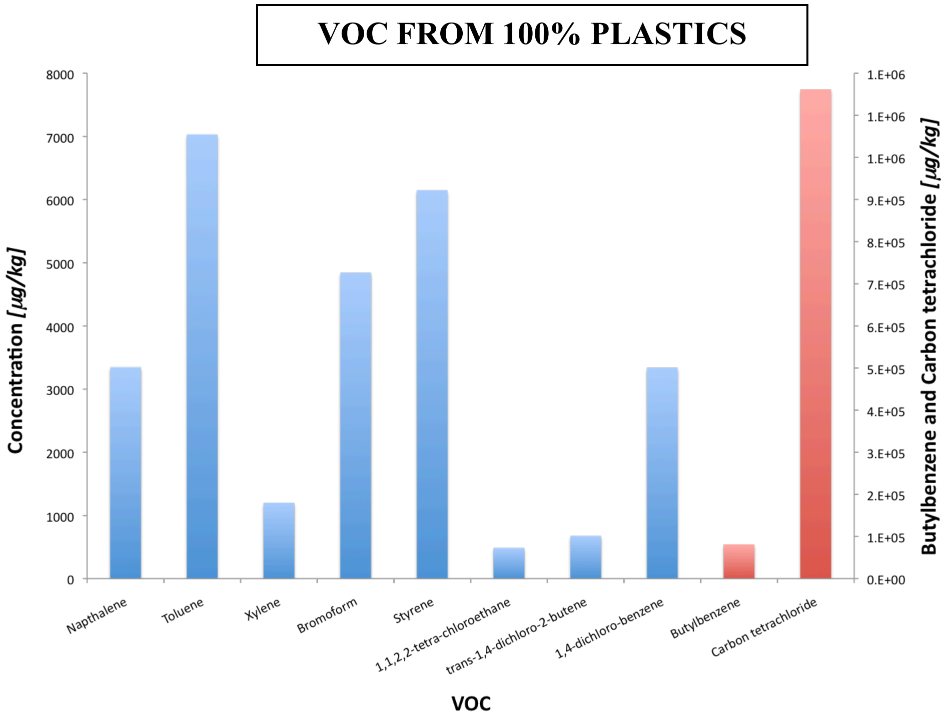


Figure 14: VOC collected in TDT during the combustion of 100% plastics in tube furnace

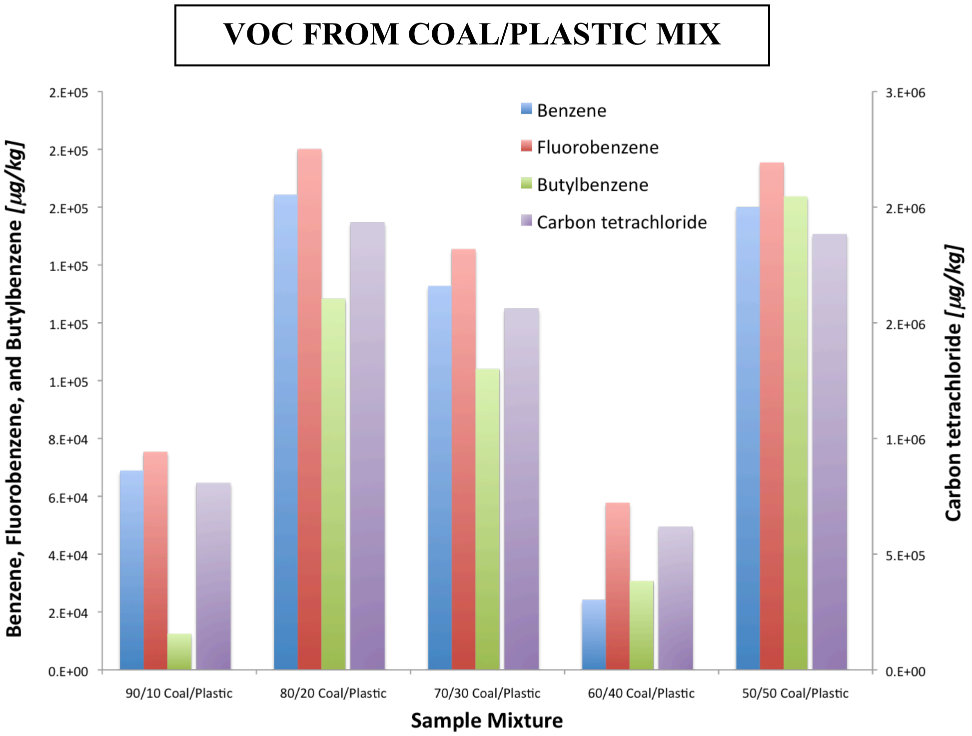


Figure 15: Detected benzene, fluorobenzene, butyl benzene and carbon tetrachloride for coal/plastic combustion test

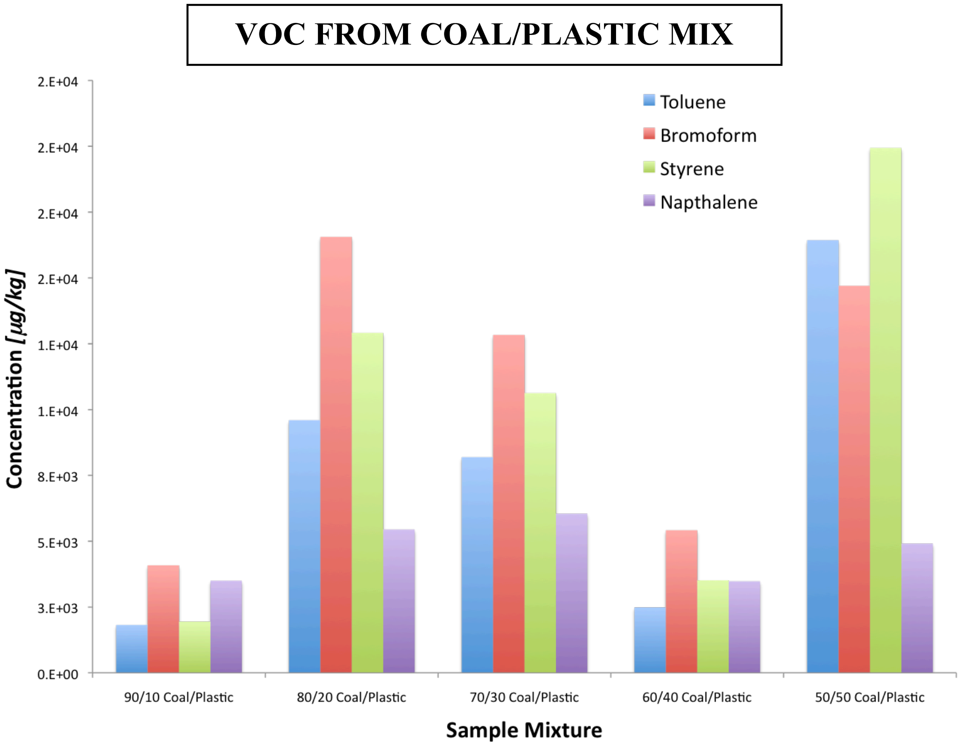


Figure 16: Detected toluene, bromoform, styrene and naphthalene for coal/plastic combustion test

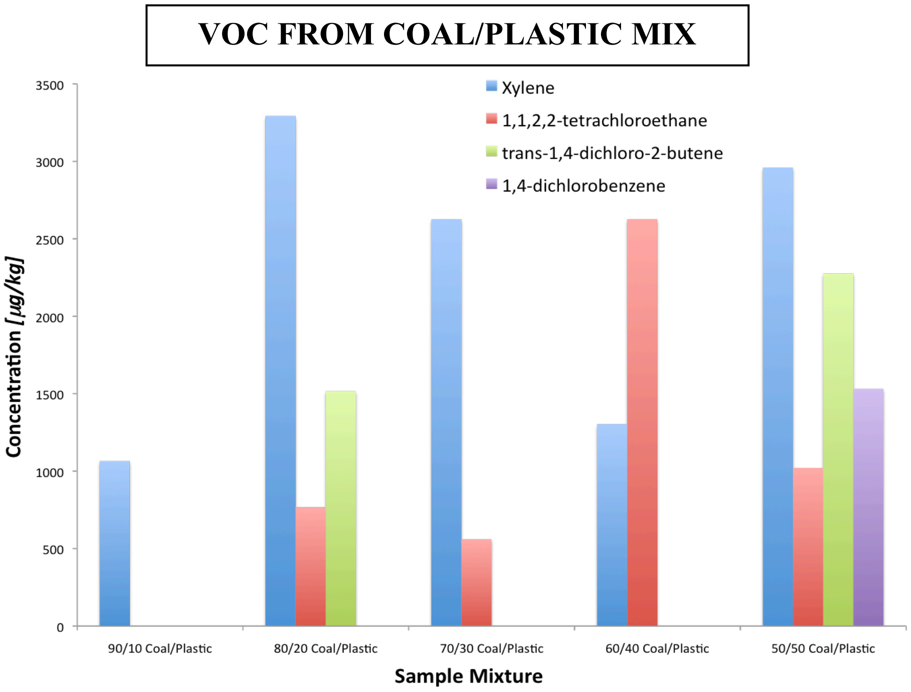


Figure 17: Detection of xylene; 1, 1, 2, 2-tertachloroethane; trans-1, 4-dichloro-2-butene; 1, 4-dichlorobenzene for coal/plastic combustion test.

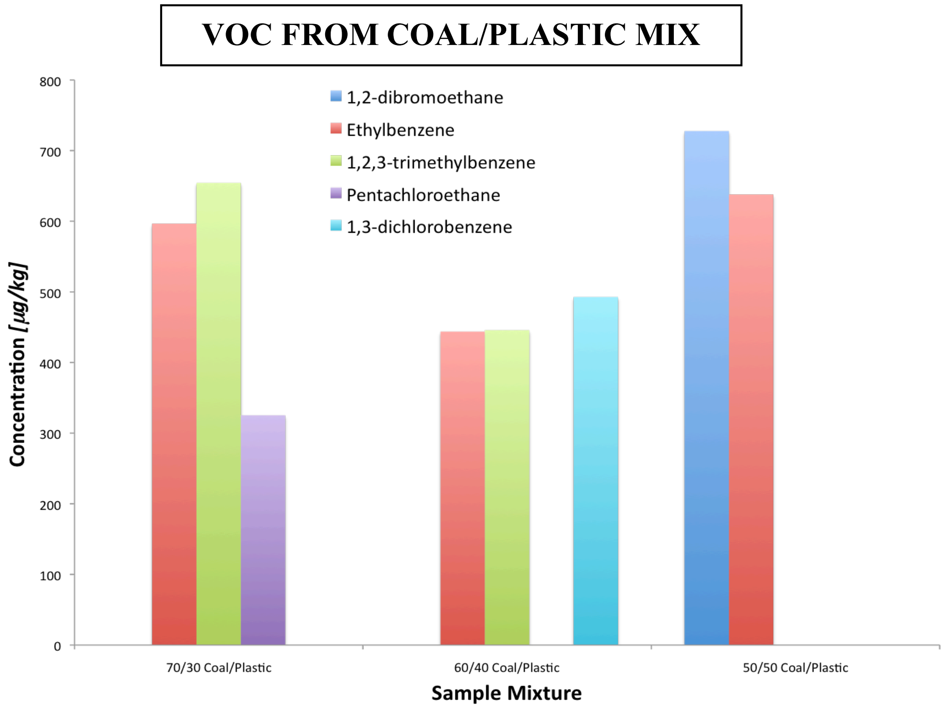


Figure 18: Detection of 1, 2-dibromoethane; ethylbenzene; 1, 2, 3-trimethylbenzene; pentachloroethane and 1, 3-dichlorobenzene for coal/plastic combustion test.

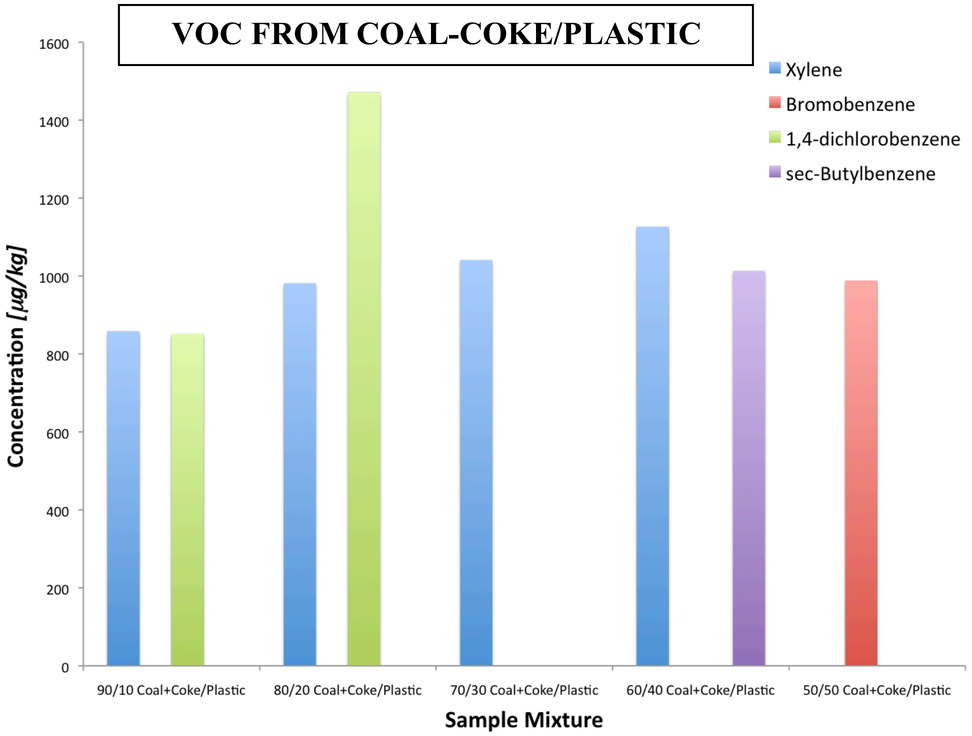


Figure 19: Detection of xylene; bromobenezene; 1, 4-dichlorobenzene; sec-butylbenzene for coal-coke/plastic combustion test.

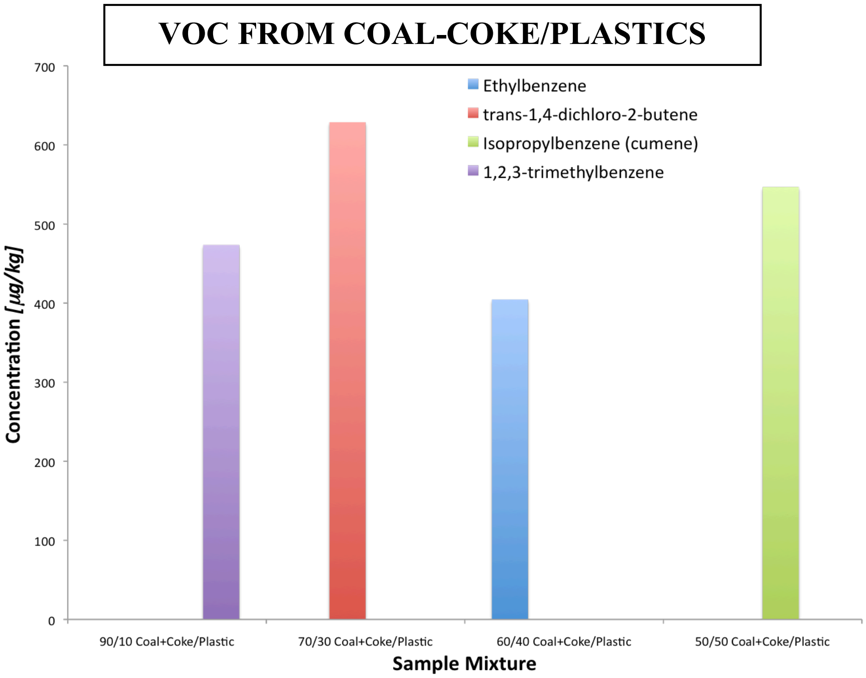


Figure 20: Detection of ethylbenzene; trans-1,4-dichloro-2-butene; isopropylbenzene and 1, 2, 3-trimethylbenzene for coal-coke/plastic combustion test

The absence of 1,1-dichloropropene which was detected for 100% coal but not for coal/plastic; and the emergence of VOCs such as fluorobenzene, ethylbenzene, 1, 2, 3-trimethylbenzene and 1, 4-dichlorobenzene indicate that interactions occur among the VOCs generated from pure samples during combustion yielding newer species and eliminating older ones. For the coal-coke/plastic samples, the VOCs detected also included all the expected VOCs from pure plastics. All the VOCs detected for 100% coke were also present in the detected VOCs for the coal-coke/plastic samples. 2-chlorotoluene and 4-chlorotoluene which were detected for the 50/50 coal/coke samples were not detected when the composition included plastics. Sec-butylbenzene which was detected for coal/coke only was also detected for coal-coke/plastics. Similar to coal/plastics, coal-coke/plastics also generated VOCs which were absent in the combustion products of all three components. The lack of a definite trend in the emission of VOCs could be attributed to the heterogeneity of the mixed plastic samples. As mentioned earlier, there were heavier chip-like components and lighter ones: in preparing the samples for testing, the mix of light and heavy plastics was random as long as the combination provided the required mass.

Discussion

Over twenty VOCs were detected in low concentrations. This number confirms the assertion that residence times of the flue gases in the hot zone of the tube furnace may not be long enough to thermally degrade these organic compounds. The limited number of emergent species compared to the VOCs associated with pure samples also gives credence to the assertion that thermal degradation was not as extensive as would be in an industrial kiln. This limitation has been highlighted in the description of our experimental methods.

Variations in the quantity of VOCs produced from the mixture of coal, coke and plastics could be attributed to the heterogeneity of the plastic fractions which consisted of fluffy and chip-like plastics randomly mixed to meet the target mass for each test. The optimum fraction of plastics in the fuel mix could be verified via full scale industrial trials.

It is however safe to conclude that plastics will contribute a significant amount of volatiles which when consumed in a kiln will generate large amounts of energy for the clinkerization of crushed limestone. The temperature regime and residence time of flue gas in the cement kiln at Lafarge can sufficiently thermally degrade these VOCs as shown in the literature review section. For example a compound such as benzene (C_6H_6) should thermally breakdown in the following manner at temperature > 1000°C:

$$C_6H_6 \ + \left(\frac{9}{2}\right) O_2 \rightarrow 6CO + 3H_2O\ ;\ then\ CO + \frac{1}{2}\ CO_2 \rightarrow CO_2$$

Similar degradation is expected for the other detected VOCs. The produced CO_2 and H_2O from the oxidation of VOCs are already quantified in the theoretical prediction for the mass of combustion products from stoichiometry and elemental analysis. These are not additional emissions that should awake any additional concerns.

5. CONCLUSION AND RECOMMENDATION

The data collected by the methods described in this report provide a reliable preliminary guide to the possible changes in emissions which may occur when an equivalent heat amount of a coal-coke fuel blend is replaced with plastics. The results have been discussed and analysed in light of limitations of equipment, materials and methods. Comparative study of the fuel blends provided the following findings:

1. Prediction of flue gas composition from the elemental analysis of plastics, coal and coke, show that replacing coal/coke with waste plastics should decrease the potential to form PCDD/F, SO_2, NO_x, secondary PM and secondary O_3. Based on equivalent heat amounts, our analysis projects 34% decrease in fuel CO_2; 80% reduction of fuel NO_x; and 98% reduction in fuel SO_2 emissions. Also, plastics provide a 30% reduction in fuel mass requirement for equivalent heat content of coal/coke.
2. From elemental analysis of equivalent heat quantities of plastics and coal/coke, PM emissions should decrease by more than 50% with the use of plastics. After applying heat content compensation factor of 0.7 to results obtained from experimental tests in the tube furnace, particulate emission from plastics were found to fall within similar ranges as coal. Based on these projections, the expected changes in particulate emissions should have minimal effect on ESP presently in use at the Brookfield plant.
3. Recorded experimental data showed clearly that the presence of plastics resulted in the increase of VOCs species. This agreed with predictions from literature and chemical analysis. These VOCs are expected to thermally degrade into products of complete combustion (CO_2 and H_2O) under industrial cement kiln conditions and an extended residence time.

With results from this comparative study and available literature on one hand; and the Brookfield cement kiln emissions control technology on the other, it is recommended that full scale field trials with stack emissions monitoring targeted towards PM, CO_2, SO_2 and VOCs downstream of the ESP should proceed. This should provide more data to confirm; or identify any deviations from expectations drawn from elemental analysis and the presented experimental results. Field trials would also provide the opportunity to quantify the effect of the ESP in the comparative analysis, an aspect that could not be fully evaluated in the bench scale experiments.

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