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Candidate: W.K. Hiromi Ariyaratne

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Telemark University College
Faculty of Technology
Kjølnes
3914 Porsgrunn
Norway
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Abstract:

In this thesis, the possibilities and limitations of using alternative fuels in cement kilns are considered. A literature study on agricultural biomass, non-agricultural biomass, petroleum based waste, chemical & hazardous waste and other miscellaneous waste is carried out.

The cement manufacturing process is overviewed and a modern "Pfister feeder" system installed at the Norcem cement plant in Brevik-Norway is thoroughly discussed.

The biomass content of RDF is experimentally determined by the selective dissolution method. The average biomass, non-biomass and ash content are 43.75% (dry), 14.65% (dry) and 41.60% (dry) respectively. However, some unlikely values were found when determining the biomass content of RDF by calorific value (average 36.4% (dry) of biomass and 63.6% (dry) of non-biomass) and it should be further investigated.

The RDF is further characterized by thermogravimetric analysis for pure portions of polyethylene, rigid plastics, polystyrene, wood, cardboard, paper and fabric. Almost similar results were obtained for proximate analysis as found in the literature. Also, the coupling of TGA and FTIR through gas bag transfer is overviewed thoroughly and a procedure for manual transfer of gas samples has been given.

Full scale experiment with animal meal feeding at the main burner is carried out in kiln 6 at Norcem-Brevik with the new feeder system. No operational, process or emission problems could be observed when feeding up to 7 t/hr of animal meal at a moderate raw meal feed rate (220 t/hr). However, the clinker quality could be accepted only up to 6 t/hr of animal meal feed rate. An increase of free lime content with animal meal feeding is either due to a reduction of flame temperature or the introduction of extra calcium at the kiln outlet via the high calcium phosphate content in animal meal, which will add to the clinker without proper burning.

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Preface

I wish to express my sincere and profound gratitude to my supervisor, Ass. Prof. Lars-André Tokheim for supervising my research project and the invaluable assistance, guidance, advice and encouragement given during the course of this study.

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Porsgrunn, May 14, 2009

Hiromi Ariyaratne

Overview of tables and figures

Abbreviations

APCD	Air Pollution Control Device
ASR	Automobile Shredder Residue
BSE	Bovine Spongiform Encephalopathy
CDM	Clean Development Mechanism
CFD	Computational Fluid Dynamics
CKD	Cement Kiln Dust
CSS	Combustible Solid Substances
CV	Calorific Value
DRE	Destruction & Removal Efficiency
DTG	Time Derivative of ThermoGravimetry
EGA	Evolved Gas Analysis
ESP	Electro Static Precipitator
FTIR	Fourier Transform Infra Red Spectrometer
GCV	Gross Calorific Value
GHG	Green House Gas
HCB	Hexa Chloro Benzene
HHV	Higher Heating Value
HWF	Hazardous Waste Fuel
ID	Induced Draft
LA	Low Alkaline
LDPE	Low Density Polyethylene
LHV	Lower Heating Value
LHW	Liquid Hazardous Waste
MBM	Meat & Bone Meal
MSW	Municipal Solid Waste

NOK	Norwegian Krone
OPC	Ordinary Portland Cement
PAH	Poly Aromatic Hydrocarbon
PCB	Poly Chlorinated Biphenyl
PCDD	Poly Chlorinated Di-benzo Dioxins
PCDF	Poly Chlorinated Di-benzo Furanes
PE	Polyethylene
PET	Polyethylene Terephthalate
PHD	Process History Database
PP	Polypropylene
PS	Polystyrene
PSR	Perfectly Stirred Reactor
PVC	Poly Vinyl Chloride
RDF	Refuse Derived Fuel
SHW	Solid Hazardous Waste
SLC	Separate Line Calciner
SLF	Substitute Liquid Fuel
SPL	Spent Aluminium Pot Liner
SR	Shredder Residue
SRF	Solid Recovered Fuel
TDF	Tyre Derived Fuel
TGA	ThermoGravimetric Analyzer/Analysis
THC	Total Hydro Carbon
TOC	Total Organic Carbon
TUC	Telemark University College
VOC	Volatile Organic Compound
XRF	X-Ray Fluorescence

1 Introduction

1.1 Background

Cement is an important binding agent for construction industry and is produced world-wide in large amounts. Cement manufacturing is an energy-intensive process due to the high temperatures required in the kilns for clinkerization (Murray & Price, 2008). Typically cement production requires approximately 3.3-4 MJ/kg clinker of thermal energy depending on the process (Demján, 2005). In General, the energy cost in a cement plant is around 30 – 40% of the total production costs (Rasul, Widianto & Mohanty, 2005).

On the other hand, cement production generates an average world carbon emission of 0.81 kg CO_2 per kg cement produced (Huntzinger & Eatmon, 2009). The calcination of carbonates accounts for roughly 60% of the CO_2 emitted, while the remaining CO_2 results from energy usage during the production process (Tokheim, 1999). It has been estimated that the CO_2 emissions from the cement manufacturing contribute 5% of global CO_2 emissions and hence major impact on the environmental threat; global warming (Murray & Price, 2008).

Now the cement industry is close to the limit of what can be achieved through technical improvements. In order to keep its competitiveness the cement industry tries to combine the energy efficiency and the use of alternative fuels and alternative raw materials. Although coal, petroleum coke, and other fossil fuels have been traditionally burned in cement kilns, because of the high energy usage and high environmental impact of the process, many cement companies have turned to energy-rich alternative fuels. Further, due to their high burning temperatures, cement kilns are well-suited for accepting and efficiently utilizing a wide range of wastes that can present a disposal challenge. Besides, this integrated activity offers additional revenues to the cement industry as the disposal of wastes normally receives a financial incentive (Andrade, Maringolo & Kihara, 2003).

Today, many plants meet between 20-70% of their energy requirements with alternative fuels such as animal meal, waste tyres, waste oils, solvents, plastics, paper, wood, rubber, sewage, refused derived fuels, etc (Cement manufacturing, 2008). This type of energy recovery conserves not only the valuable fossil fuels for future generations while safely destroying wastes that would otherwise be deposited in landfills but also the fuel expenses.

The range of alternative fuels is extremely wide. In order to complete the thermal destruction of certain waste, it is necessary to analyze the physical, chemical and thermal characteristics of each waste and its compatibility to the clinking process. It is important to know the physical state of the fuel, calorific value, content of ash, volatiles, moisture, fixed carbon, toxicity and some other physical properties like particle size, bulk density, etc. The safety of the process is related to both the efficient control of the temperature of the flame and the heat transfer process, as well as the accurate mixture of the raw material, and hence the quality of the final product and a balanced operation of the kiln (Ottoboni et al., 1998). A cement kiln using waste materials retains ash and other residual constituents incorporating them into the clinker and it is important to observe them before burning.

1.2 Problem statement

This research project basically focuses on the use of alternative fuels in cement kilns and it will be analyzed in detail. The following points will be mainly concerned under main objective. The detailed task description is shown in Appendix 1.

- Carry out literature study on the use of alternative fuels in the cement kilns
- Determination of biomass content of RDF through laboratory experiments
- Perform laboratory experiments in TGA instrument for the characterization of refuse derived fuel (RDF)
- Further development of a fuel characterization procedure using a combined TGA/FTIR system
- Carry out animal meal capacity test in full scale with a modern alternative fuel feeding system (Pfister feeding system)

Norcem cement plant in Brevik, Norway has initiated the utilization of alternative fuel in 1987 and it is still being improving because of their motivation on the benefits for the society, environment and plant itself (Tokheim, 2005). However, when optimizing the replacement of fossil fuels by alternative fuels, it faces several limitations and further investigations and modifications are required to overcome these restrictions. Therefore, the objectives of this project has been decided by concerning those matters and Norcem cement plant in Brevik, Norway will be taken as a case study.

1.3 Structure of the thesis

This chapter lists the project objectives and a general introduction for the utilization of alternative fuels in the cement kilns. The chapter 2 presents a literature study of the different types of alternative fuels used in cement kilns and their characteristics. Chapter 3 includes brief description of cement manufacturing process. The alternative fuel system at Norcem-Brevik is also reviewed in chapter 3. The determination of biomass content in RDF is discussed in chapter 4. In chapter 5, the laboratory scale experimental work with TGA instrument for sorted materials of RDF is presented. The full-scale combustion experiments with a modern feeding system are presented in chapter 6. Finally Chapter 7 presents the conclusions and recommendations for the future work.

2 The literature study on the use of alternative fuels in cement kilns

2.1 Introduction

Cement kilns represent a very energy intensive sector, requiring energy inputs ranging from 3.2 to 5 MJ/kg of clinker produced depending on the process conditions (Lemieux et al., 2004). The reaction of decarbonization of limestone and dehydration of kaolinite, which are highly endothermic, needs energy around 2.2 MJ/kg and the exothermic reaction of phase forming (C_3S, C_2S, C_3A and C_4AF; See 3.1) releases energy around 0.45 MJ/kg. In the dry process, approximately 50% of the energy is needed for chemical reaction and the rest is contributed for the radiation loss (approx. 10-12%), exhaust air (about 10%), exhaust gas (up to 20%) and clinker (approx. 2%) (Willitsch et al., 2009). Cement manufacturers are using a variety of energy inputs. Among the most common types of fuels are fuel oils, miscellaneous coal, petroleum coke and natural gas (Jacott et al., 2003). It is pointed out that energy makes up about 30-40% of the cost of cement production (Rasul, Widianto & Mohanty, 2005). Not only to reduce energy costs but also for the saving natural resources, decreasing emissions, decreasing the need for landfills and other disposal options and decreasing the CO_2 footprint of emissions, the cement manufacturers around the world are adopting the practice of using waste products and other alternatives to replace fossil fuels in cement manufacturing (Gossman, 2007).

Researches carried out for a number of years in cement plants all over the world have clearly shown the advantages of waste utilisation in clinkering processes and cement production. Industrialized countries have over 20 years of successful experience of using alternative fuels. In the US, it is common for cement plants to derive 20-70% of their energy needs from alternative fuels (Murray & Price, 2008).

The conditions of incineration in cement furnaces are perfect for the use of alternative fuels made from waste since the gross chemical make up of many wastes is similar and compatible with the raw materials used to manufacture portland cement. The decisive factors promoting the use of cement kilns for the utilization of wastes are:

1. The cement kiln sustains high temperatures: the temperature of the material in the clinkering zone reaches at least 1700 K and flame temperatures 1900–2100 K and

significantly exceed the level of temperatures necessary for complete incineration of high-molecular hydrocarbons, as well as the de-chlorination of dioxins and furans (Mokrzycki, Uliasz-Bochenczyk & Sarna, 2003).

2. Long residence time at high temperature (since the significant length of kiln), which guarantees a great efficiency of thermal destruction: A gas stream with a temperature exceeding 1670 K flows through this zone within about 2.7 s, while the time for gas streams to flow through the zone with a temperature exceeding 1470 K amounts to between 4.1 and 5.0 s (Mokrzycki, Uliasz-Bochenczyk & Sarna, 2003).

3. Surplus oxygen during and after combustion (Karstensen et al., 2006).

4. The process is enhanced by an alkaline environment that tends to scrub combustion gases: neutralization and capture of the HCl acid or other compounds (Giannopoulos et al., 2007).

5. Fixation of the traces of heavy metals in the clinker structure which promotes the immobilization of the heavy metals since it is finally bound to the concrete: no production of by-products such as slag, ashes or liquid residues (Karstensen et al., 2006)

6. Highly turbulent nature leads to the formation of a highly homogeneous mixture: Actual gas flow velocities through the high temperature zones fall within the range of 12.1–13.5 m/s (Mokrzycki, Uliasz-Bochenczyk & Sarna, 2003).

7. Large area of the furnace and continuous fuel supply.

In addition to above factors, the cement kiln dust (CKD) and particulates contained in the exhaust gas are collected through electro static precipitators and recycled to the system (Giannopoulos et al., 2007).

Moreover, the ecological, economical and social benefits of using alternative fuels in cement kilns are thoroughly discussed below.

2.2 Benefits of using alternative fuels in cement kilns

As discussed in detail below, the potential benefits of burning alternative fuels at cement plants are numerous and fairly obvious, however only with proper planning.

1. The acquisition of primary sources of energy negatively influences the environment. The use of waste as alternative fuels reduces the use of non-renewable fossil fuels such as coal and hence prevents resource depletion of valuable non-renewable fossil fuels which takes long period of time for the creation (CEMBUREAU, 1997).

2. The use of alternative fuels has the potential to reduce emissions to the environment by replacing the use of conventional fossil fuels with materials that would otherwise have to be incinerated in a separate dedicated incinerator with corresponding emissions and final residues (figure 2.1). It has been demonstrated that the substitution of conventional fossil fuels with alternative fuels based on waste can make an important contribution to sustainable development through the reduction of the global burden of greenhouse gases such as carbon dioxide and hence slow down of global climate changes which is the Kyoto target (CEMBUREAU, 1999). The cement industry is responsible for 5% of global CO_2 emissions, nearly 50% of which are due to the combustion of fossil fuels (Murray & Price, 2008). As illustrated in figure 2.2, in a coal fired cement plant, 0.83 ton of CO_2 is emitted when 1 ton of cement produced and 54% out of that is due to decarbonation of limestone, 34% is due to combustion of coal and the rest of 12% is due to other electricity utilities for the cement production process.

3. The use of alternative fuels in cement kilns maximizes the recovery of energy from waste. All the energy is used directly in the kiln for clinker production. Also, when alternative fuels are combusted in cement kilns, the inorganic part is bound into crystal structure of the clinker indicating the whole recovery of waste material. Unlike with dedicated waste incineration facilities, no any liquid waste is generated and all solid waste is recycled within the kiln hence no need of separate disposal of ash and slag (CEMBUREAU, 1997).

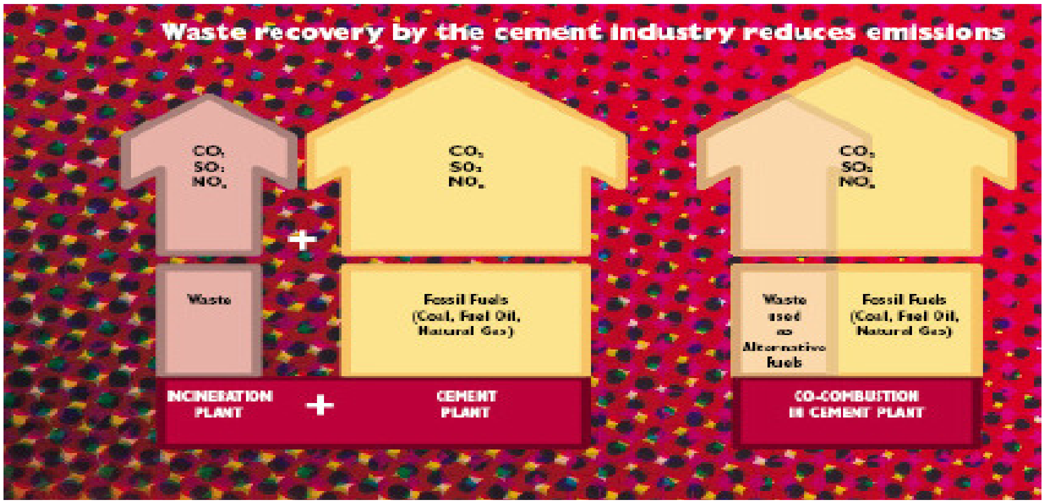


Figure 2.1: Benefits of emissions in co-combustion of alternative fuels in a cement plant (Murray & Price, 2008)

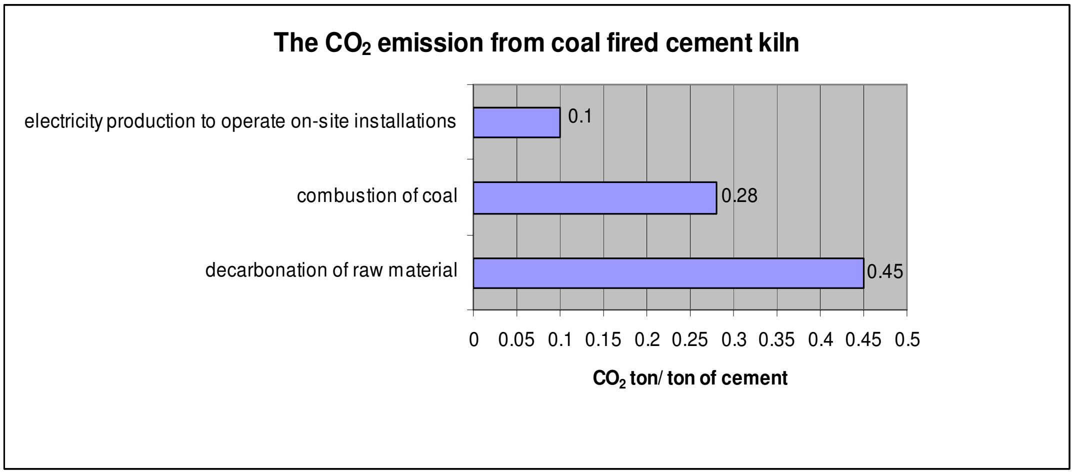


Figure 2.2: The CO_2 emissions from coal fired cement kiln (CEMBUREAU, 1999)

4. Alternative fuels are essentially the waste products of other industrial or agricultural processes, and due to their high volume and potentially their toxicity, they pose a major solid waste management challenge in many countries. In all cases these waste materials would either have been land filled or combusted in dedicated incinerators. By utilizing pre-existing kiln infrastructure and energy demand, cement kilns offer an environmentally safe and secure alternative for the conventional disposal of waste in dedicated waste incinerators or in landfills. This leads to a reduced number of new disposal sites, a limitation of the expansion of existing sites and obviating the need to build dedicated, specialist incineration facilities which may have significant negative impacts on the environment. Moreover, the specialist waste incinerators are very inefficient converters of the heat content of wastes, whereas a cement kiln approaches 100% efficiency (CEMBUREAU, 1999). In fact, employing alternative fuels in cement plants is an important element of a sound waste management policy.

In addition to the aforementioned environmental benefits of using alternative fuels for cement manufacturing, there are numerous economical and social benefits have been realized.

1. Reduces the cement production costs and thereby improving the competitiveness of the industry: Cement plants are often paid to accept alternative fuels; other times the fuels are acquired for free, or at a much lower cost than the energy equivalent in coal (Murray & Price, 2008).
2. Reduces the incinerator or waste disposal costs.
3. GHG mitigation undertaking has the chance of earning carbon credits through the Clean Development Mechanism (CDM) for the cement manufacturer (National Technical Experts Team from Geosphere Technologies, 2005).

4. The collection, handling and transport of alternative fuels to the cement plants can generate employment and business opportunities in local communities.

2.3 Classification of alternative fuels used in cement kilns

There are several simple categorizations have been made by several authorities to classify the alternative fuels used in cement industry. Mokrzycki & Uliasz-Bochenczyk, 2003 reported following classifications for the alternative fuels in cement kilns.

According to the concentration criterion:

- Gas (landfill gas, pyrolysis gas)
- Liquid (pasty wastes, solvents, waste oils, greases, chemical waste from pharmaceutical and chemical manufacturing, distillation residues, wax suspensions, petrochemical waste, asphalt slurry, paint waste)
- Solid (meat and bone meal, paper, tyres, ruber wastes, plastics, fluff, electronic scraps, coconut residue, bagasse, pulp sludge, battery cases, wood waste, domestic refuse, refuse derived fuel, oil-bearing soils, sewage sludge, auto residues, agricultural waste)

According to the classification by Cembureau classification:

- Class 1: gaseous alternative fuels (examples: refinery waste gas, landfill gas)
- Class 2: liquid alternative fuels (examples: low chlorine spent solvents, hydraulic oils)
- Class 3: pulverized, granulated or finely-crushed solid alternative fuels (examples: sawdust, dried sewage sludge, granulated plastic, animal flours, fine crushed tyres)
- Class 4: coarse-crushed solid alternative fuels (examples: crushed tyres, rubber/ plastic waste, wood waste, reagglomerated organic matter)
- Class 5: lump alternative fuels (examples: whole tyres, plastic bales)

Solid alternative fuels may be divided into four groups:

- Group 1: solid, dry fuels of relative fine size, which do not adhere (dimensions: <2 mm, humidity: <10–15%); for example: wood dust, bark powder, rice husk
- Group 2: solid, dry fuels of coarse size, which do not adhere (dimensions: <20 mm, humidity: <10–15%); for example: plastic waste, wood chips, waste wood
- Group 3: solid, dry fuels which tend to stick (dimensions: <20 mm, humidity: <10–15%); for example: animal powder, impregnated wood dust

- Group 4: mixtures of different lumpy fuels (dimensions: <200 mm, humidity: <20%); for example: fluff, paper, cardboard

There is also another classification of solid and liquid fuels used in the cement industry.

Solid fuels are divided into three categories:

- Vegetable compounds or natural products (oil shale, peat, barks, sawdust, etc.)
- Synthetic products (used tyres, rubber waste, waste plastics, etc.)
- Others (parts of shredded cars, fuels derived from rejects, household garbage, etc.)

Liquid fuels are divided into:

- Liquid substitute fuels; easily decomposed, slightly toxic (acid tar, oil residues, etc.)
- Liquid substitute fuels, stable toxic (poly aromatic hydrocarbons (PAH), polychlorinated biphenyl (PCB), etc.)

Generally, the amount of coal or other fossil fuel demand that is displaced depends on the calorific value and water content of the alternative fuel in comparison to coal. A general illustration of average volumes required to replace one ton of coal are shown in figure 2.3. (Values are dependent on material's energy and water content. Substitution assumes coal has a LHV of 26.3 GJ/ton). While LDPE shows the less requirement to replace one ton of coal, the sludge needs in higher quantities due to high moisture content.

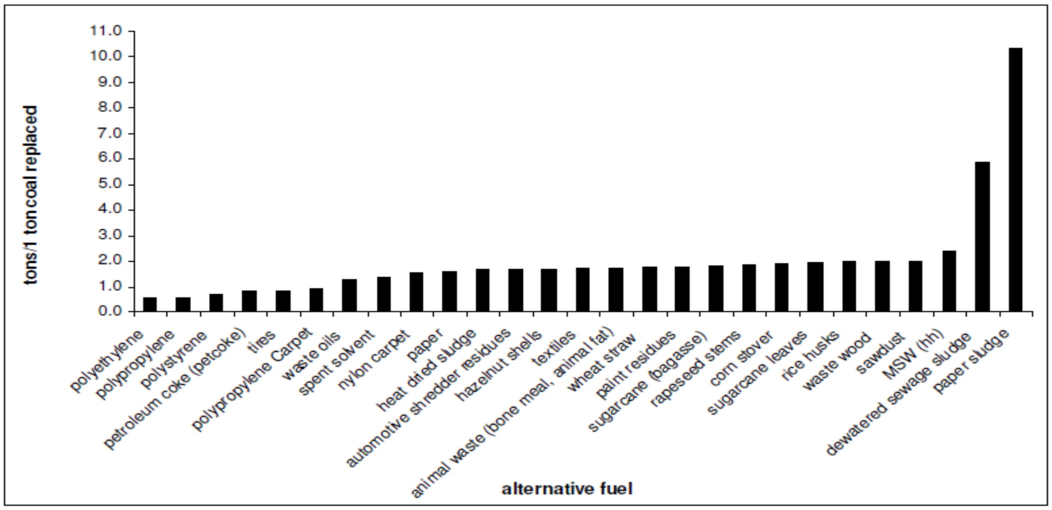


Figure 2.3: Tons of alternative fuel required to replace 1 ton of coal (Murray & Price, 2008)

2.4 Why characterization is important?

Before any alternative fuel is considered for the use in cement kilns, its characteristics and impacts to clinker quality and plant stack emissions should be determined in order to take actions for the optimum thermal destruction of certain fuel.

The calorific value must be stable enough to allow the control of the energy supply to the kiln. As Willitsch et.al., 2009 reported, for a continuously running operation of the cement kiln, the calorific value should not undergo the limit of 18 MJ/kg fuel. However, at secondary combustion the calorific value could be below 10 MJ/kg.

All kinds of varieties from liquid to solids, powdered or as big lumps can be encountered when dealing with alternative fuels (Kääntee et al., 2002). Therefore in order to achieve consistent (fairly homogeneous) material characteristics in the kiln, some fuels demand previous preparation before use. Certain kinds must be dried and pulverized. Other wastes require cutting or compressing (Ottoboni et al, 1998). Simply, the physical form must allow easy handling of the material for transportation and a stable, adjustable flow of material in the cement plant. Some fuel types can only be fed into particular sections in the system and may be needed the flexible fuel feeding systems. It may be fed directly into the burning zone in the kiln itself or into the pre-heating system for dissociating part of the carbonates from the meal before it enters the kiln for clinker formation (Kääntee et al., 2002). Burner modifications are also needed for certain fuels.

Moreover, the chemical quality of the fuel must meet regulatory standards assuring environmental protection. Especially when concern the waste derived fuels, physical and chemical characteristics vary substantially, since they are often very heterogeneous.

The following properties of the fuel can be considered as more important;

- Physical state of the fuel (solid, liquid, gaseous)
- Content of circulating elements (Na, K, Cl, S)
- Toxicity (organic compounds, heavy metals)
- Composition and content of ash
- Content volatiles
- Calorific value
- Physical properties (scrap size, density, homogeneity)
- Grinding properties
- Humidity content

- Proportioning technology

(Mokrzycki & Uliasz-Bochenczyk, 2003)

The following subsections of this report consist of an overview of the types of alternative fuels used in cement kilns and their combustion characteristics, focusing on energy and environmental considerations. The types of fuels covered are agricultural biomass, non-agricultural biomass, chemical and hazardous waste, petroleum-based fuels and miscellaneous alternative fuels. Information is provided with emphasis of physical, chemical characteristics, material pre treatment-storage & handling, process condition requirements, emission impacts and product quality impacts. A summary of ultimate analysis, proximate analysis, elementary analysis, etc for alternative fuels reported by different authors are presented in Appendix 2.

2.5 Agricultural biomass

Globally, agricultural biomass residues accounted for 0.25% of fuel substitutes used in cement manufacturing in 2001 (Murray & Price, 2008). The use of them in cement manufacturing is less common in industrialized countries and appears to be concentrated in more rural developing regions, even in developing countries, its share as kiln fuel is under 5% (Müller & Harnisch, 2009). The type of biomass utilized by cement plants is highly variable, and is based on the crops that are locally grown. Rice husks, wheat straw and corn stover which are most widely available and used as alternative fuels and further more coconut husks, sugar cane leaves and bagasse, rapeseed stems, shells of hazelnut and palm nut, coffee pods are some other common fuels.

- **Material Analysis**

As a rule of thumb, a 20% substitution rate of agricultural biomass residues for fossil fuel (on a thermal energy basis) is quite feasible in cement kilns. The range in LHV of agricultural biomass is from 9.2 – 19.4 MJ/dry kg; corn stover represents the low end and sugarcane bagasse the high end. Nevertheless, different reporters have published enormous range in energy values for these fuels. The water contents of the various types of agricultural biomass also vary dramatically. The presence of halogens (e.g. chlorine) found in biomass likely in wheat straw and rice husks may be a concern for slagging and corrosion in the kiln.

(Murray & Price, 2008)

- **Material pre-treatment, storage & handling**

Rice hulls, bagasse, coconut residues, etc can be stored in an open stockpile. Biomass is prone to change with time, thus care must be taken to use the material before it begins to breakdown. Importantly, new biomass should be rotated into the bottom of storage facilities such that the oldest material is injected into the kiln first. Dedusting systems might be needed as the particles are highly spreadable.

They are fed through the kiln inlet, calciner or the main burner through a mechanical conveyor or through pneumatic feeding.

- **Feeding & process requirements**

Biomass is often used as a secondary fuel, thus is injected during secondary firing at the pre-heater.

Low calorific value of biomass can cause flame instability but this is overcome with lower substitution rates (up to 20%), and the ability to adjust air flow and flame shape. However, substitution rates of greater than 50% have been achieved but require boilers specifically designed for biomass handling. Related to biomass conveyance, the flow behavior of different materials is quite variable, therefore, cement kiln operators must choose the method for injecting fuel into the kiln that will facilitate a constant and appropriate heat value.

Studies have shown that halogenated biomass are better to co-fired with sulphur containing fuels (such as coal) to prevent the formation of alkaline and chlorine compounds on the furnaces and hence prevent from kiln corrosion. However, ash deposits may decrease heat transfer in the kiln (Murray & Price, 2008). A comparison of ash analysis for coal and few agricultural biomasses is presented in Appendix 2.

- **Product quality and stack emissions**

Agricultural biomass is considered as CO_2 neutral because the carbon released during combustion is taken out of the atmosphere by the species during the growth phase. However, the transportation, preparation and fertilizers in biomass cultivation should be considered. On the basis of the assumptions, biomass offsets 2.5 tons of CO_2 for every ton of coal that it replaces (Murray & Price, 2008).

In addition to serving as an offset for non-renewable fuel demand, the use of biomass residues has the added benefit of reducing a cement kiln's nitrogen oxide (NO_x) emissions. Empirical evidence suggests that the reductions in NO_x are due to the fact that most of the nitrogen in biomass is released as ammonia (NH_3) which acts as a reducing agent with NO_x to form nitrogen (N_2). Interestingly, there does not seem to be a strong relationship between the N content in the biomass and the subsequent NO_x emissions reductions (Murray & Price, 2008).

With respect to combustion emissions, though the particulate emissions are increased, biomass does not contain any components that standard cement kiln emissions controls cannot manage.

2.6 Non-agricultural biomass

Globally, non-agricultural biomass accounts for approximately 30% of alternative fuel substitution in cement kilns with animal byproducts including fat, meat and bone meal making up 20% of the total (Murray & Price, 2008). Other varieties of non-agricultural biomass include sewage sludge, paper sludge, waste paper and sawdust.

2.6.1 Paper & wood

Though the best option for waste paper is recycling, the paper cannot be recycled indefinitely, as the fibre strength decreases. The waste paper used in cement industry may contain newsprint, graphics, boxes and casing, cardboard, magazine print, sanitary uses, sludge or residues from production or recycling of paper, etc. Wood based fuels originate from demolished timbers, construction waste, old furniture, etc.

- **Material Analysis**

Relative to other fuel substitutes such as petroleum-based wastes and some chemical and hazardous wastes, biomass has a low calorific value; nevertheless the carbon neutrality of biomass is one incentive for using biomass. Calorific value of paper, paper sludge, wood materials typically is around 12.5-22, 8.5, 17 MJ/kg respectively (Twigger et al., 2001). The filler used in paper industry contains limestone and kaolin which are really beneficial raw materials in cement industry. However, the impregnated wood might be problematic, since it usually involves heavy metal salt of copper, chromium and arsenic, which are fixed to the cell walls of the wood matrix (Ollila et al., 2006). Also paper, paper sludge and woody materials can possibly be contaminated with chlorine.

- **Material pre-treatment, storage & handling**

No plants have been identified where paper waste is the sole alternative fuel type used. Generally if fuels are originated from municipal solid waste, the paper is made up with mixture of plastics and some other materials and then shredded to 10-20 mm. The paper fibre residue can be difficult to use because it requires drying (Twigger et al., 2001). In the case of wood, the impregnated wood is separated out. However, it can be difficult to separate impregnated wood visually or mechanically from untreated wood, especially if the wood is old. Then the woody materials are crushed into small pieces depending on the requirements by primary or secondary combustion.

Bulk feedstock (waiting shredding), shredded or pre-shredded materials are stored in covered storage facilities; typically warehouse facilities to prevent the material getting wet which can cause variability in feed metering and leachate problems. The storage facilities might need odour abatement/hygiene systems. If it is dry paper, the dust suppression and fire detection and extinction is needed. Paper sludge is more likely stored in drums and suitable for blending into wet process slurries for easy handling.

The fuels can be transferred via typical solid fuel conveying method. For an instance, the Castle Cement at Ketton transfers the fuel (plastic and paper mixture) from storage by a front end loader and put on a conveyor, into a hopper, and then into a "Pfister" feeder unit which measured the flow rate. It was then pneumatically conveyed to the kilns (Twigger et al., 2001).

- **Feeding & process requirements**

The fuel can be burnt in calciner or main burner. 10-20 mm size of plastic/ paper mixed fuel is suitable for use in the calciner, however finer shredding may be needed if the fuel is to be used in the front of the kiln. For using of woody materials at primary conveying, a particle size of 6mm has shown as optimal size for combustion (Willitsch et al., 2009).

- **Product quality and stack emissions**

The carbon neutrality of biomass is one incentive for using biomass however depends on sustainable harvesting of trees, and carbon emission associated with transportation and preparation. Assuming biomass as CO_2 neutral fuel, 2.5 ton of CO_2 reduction is achieved with 1 ton of replaced coal (Murray & Price, 2008).

The chlorine present in treated wood can enhance the volatilization of heavy metals like mercury (Hg), cadmium (Cd) and lead (Pb). The formation of PCDD/PCDFs is likely to increase if the biomass is contaminated with substances such as paint, pesticides, preservatives, coatings, or anti-fouling agents (Murray & Price, 2008).

Trials conducted and emissions monitored for demolition timber in cement kiln found there was no increase in heavy metals or organics, which include dioxins. Also a drop in nitrogen dioxide emissions was proved (CIF, 2009).

2.6.2 Meat & bone meal (animal meal)

A major potential source of animal waste for cement kilns is cattle slaughtered for the purpose of public protection from Bovine Spongiform Encephalopathy (BSE) or "Mad Cow" disease in 1992. Some plants use these wastes on a regular basis, whereas other plants burn dioxin-contaminated meat at the request of the government, while few plants (e.g. CCB in Belgium) burn MBM and tallow from an animal feed production plant (Twigger et al., 2001).

- **Material Analysis**

Animal waste typically has a calorific value of 16-17 MJ/kg. The most important point of animal meal using in cement kiln is higher phosphorous content (P_2O_5 up to 15%). Furthermore, chlorine 0.7%, sulfur 0.6%, heavy metals such as Cd<0.5, mercury 0.008, Tl<2 mg/kg are also to be concerned.

- **Material pre-treatment, storage & handling**

The animal waste should be provided by a reputable and established supplier. Typically it is granulated under 10 mm size.

The following guidelines for storage and handling of animal meal are reported in Twigger et al. (2001).

Animal material must only be stored in dedicated areas, which must be of an adequate size for the volumes to be used, and must be located close to where the material will be used. The storage areas should be totally enclosed may be with dedusting system to avoid emissions and to keep maintenance tasks as low and with a lockable, self-closing door in order to be secure from thieves, birds, insects and rodents. The storage areas should usually be refrigerated, and may need additional odour treatment to prevent odour problems beyond the site boundary, for example wet scrubbing or biofiltration. If tallow is used in conjunction with MBM, it may require heated storage. Continental Cement in the US keeps its storage buildings under negative pressure, with emissions vented to the kilns.

A regular cleaning and disinfection programme should be implemented for all areas where animal matter is stored or handled. All handling, including unloading and transfer, should take place under cover, especially for MBM which is dusty and can be subject to wind whip. Extraction fans with filters can reduce odour emissions from the handling areas. As well as being dusty, MBM can form into clumps, which must be broken down.

Any animal carcasses should be lifted and not dragged. Any spillage of animal material should be cleaned up immediately, with solids cleared by vacuum or by wet methods, rather than by dry sweeping. Floors must be resistant and slope to a holding pit. The wash down water should preferably be incinerated, with special care taken if this water contains additional chlorine from disinfectant, or should be treated if adequate water disposal facilities exist on site. Any vehicles, containers or equipment used in conjunction with animal waste should be impervious and designed for easy cleaning, and cleaning must take place regularly.

- **Feeding & process requirements**

Most of the cement plants burn animal meal in main burner, occasionally in precalciner. If only higher quantities of meat and bone meal are fed to the riser as alternative fuel, it was found that slightly higher amount of air (3-4%) is required than traditional fuel feeding systems. If meat and bone meal is fed to the burning zone and replacing part of the primary fuel, the results show that approximately 5 to 10% more air is needed for combustion (Kääntee et al., 2002).

- **Product quality and stack emissions**

Though the phosphorous content of animal meal affects the clinker quality, there are no reported adverse emissions from animal meal burning. The CBR cement company in Beligium reports that increased presence of P_2O_5 in cement clinker, i.e. utilization of animal meal in the cement kiln, at levels above 1% has negative influence on cement performance (Axelsen, 2002).

2.6.3 Sewage sludge

Denmark, Netherlands and Switzerland have few plants which use sewage sludge in conjunction with other solid waste fuel types. The sewage sludge currently accounts for less than 2% of fuel substitution but is likely to increase in the future as wastewater treatment plants become more prevalent and more over due to strict environmental legislations (Murray & Price, 2008).

- **Material Analysis**

Sewage sludge typically has a calorific value of 16-17 MJ/kg (Twigger et al., 2001). The range in calorific values of sewage sludge is enormous and depends on the characteristics of the wastewater that it derives from and the treatment the sludge receives. The levels of mercury (Hg) and thallium (Tl) are high in sewage sludge. Normally mercury in the sludge comes from either the cleaning process at the sewage plant and/or from the incoming sewerage where it is present. Although the mercury level in the sludge fuel can reach 16 mg/kg the cement industry aims to fire sludge with a maximum mercury content of 0.5 mg/kg

(Zabaniotou & Theofilou, 2008). In addition to heavy metals, unpleasant odor and high content of moisture, makes utilization of sewage sludge more difficult. A detailed analysis of sewage sludge is presented in Appendix 2.

- **Material pre-treatment, storage & handling**

The wet sewage sludge is better for blending into wet process slurries and use in wet process kilns. However, any sludge treatment should be directed towards reduction of its odor, reduction of organic solids, minimization of pathogens, improving de-watering characteristics and reduction of moisture content. In the dry cement process the sludge must be dried to 1% moisture before firing. It is observed that the calorific value for high volatile solids content dry sludge is quite high, whereas for low volatile solids content this drops drastically and therefore it is questioned that what volatile solids levels of treatment have to be reached. Normally, the sludge can be dried with some lime present (to raise the carbonization temperature and hence reducing mercury emissions) at temperature 180–200 °C. Drying of the sludge with hot gases should be performed in an inert atmosphere (hot air with O_2>16% can cause ignition). The following stages are recommended for good stabilization of the sludge.

(a) Digestion (aerobic or anaerobic)

(b) Lime addition on raw sludge

(c) Thermal treatment 30–75 °C and 75–90 °C

(d) Composting

(e) De-watering (centrifuge, filter press, vacuum filters etc)

(f) Drying if required- Sun or open drying is normally the method used to reduce further the sludge moisture

If the wet sewage sludge mixed, dried and ground with another solid fuel like pet coke in order to avoid its nuisance odor, the care must be taken to prevent from danger of ignition. Mixing should be performed in a properly designed effective mixing drum.

(Zabaniotou & Theofilou, 2008)

Dried sewage sludge can exhibit self-heating properties under certain composition and size criteria. Consequently dried sewage sludge granulates or pellets can be stored in silos fitted with temperature and carbon monoxide (CO) measurement devices for indication of possible overheating. If the CO content rises beyond a pre-set maximum value inertisation of the silos can be initiated by injecting nitrogen or carbon dioxide into the silo. If inertisation does not rectify the combustion issue then the silos may be manually flooded with water if necessary. The storage depth, the length of storage time and moisture content should be limited to avoid self-heating. A dehumidification device can be installed. The air displaced as a result of the dried sludge being fed in by the distribution screw can be cleaned in a bag filter that is switched on and off depending upon the filling and emptying cycle.

Dried sewage sludge can be pneumatically or mechanically conveyed around the process. It should be recognized that where pneumatic conveying or any open transfer systems for granulates or pellets occur, the air will be odorous and dusty, consequently conveying air has been treated in proprietary odour abatement equipment, such as biological filters.

(Twigger et al., 2001)

- **Feeding & process requirements**

If only higher quantities of sewage sludge is fed to the riser as alternative fuel, it was found that slightly higher amount of air (3-4%) is required than traditional fuel feeding systems. If sewage sludge is fed to the burning zone and replacing part of the primary fuel, the results show that approximately 5 to 10% more air is needed for combustion (Kääntee et al., 2002). All in all, Kääntee et al. (2002) suggests that as a rule of thumb, the maximal sewage sludge feed rate should not be more than 5% of the clinker production capacity of the cement plant (Zabaniotou & Theofilou, 2008).

- **Product quality and stack emissions**

It was reported that the high sludge volatile matter enforces a better primary fuel ignition and the ash constituents are similar to those of clinker produced without sludge firing in fact, the ash serves as a 28-day strength improver of cement (Zabaniotou & Theofilou, 2008).

In addition to possible CO_2 offsets, cement plants burning sewage sludge have documented a subsequent reduction in NO_x emissions (Murray & Price, 2008). However, some experimental studies have shown that increase of the sludge ratio in the fuel have resulted to increase of nitric oxides and sulfur oxides and controlling the ratio of sludge/coal in the fuel must be considered (Zabaniotou & Theofilou, 2008) .

In terms of emissions, the suspended fine limestone particles are effective in the removal of acidic gaseous pollutants like HCl and HF from sludge combustion. However, one may expect clogging of the cyclone pre-heater if the sludge has more than 0.2–0.5% Cl. The high cement kiln temperature and the rapid cooling of gases hinder the formation of dioxins/furans.

In the study carried out by Zabaniotou & Theofilou (2008) for burning mixture of sewage sludge which had 65-70% moisture and pet coke at main burner, it has been shown that the sum of different dioxins and furans emissions are only around 0.006 ng/Nm^3.

Any heavy metals present in the sludge are frapped in the liquid fraction of the raw materials at the kiln's sintering zone. Eventhough the chlorine present in sewage sludge can enhance the volatilization of heavy metals like Hg, Cd and Pb, Zabaniotou & Theofilou (2008) reported that the sum of basic heavy metal emissions were in total of 0.7960 mg/Nm^3 versus allowable of 5 mg/Nm^3. In the case of mercury, the sludge fuel meets too high levels of CaO and this avoids rapid Hg evaporation. With the presence of minute amounts of copper in the kiln, the Hg is trapped as an amalgam. However, an activated carbon filter could be used to reduce mercury emissions.

2.7 Chemical & hazardous waste fuel

Cement plants have been utilizing certain approved hazardous wastes as an alternative fuel since the 1970s. By 2005, chemical and hazardous wastes account for approximately 12% of global fuel substitution in cement kilns (Murray & Price, 2008). This category includes variety of materials such as spent solvents and residues in paint operations, obsolete pesticides, residues from electronic industry (oils and resins), metal cleaning fluids (working and machining lubricants, coolants, cutting fluids), anodes and chemical cokes, etc. However, some authors reported that there are some hazardous wastes that are unsuitable for co-processing in cement kilns including electronic waste, whole batteries, explosives, radioactive waste, mineral acids and corrosives. In Norway, the disposal fee of hazardous waste is typically NOK 1,000/ ton of waste (Tokheim, 2000).

- **Material Analysis**

Because the characteristics and types of chemical and hazardous wastes vary greatly, it is difficult to generalize a typical analysis for chemical and hazardous waste. Spent solvent is reported to have a LHV of approximately 25 MJ/kg. An obsolete solvent-based insecticide has a LHV of approximately 37 MJ/kg. Paint residues are at approximately 16 MJ/kg, which has a calorific value in the same range as biomass (Murray & Price, 2008). In the case of hazardous waste, a special concern should be taken for the content of chlorine (0.5-2%) which leading for higher sulphatization degree and sulfur and metals (Pb, Cr, Zn, Fe and Ti) to maintain the product quality. Most of the sources of chlorine is a group of chlorinated solvents, the most common of which are; perchloroethylene (from metal parts cleaning), 1,1,1-trichloroethane & tri-chloroethylene (coatings and adhesives), methylene chloride (commercial paint strippers and as a solvent in high performance adhesives) and a variety of chloro-fluoro carbons (non-toxic cleaners as well as refrigerants) (Constans, 1995).

- **Material pre-treatment, storage & handling**

A cement manufacturing plant can have three different systems for receiving and injecting hazardous wastes: one for pumpable wastes (liquid), one for containerized wastes, and a bulk pneumatic loader for solid wastes. With respect to pumpable wastes, consideration must be given to the ambient viscosity of the material, as some wastes may require heating to be pumpable. Some fuels might need mixing to avoid settling solid particles in the tanks. Even though, the grinding and shredding step is eliminated for most of liquid hazardous fuels, to prevent from suspended solids clogging in the pipe lines, burner nozzles and flow control valves, grinders might be needed in the same time of mixers. "Muffin monsters" are typical grinders and some cement plants use the ball mill for suspended solid particle size reduction (Constans, 1999). pH and fuel freezing points (for liquids) are also important when handling hazardous waste. Both liquid and solid fuels can be blended with some other fuels to match the calorific value of the fossil fuel used at the plant and for easy and safe handling (e.g. mix with saw dust or wooden chips). This approach helps to avoid over-heating in the kiln and minimizes the need for other operating adjustments.

The storage area must be designed and maintained such that the integrity of the ground water is assured. Also it must be designed to minimize hazards to human health or the environment from fires, explosions or any unplanned sudden or un-sudden release of hazardous waste to air, soil or surface water (Mantus, 1992). Because of the potential for chemical and hazardous wastes to contribute to unwanted emissions, adherence to proper storage and handling protocols is critical for cement kiln operators.

- **Feeding & process requirements**

Kiln injection protocols have been developed to avoid harmful emissions: chemical and hazardous waste fuels that are free of organic compounds may be added to the raw slurry or mix, and materials with high organic contents must be introduced directly into the main burner, the secondary firing, or to the calcining zone of a long wet or dry kiln. Following these loading schemes will prevent the formation of harmful emissions such as PCDDs. The sulphur content in coal has been shown to reduce PCDD/PCDF emissions; co-firing hazardous wastes with coal is desirable. It is also essential that materials are fully combusted, thus retention time, mixing conditions, temperature and oxygen content must be carefully monitored and adjusted as necessitated by the waste fuel's heating value (Murray & Price, 2008). A stable cement kiln will comply with the US TSCA PCB incineration criteria which require a temperature of 1200 °C and 2 s retention time at 3% oxygen or the EU Directive 2000/76/EU requiring a temperature of 850 °C for at least 2 s for the incineration of non-chlorinated hazardous waste whilst 1100 °C and 2 s retention time at 2% oxygen for organic substances containing more than 1% halogen (Karstensen, 2008).

- **Product quality and stack emissions**

The study with solid hazardous waste mixed with (about 30 %) wooden chips, carried out by Tokehiem, 2000 reported that neither negative impact on clinker quality nor on the environment were detected.

The use of waste solvents from ink and paint manufacturing processes and liquid industrial wastes in coal-fired cement kilns has been shown a substantial (up to 40%) reduction in NO_x emissions. However increases in unburnt hydrocarbons and/or particulate levels were reported. It is also reported that the partial substitution of conventional fuels with a low heating value water emulsion which also resulted in significant NO_x reductions (Giannopoulos et al., 2007).

Murray & Price (2008) reported that even though the spent solvent avoid CO_2 emissions in substantial at 0.95 t CO_2/t coal replaced, the use of paint residue to replace coal leads to a positive but small addition of CO_2. A small increment of CO was observed by Tokheim (2000) only in some occations but it was reported as poor burn out.

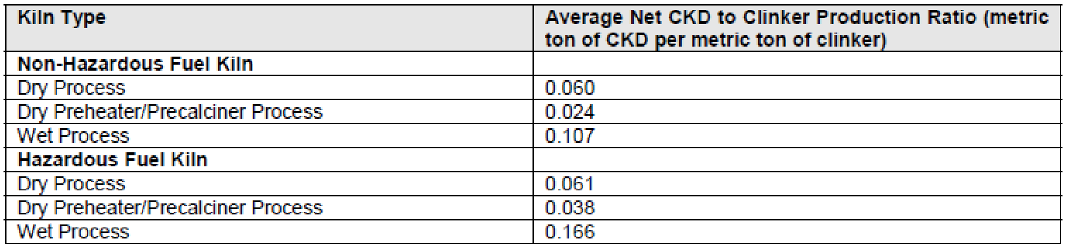
The study carried out by Gossman, Black & Ward (1990) for heavy metals in wet process cement kilns with hazardous waste fuel consents the conclusion by Tokheim (2000); that most of trace metals are present in the kiln is from raw material and coal rather than from HWF. The table 2.1 provides the conclusions from the study in wet cement kilns. However, the technique called "dry sorbent adsorption" (which injects relatively inert fine particulate to act as a medium for volatile metal condensation and capture the metals) is generally used by cement kilns but again it is another cause for higher particulate emissions (Gossman, 1993).

The CKD production is compared by Jacott et al. (2003) and mentioned that wet kilns that burn hazardous wastes generated significantly more CKD waste and even with high toxicity but not dry kilns (Table 2.2).

Table 2.1: Fate of metals in wet process cement kilns (Gossman, Black & Ward, 1990)

Concentrate in kiln dust	Concentrate in clinker	Evenly distributed	Dependent on where input	Likely to develop recirculating loads
As	Be		Sb	Sb
Cd	Cr	Ba	As	As
Pb	Ag	Ni	Ba	Pb
Hg	V	V	Be	Se
Se			Cr	Zn
Tl			Ni	
			Se	
			Zn	

Table 2.2: CKD production with hazardous and non-hazardous fuel (Jacott et al., 2003)



Kiln Type	**Average Net CKD to Clinker Production Ratio (metric ton of CKD per metric ton of clinker)**
Non-Hazardous Fuel Kiln	
Dry Process	0.060
Dry Preheater/Precalciner Process	0.024
Wet Process	0.107
Hazardous Fuel Kiln	
Dry Process	0.061
Dry Preheater/Precalciner Process	0.038
Wet Process	0.166

By 1980-1990, the emission of PCDD/F was identified too worse when using hazardous waste fuels. However, recent studies have shown that those tests were carried out under “worst” scenario of burning conditions, i.e. typically high waste feeding rates and high temperatures in the air pollution control device (APCD). Research on the combustion of hazardous wastes indicates that the potential for PCDD/PCDF formation in cement kilns is limited to the cyclone preheater and the post-preheater zones, the coolest zones of the system.

According to Karstensen reported, the studies on preheater/pre-calciner dry process kilns conducted by the Thai Pollution Control Department and UNEP, Holcim Columbia cement manufacturing, and researchers in Egypt have all found non significant increases in PCDD/PDCF emissions compared to the baseline coal-fired kilns, and all fell well within compliance standards (Murray & Price, 2008). The PCDD/PCDF data presented in the SINTEF study shows that no matter the feeding point, most cement kilns can meet an emission level of 0.1 ng TEQ/Nm^3 (well below 10 ng TEQ/kg which is found in foods like fish, butter, breast milk) if primary measures are applied (Loo, 2008).

PCDD/Fs, PCBs (polychlorinated biphenyls) and HCB (hexa chloro benzene) were measured with two hazardous insecticides in an industrial facility in Vietnam and all the results were below the detection limits. No PCDD/Fs were detected in dust samples in the study carried out with obsolete solid and concentrated liquid pesticides dissolved in kerosene and fuel oil at main kiln in Malaysia. Test burns carried out with hazardous chlorinated hydrocarbons containing up to 46% chlorine in a wet cement kiln in Canada concluded that all starting materials including 50% PCB were destroyed and another study showed that no significant difference in stack emissions when 20–40% of the conventional fuel is replaced by liquid wastes. Similar tests with chlorinated and fluorinated hydrocarbons conducted in a wet kiln in Sweden showed that the DRE (Destruction and removal efficiency) of PCBs were better than 99.99998% and that there were no change in product quality or any influence on process conditions with a chlorine input up to 0.7% of the clinker production. Two studies carried out for test burns in a wet kiln and dry kiln in Norway feeding 50 kg PCBs/hour, showing a DRE better than 99.9999% and no traces of PCB in clinker or dusts could be detected.

(Karstensen et al., 2006)

However, the most important primary measures to achieve compliance with an emission level is quick cooling of the kiln exhaust gases to lower than 200 °C in long wet and long dry kilns without pre-heating to avoid high temperatures at APCD inlet which believed that prevent the post-combustion de-novo synthesis of PCDD/PCDF. Modern pre-heater and pre-calciner kilns have this feature already inherent in the process design. Feeding of alternative raw materials as part of raw-material-mix should be avoided if it includes organic precursors and no alternative fuels should be fed during start-up and shut down (Loo, 2008).

2.8 Petroleum-based waste

Tires, waste oil, different kind of plastics, pet coke can be categorized under petroleum based wastes.

2.8.1 Tyre derived fuels

Tyres are the oldest secondary solid waste fuel utilized within the cement process. The annual generation rate of used car tyres in Norway is about 15,000 tons. The disposal fee received for whole car tyres is typically NOK 500/ ton and 200/ton for shredded tyres (Tokheim, 2000).

- **Material Analysis**

The composition of tyres is variable with respect to the levels of bracing material within the tyre or tyre chips. The composition can also change with manufacturer and tyre wear (Twigger et al., 2001). Generally, TDF is very high quality fuel having 30-35 MJ/kg about the same as a superior quality coal. The nitrogen content of TDF is lower than that of coal while the chlorine content of TDF is higher (Barlaz, Eleazer & Whittle, 1993). TDF typically has 0.5-2.0% sulfur, this is less than or equal to most coals and coke. TDF may have metals such as lead, cadmium and zinc (Constans & Gossman, 1997).

- **Material pre-treatment, storage & handling**

TDF can be provided in a number of forms. Few advantages and disadvantages are addressed in the table 2.3 for different form of tyre derived fuels.

The storage of whole tyres is essentially by size and type (separation of truck and vehicle). Sorting and storage can be performed at the site or by the supplier. Whole tyre requires more storage capacity due to less bulk density. Although the storage is typically undertaken in open stockpiles, sometimes they are delivered in trailers or multi trucks that act as storage containers and can be fed directly to the kilns or conveyor belts to prevent from pile fire. In the same time, some operators do warehouse the feed to prevent water ingress and hence entering the water to the kiln. Chipped tyres have a higher bulk density and therefore storing under roofing or in warehousing is employed.

Today, a number of systems have been fully integrated in conveying, weighing and discharging. For whole tyres, the important techniques are mechanical transfer from storage (or via trucks and unload to the end of conveyor), control the addition rate to the kiln and minimize the fate air by means of double pendulum flaps or special designed dampers. The conveying of shredded tyres into the kiln is typically by mechanical means, e.g. belt and roller conveyers, with entry into the kiln by a series of sluices or clappers. Some systems incorporate rotary valves, e.g. three way valves, which allow other fuel additions with the shredded tyres (Twigger et al., 2001).

Table 2.3: Advantages and disadvantages of different forms of tyre derived fuels (Constans & Gossman, 1997)

Form	Advantages	Disadvantages
Ground tyres (crumb)	The steel in the bead and radial bands can be removed via air classification The crumb can then be blown in with powdered coal fuel directly substituting for the powdered coal The transportation storage and management of the crumb is very similar to managing coal fines	The removal of the steel is unnecessary (disadvantage) since cement kilns have a need for iron in its process Producing the crumb is quite expensive dust suppression and fire suppression on storage may be required due to high bulk density
Tyre chips (from 2x2 to 15x15 cm^2)	Feed rate can be continuous and carefully regulated There is very little manual labor involved in handling chips versus whole tires	Still expensive The wire in the bead and radial belts do not shear smoothly when the tires are chipped. Consequently, the chips are ragged with these wires hooking onto everything they come in contact with.Utilizing tire chips, after several months of use, plugged their raw mill with migrating chips will cause for shut down the mill dust suppression and fire suppression on storage may be required
Whole tyres	No processing costs in addition to the acquisition costs Do not migrate throughout the facility Dust suppression and fire suppression on storage are not required	Transportation, storage and management of whole tires requires more logistical care and more manual labor and difficult to automate

- **Feeding & process requirements**

Using tyres as fuel in cement kilns gives complete destruction of the rubber and cotton content of the tyres, no black smoke or odour is produced. The method of introduction is dependent upon kiln configuration and fundamental process type. Long wet or long dry kilns can utilize tires in two ways. Tire crumb and smaller chipped tires may be blown in with the powdered coal or through a separate feed system. However, the hooking wires of chips will create a feed problem since the feeding totally depends on gravity. Whole tires can be injected mid-kiln through a Cadence gate attached to the wall of the kiln. The Cadence System incorporates a feed fork system, external to the kiln, that picks up the tyres and delivers them into the mid kiln region through a flap system, using gravity. Up to 10 -15 % of the combustion air for the process is added mid kiln to create an oxidizing re-burn zone and to ensure complete burn out of the tyre fuel (Twigger et al., 2001).

The preheater/ precalciner process, however, allow the injection of whole or chip tires into the kiln quite simply through a chute down on to the kiln feed as it enters the kiln from the last stage of the preheater/precalciner. Whole tires or tire chips can be fed to a double gated chute into the duct between the kiln and the kiln feed discharge of the last stage. With the outer gate closed, the inner gate opens and drops the tire or the chips directly into the kiln feed or into a chute which drops the tire or chips into the feed (Constans & Gossman, 1997). Whole tyres can also be introduced on fingers into the gas riser of the kiln. This is stated as having a positive impact upon the internal sulphate cycle and reduces deposition in that part of the process, possibly due to the temperature of the system. However, the feed of whole tyres in the beginning of the kiln produce a reducing atmosphere to break down part of the NO_x generated in the sinterization zone. The long and short kilns can accept respectively 5% and 20% of total energy requirement through trye burning (Barlaz, Eleazer & Whittle, 1993).

- **Product quality and stack emissions**

According to the theoretical considerations, sulfur released during the combustion of TDF or coal is expected to be incorporated into the calcining limestone to form gypsum, a raw material of cement. It has also been predicted that production of nitrous oxides will be reduced when TDF is substituted. However, some plants may also experience changes in SO_x and NO_x levels depending on where and when the TDF is burned, and changes in O_2 levels. In the trials carried out by Tokheim (2000), with the whole car tyres at the kiln inlet at a maximum feeding rate of 1 t/h, a 25% NO_x reduction has been achieved and the sulphur concentration in the precalcined meal has increased from 4 % to a level of about 6 %. In the same study with shredded car tyres in the kiln inlet has shown reduced NO_x emission by 30-50 % and accumulation of sulphur in precalcined meal.The statistical analysis done by Prisciandaro, Mazziotti & Veglio´ (2003) shows if less than 20% of regular fuel is replaced with tyres, the stack emissions including SO_2, NO_x and CO will slightly be increased. The disagreement for NO_x and SO_2 was explained by major air supply, different moisture and incomplete combustion of tyres used in analysis. Mokrzycki et al. reported an increase in emissions occurs only if the alternative fuel is fed to the kiln inlet (Conesa et al., 2008).

The alkaline environment of a cement kiln is expected to neutralize the majority of the HCl acid generated. As Conesa et al. (2008) reported, some authors have experienced a 24% increase in SO_2, an 11% decrease in NO_x and 37% increase in CO when using a combination of tyres and coal. Nevertheless, the authors indicate a decrease of the rate of emission of organic compounds that is 45% for dioxins and furans. According to Tokheim (2000), there are any no significant increases in the emissions of dioxins/furans or heavy metals when shredded car tyres are used at kiln inlet. However, in a study carried out by Hsu and Ling, levels of dioxins and furans in the cement did increase, when adding tyres to the kiln. Also, the emission of VOC and PAH seems to increase with the amount of tyres fed to the kiln, probably due to the feeding point which was kiln inlet (Conesa et al., 2008). A uniform feed rate of crumb or chips will allow the operator to increase the kiln exit oxygen, however, the insertion of whole tires at one to two minute intervals will often produce a CO spike and/or an oxygen dip in the kiln exit gases. This can be compensated for by increasing the interval between tire insertions and/or by increasing the normal kiln exit oxygen (Constans & Gossman, 1997).

The available data on hazardous waste combustion in kilns suggest that the release of metals from cement produced in kilns accepting tires is likely to be minimal. The presence of iron in the bead and radial belts in tyres reduces the need to purchase iron, since its raw material of the cement production. Conesa et al. (2008) have found the increment of nickel and lead in stack emissions when feeding tyres. They have concluded that it might be due to the tyre feeding point which was the kiln inlet therefore the metals contained in the tyres that are volatilized in the kiln have lower residence time in the kiln to be absorbed by the cement. The statistical analysis done by Prisciandaro, Mazziotti & Veglio´ (2003) have reported an increase of Zn was detected on the dust and no statistical differences were observed for the dust content in the emissions from tyre feeding plants.

2.8.2 Plastic derived fuels

No plants were identified using plastic wastes alone as alternative fuels but as part of. Because of the general high quality, the price of waste plastic is typically around NOK 100/ ton, which is well below the price of coal (Tokheim, 2000).

- **Material analysis**

The chemical composition of the plastics used must be checked in order to determine the suitability for combustion. It is usually the case that the chlorine content of plastics is a limiting factor. Plastics which is rejected from industrial processes typically have a calorific value of 29 to 40 MJ/kg, which is slightly higher than coal whilst the plastic bags (packaging waste) come out from retail outlets have a calorific value of 12.5 to 18.5 MJ/kg (Twigger et al., 2001). However, PVC, which contains nearly 50 % chlorine, and PET, which has a high oxygen content, both have rather low heating values (Tokheim, 2000). It might potentially contain minor traces of metals.

- **Material pretreatment, storage and handling**

Some plants use plastics in the form of sorted municipal solid waste, whilst some plants use only the plastics that are unsuitable for recycling. Following the separation at source, the plastics collected are further separated, as not all are suitable for use as fuels (high chlorine & sulfur content). Typically plastics are shredded about 2 to 20mm and may be granulated to smaller size fractions to meet the size specification and analytical specification by the plant. The material preparation can be done in on-site or off-site. However, plastic is used as a number of blended materials in different countries. For instance, Combustible Solid Substances (CSS) which consists of plastic, sawdust, oils and lacquers in Austria, Resofuel which consists Substitute Liquid Fuel (SLF) and impregnated paper/plastic adsorbent in Belgium and Profuel which consists blend of paper, plastic, carpet off-cuts and photographic film in UK.

Bulk feedstock (waiting shredding), shredded or pre-shredded materials are stored in covered storage facilities; typically warehouse facilities to prevent the material getting wet which can cause variability in feed metering. The storage facilities do not need odour abatement/hygiene systems. Due to their chemical composition, plastics can often easily ignite when exposed to sufficient heat in the presence of oxygen. Therefore dust suppression and fire detection and extinction is needed especially for shredded materials of polystyrene, polyethylene, etc.

The pre-shredded material is typically loaded into the process, from storage, by vehicles with buckets and a loading chute. The material is then typically transferred mechanically nearer to the injection point of the kiln by belt conveying. This allows the shredded materials to be subject to magnetic separation, to remove any entrained ferrous metal materials, from the belt. The material is then normally blown into the kiln via a pneumatic system, after having been subject to a metering system (typically a weigh cell) to ensure consistent feed rate into the kiln.

(Twigger et al., 2001)

- **Feeding & process requirements**

Plastic is conveyed either to the main burner or to the secondary combustion at precalciner. The material is conveyed from an intermediate bin over a weigh-belt feeder and rotary gate, by using compressed air, to the burner. This system is simple designed and simple to maintain. However, some important points are discussed below.

- ➢ The composition of feedstock should be controlled to minimise their impacts upon the process, product and emissions. For instance, using PVC free feed or with feedstock with limited chlorine input (e.g. 0.5% by weight) according to the cement specification
- ➢ The alternative fuels had to be supplied in such a way that simultaneous contact between fuel, precalcined meal and kiln gas was avoided (Tokheim, 2000)
- ➢ The oxygen level in the process is maintained at optimum to ensure minimum generation of pollutants
- ➢ The feed rate of the paper and/or plastic is consistent and controlled on temperature, together with the feed rate of support fuel (coal/pet coke)
- ➢ For the use in primary combustion, the particle size of 10 mm edge length has shown to be optimal for higher dosing rates. Combustion of bigger sized plastic material performs at entrance into the high temperature area of the flame a ball-shaped profile instantly, due to the material structure (decreasing of surface). The reason is to avoid a too fast burn-off - jeopardy of burning out at the clinker bed creating of reducing condition (Willitsch et al., 2009).

- **Product quality & emissions**

The carbon offsets associated with replacing coal with petroleum-based waste fuels are highest for polyethylene and polystyrene plastics, at approximately -1.0 tons CO_2/ton coal. Chlorine is a specific problem in certain plastic varieties, particularly PVC. However the capture of particles through a bag filter and send them back into the clinker is a acceptable solution. Chlorine may impact the quality and strength of the clinker if concentrations exceed 0.7% (Murray & Price, 2008).

The trials done by Tokheim (2000) reported, with supply of a high-grade plastic mixture at the kiln inlet (15% energy substitution) resulting in NO_x reductions of up to 40 % and plastic feeding at the riser duct results only 20% NO_x reduction. However, when the feeding point is at kiln inlet, some other operational problems were arisen. The reducing environment disturbed the internal circulation of sulphur, leading to an accumulation of sulphates in the precalcined meal and increased deposit formation in the precalciner and the lower cyclone stages. The energy transfer from the rotary kiln to the precalciner was also increased hence free-lime concentration in the clinker was increased which is badly affected to the product quality.

The following figure shows the influence in which 40% fuel substitution by thermal fraction of industrial waste mainly plastic on clinker quality.

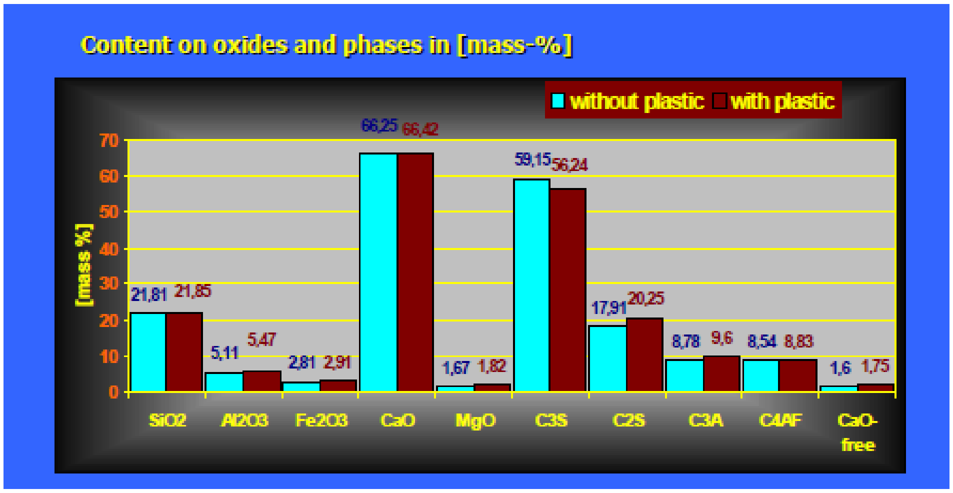


Figure 2.4: Influence of plastic burning on clinker quality (Willitsch et al., 2009)

The reported data for dioxin emissions could not be found for sole burning of plastics but when burning with other alternative fuels at kiln inlet/ precalciner were reported Karstensen (2008). In this study, first a mix of animal meal, plastics and textile, second a mix of pet coke, plastic and waste oil and finally coal, plastic and tyres show 0.0025, 0.001 and 0.0021-0.0041 ng I-TEQ/m^3 of PCDD/PCDF emissions respectively.

The more volatile metals (mercury and thallium), potentially present in fuel, would pass through the cement process and are potentially directly released to air, nevertheless these metals tend to condense on dust as the stream is cool and therefore are removed by the ESPs. However, the semi-volatile metals (Cd, Pb, Zn) can cause problems by accumulation within the processes and so require limiting at source (Twigger et al., 2001).

2.8.3 Waste oil

Waste oils which can also be categorized under hazardous waste category, originate from automotive, railway, marine, farm and industrial sources. In the countries of EU, of the approximately 1.7 million tons of waste oil collected every year, 63% is used by cement kilns (Murray & Price, 2008).

- **Material Analysis**

Waste oils in general are increasingly used as alternative fuels in the cement industry, since they are characterised by a relatively high calorific value (33-41 MJ/kg) but are mostly hazardous due to high concentrations of trace elements resulting from contamination by the materials they have previously come in contact with. In comparison to crude based heavy fuel oils, waste oil is far more concentrated with heavy metals, sulfur, phosphorus, and total halogens. However, it depends on the originated source of waste oil. Common salt "sodium chloride" often appears in waste oils from marine sector due to contamination with sea water (ships' bilges). There are often some chloride salts that are by-products of chemical production (Constans, 1995).

- **Material pretreatment, storage and handling**

Pretreatment is not essential however, it can be pre-treated before firing by blending at the blending tank and filtering to remove sediments after the transfer pump. The higher energy value oils, petroleum fractions, and distillates will help in blending other liquids up to the desired average heating value for use in the cement kiln.

Waste oil shall be stored in an oil-receiving tank, however with special safety guidelines for explosion and fire (National Technical Experts Team from Geosphere Technologies, 2005).

- **Feeding & process requirements**

It can be fed through the main burner or the calciner using a fuel oil firing system. Generally, un-blended waste oil is used to start-up or heat up process of the main burner. Typically, a liquid fuel and atomizing air burner nozzle is constructed and is installed in the center of the coal burner pipe (Constans, 1995).

- **Product quality & emissions**

The carbon reduction associated with replacing coal with waste oils yield approximately 0.5 tons CO_2/ton coal replaced (Murray & Price, 2008).

A detailed kinetic PSR modelling study for cutting oil emulsions done by Giannopoulos et al. (2007) demonstrated that although NO_x emissions from the precalciner are generally substantially lower than those from the cement kiln, cutting oil emulsion injection in the latter appears to be favourable and can lead up to 50% reductions in NO levels. However, injection of cutting oil emulsion with relatively high nitrogen content in the precalciner may result, under lean conditions, to increases in the emitted NO levels.

The study in a dry process cement kiln carried out by Berry & MacDonald (1975/76) with burning used automotive crankcase oil which is heavily contaminated with toxic components reported some emission results about lead, phosphorous, zinc and particulate matter. Lead, zinc and phosphorus emissions in the kiln exhaust gases were not found to be increased whilst a small increase in bromide emissions (0.7% of bromine input with waste oil) could be found. In the particulate materials, lead and bromine were found in slightly increased concentrations and zinc and phosphorous were not found to be related in any way to used oil burning. A small reduction in particulate emissions was found during the study and part of this improvement may have been due to the additional water introduced with used oil and hence improved precipitator efficiency. In the same study, the results of the mass balance showed that 89% of the lead, (70%-80% in the clinker along with some bromine, 9% in the conditioning tower solids whilst less than 4% in the by pass duct), 72% of the bromine (the majority of the bromide was found in the by-pass precipitator dust as potassium bromide) and 100% of both zinc and phosphorous were retained in the process solids. Authors also reported, in any system, good precipitator performance would be important for successful emission control when burning used oils.

Used oils fed into dry preheater kilns equipped with electrostatic precipitators in Germany found no significant difference in PCDD/PCDF emissions compared to traditional fuels (Murray & Price, 2008).

However, as Boughton (2004) reported, the environmental impacts of burning untreated waste oil are significant, thus the practice cannot be recommended for cement kilns (Murray & Price, 2008).

2.8.4 Miscellaneous waste

There are a variety of miscellaneous waste fuels that are burned in cement kilns such as automobile shredder residue (ASR), carpet residue, nappy manufacturing wastes, wax residue, municipal solids waste or RDF, power station ashes, coal shale/bed coke/fine coke, textiles which has around16 MJ/kg and can be substituted at a rate as high as 30% in cement kilns, landfill gas which has CO_2 reduction potential of 1 ton CO_2/ ton coal replaced, etc (Murray & Price, 2008). The majority of these are used when the sources are closed to the plant and readily available.

2.8.4.1 MSW (Municipal Solid Waste) & RDF (Refuse Derived Fuel)

It is very rare to use unsorted MSW in cement kilns as alternative fuel due to their heterogeneous nature, as it contains materials of widely varying calorific values and sizes, and may also contain hazardous materials. RDF typically consists of pelletized or fluff MSW that remains after the removal of noncombustible materials such as ferrous materials, glass, grit, and other non- combustibles. In Norway, the disposal fee is around NOK 175/ ton of RDF, delivered on-site (Tokheim, 2000).

- **Material Analysis**

The RDF contains several materials consisting paper, plastics, rubber, wood, fabrics, organic waste and metals in different compositions depending on the origin of the waste. The generation and composition of waste depends on several local factors such as products, consumer behaviour, weather condition, etc. MSW typically has a calorific value of 8-11 MJ/kg, while RDF presents a CV in the range of 15–20 MJ/kg. As can be easily observed, RDF usually has a higher content of Sb, Hg, Cd, As, Pb, Cu, Cr and Zn than the pet coke (Genon & Brizio, 2008).

- **Material pre-treatment, storage & handling**

As stated earlier, sorting should be done for the MSW before feeding to the kiln for better performance. The pretreatment is done in several ways. The fuel can either be a sorted MSW which has some lighter fractions with mainly paper and plastics, a RDF or a MSW gasified fuel (Twigger et al., 2001). When producing RDF, MSW must be screened to remove the recyclable and inert and sometimes wet fractions. The remaining material accounts for approximately 20-50% of the original MSW weight (Murray & Price, 2008). Then it is pulverized to give a more uniform size. This stream may be subjected to a secondary screening process to produce typically three fractions: fine, medium and coarse RDF. The medium fraction is classified to remove heavy items from the paper and plastic rich stream. It can then either be used as coarse fuel or dried and pelletised to produce densified RDF (Twigger et al., 2001). Mechanical sorting is reported to be a sufficient processing technique by plants in Austria, Germany and Italy, while in the Netherlands, pelletizing is practiced (Murray & Price, 2008).

RDF needs to be stored under cover or in enclosed storage, both with adequate ventilation, as RDF is very dusty and disintegrates when exposed to moisture. This can result in leachate seeping to groundwater, which must be avoided. RDF also has a characteristic odour that must be minimised. This can be achieved by the material enclosure but it is also possible to draw combustion air from the storage area to prevent outside releases. Because of the low density of the material, the transport and storage costs are much higher than the cost of substituted fuels per unit of heat produced.

The characteristics of RDF mean that handling facilities must be designed to avoid dust emissions. RDF can have both oversized pellets and very fine material that can block the handling equipment. Handling must be minimised as RDF degrades easily to dust. It also disintegrates when exposed to moisture so handling must also be under cover. This will also help to prevent odour releases.

(Twigger et al., 2001)

- **Feeding & process requirements**

The concentration of sulphur in RDF (0.1–0.2% or may be even higher like 0.5%) is generally much lower than the reference value in conventional fossil fuels (3-5%). Therefore, any problems regarding precipitation or clogging can be excluded, although issues of alkali sequestration and transfer in the clinker must be verified. On the contrary, an increase in chlorine (0.3–0.5%), with respect to coke (<0.1%) can lead to some problems arising from reactions between alkali and chlorine, the volatilisation of chlorides and recycling with dust, therefore may be needed to operate a bypass system in order to limit the chlorides in the final clinker.

The air requirement for combustion of RDF (with composition C 53%, H 7%, O 21%, inorganic 19%) with a calorific value of 20 MJ/kg was calculated as 6.16 Nm^3/kg. Also the substitution of RDF for pet coke leads to an increase of more than 15% in the produced waste gas in wet conditions (from 0.29 Nm^3/MJ to 0.335 Nm^3/MJ).

However, the issues involving kiln thermal and mass balances are very important as they can limit the RDF substitution rate, and, in some cases, technological modifications and process parameter adjustments are required.

(Genon & Brizio, 2008)

- **Product quality and stack emissions**

The heterogeneity of MSW makes its emissions characteristics hard to generalize. Co-incineration of RDF does not seem to affect the quality of the emissions at least from the point of view of macro-pollutants (NO_x, SO_x, VOC, CO, and dust) but may be micro-pollutants. Furthermore, it is stated that no consideration has to be taken to the clinker quality during utilization of RDF up to 50% (Axelsen, 2002).

The combustion of RDF allows for a reduction of about 1.61 kg of CO_2/kg of utilized RDF compared to coal (Genon & Brizio, 2008). This is due to the chemical composition of the combustible material. However, Mokrzycki, Uliasz-Bochenczyk & Sarna (2003) suggested that an increased CO content in emissions were observed when the fuel is fed to the furnace inlet, hence the fuel must be fed to the main burner of the furnace.

Low values of N in RDF (0.3– 0.5% in comparison with 1.5–2% in fossil fuels) can lead to lower formation of NO_x. The benefit derived from the use of RDF has been quantified by the European Commission (2003) as 0.36 kg NO_x/t of burned RDF (Genon & Brizio, 2008).

Some authors reported lower SO_2 emissions during utilization of RDF. It is also reported that 50% reduction of SO_3 in the clinker during combustion of RDF. Decreases were also observed in the alkalies and in $CaSO_4$ as a direct result of the decrease in SO_3. Also, an increase in the free lime content of about 35% was observed, because the raw mix content was not adjusted for the CaO content in RDF (Axelsen, 2002).

The study, Genon & Brizio (2008), shows that by assuming RDF has 0.1–0.4 ppm mercury & 0.18–2.6 ppm Cd, the combustion of 1 t of RDF in a cement kiln, if compared to the use of hard coal, causes a small increase of around 421 mg in the emission of mercury, 4.1 mg of lead, and 1.1 mg of cadmium. However, in a subsequent simulation using a different set of RDF characteristics, (since they are quite varying) it was evident that the use of RDF can strongly worsen the emission of heavy metals, pushing them dangerously towards the limits. The transfer factors to waste gas of heavy metals can be very plant-specific and should be determined case-by-case. The transfer factors depend upon the composition of the fuel, presence of halogens, occurrence of a reducing or oxidizing atmosphere, dedusting system of the kiln vapour pressure in the waste gas and the concentration of the heavy metals recycled to the system. In any case, it is evident that the use of RDF instead of traditional fuels in a cement kiln could be dangerous in terms of the presence of larger amounts of heavy metals in the waste gas, so the quality and the quantity of RDF to be burned should be analyzed in depth.

Because of high content of chlorine in RDF may result in higher HCl and PCDD/PCDF formation. However, in some studies, no increase in the amount of PCDDs and PCDFs was detected from the stack emissions. It is suggested by some other authors that the higher chlorine/ hydrogen atom ratio in RDF compared to coal, will facilitate PAH and soot formation. Hence combustion of RDF may produce a larger amount of PAH than coal combustion (Axelsen, 2002). Genon & Brizio (2008) reported that considering a 20%

substitution rate of the combustible material by wastes in a cement kiln, 30 g of supplied RDF produce an emission of 3 Nm^3 of fumes with a PCDD/F concentration below 0.1 ng/Nm^3, a specific emission of 10 ng PCDD/F/kg RDF. However, they have concluded that it is not possible to say that all of the possible dioxins derive from the RDF.

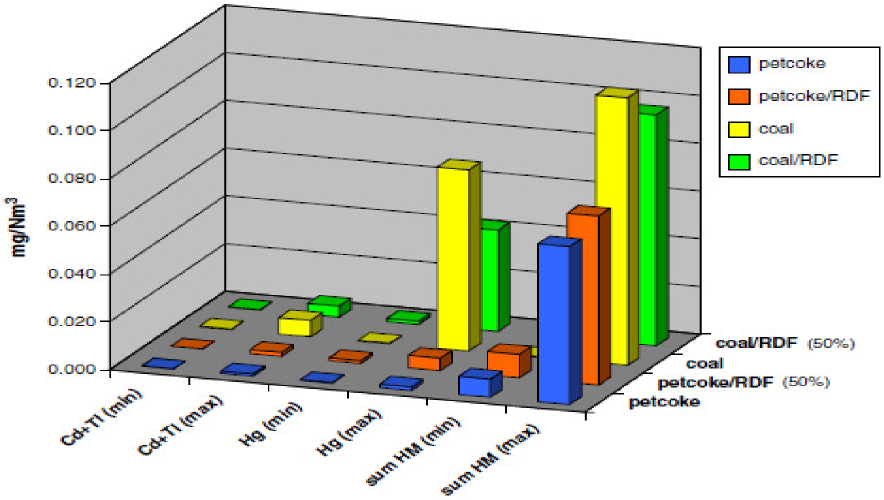


Figure 2.5: Difference of heavy metals from different alternative fuels (Genon & Brizio, 2008)

2.8.4.2 Automobile shredder residue (ASR)

ASR, otherwise known as fluff, is the term for the non-recoverable components of end-of-life vehicles. It is typically about 20% by weight of the vehicle and is an amalgam of rubber, plastic, wood, paper, dirt, fabric, and ferrous and non-ferrous metal pieces (Murray & Price, 2008). Dry SR is about 50% combustible and 50% noncombustible such as metals, glass, dirt, and residual ash (Boughton, 2007).

ASR is co-fired in cement kilns in Belgium and France and it has approximately 16 MJ/kg of LHV (Murray & Price, 2008). ASR is a heterogeneous mixture of many different materials and it is very difficult to quantify the composition. Some separation of the SR components was required to improve the energy value, as well as to reduce residual ash or remove problematic constituents such as PVC. However, SR may consist of up to 40% of mineral (silicates, calcium, aluminum and iron) equivalent to that used in cement production (Boughton, 2007).

Maintaining the kiln stability is difficult because of its heterogeneity. ASR also tends to have high alkalinity, due to potassium and calcium, which increases CKD. Burning ASR may lead to higher heavy metal emissions due to the presence of copper wire; the common presence of

PCBs in ASR is also a barrier to its use as a fuel. However, experimental results suggest that existing ASR density separation technologies that exclude fine material (<1.2 cm) can significantly reduce problems with CKD and harmful emissions (Murray & Price, 2008).

2.8.4.3 Waste carpet

Post-consumer carpet represents a high volume, high energy content almost similar to that of a low-grade coal and high $CaCO_3$ content with latex/rubber which constitutes the carpet backing filler (Lemieux et al., 2004). The LHV depends on the carpet type: polypropylene and nylon carpet residues have LHVs of approximately 28 and 17 MJ/ton, respectively (Murray & Price, 2008). A cement kiln can accept all the types of carpets with the exception of PVC backed carpet tile products. There is the potential for trace contaminants to be present in post-consumer carpet waste (Appendix 2). Chlorine is likely a contaminant (e.g. salt), resulting from either carpet manufacture or carpet use. Magnesium, sodium, silicon, and aluminum may be contaminants in the filler or contaminants resulting from carpet use. Other trace metals may be used as catalysts in carpet manufacture or may be contaminants. The presence of fluorine and bromine in the carpet fiber is likely due to flame retardant application (Lemieux et al., 2004).

If shredded fibres and fines of carpets are used, an air entrainment method is suitable feeding method due to the low bulk density of the material.

Carpet residues contribute non-trivial carbon reduction of about 0.15 and 0.54 tons CO_2/ton coal for nylon and polypropylene carpet residues, respectively (Murray & Price, 2008).

Nylon compared to polypropylene carpet residues has much higher NO_x emissions. The former contain approximately 4.5% nitrogen by mass, opposed to less than 0.05% for polypropylene residues. Both varieties of carpet residue increase nitrogen emissions in comparison to coal, the latter only slightly due to an increase in the kiln's flame temperature. Conversion of the nitrogen in nylon carpet residues to NO_x emissions is more effectively controlled by batch-fed injection schemes than continuous feed (Murray & Price, 2008). Pilot scale studies carried out by Lemieux et al. (2004) with continuous feeding of shredded carpet fiber and ground carpet backing, at rates of up to 30% of total energy input reported the following results. An XRF analysis of an ash sample taken from the kiln following testing indicated that 50–60% of the ash consists of calcium oxide, with the largest minor components being oxides of aluminum, silicon, magnesium, iron, and sulfur.

NO emission has been increased by an average of 95 ppm due to the nitrogen content of nylon fiber. In these experiments, the carpet nitrogen conversion to NO is ranged from 3 to 8% (5.3%). However, carpet preparation and feeding method are controlling factors in fuel N conversion. Conversion was higher at low carpet feed rates and high feeder-burner air ratios result in greater mixing of carpet and air during combustion. The high temperature effect could be due to enhanced conversion of fuel-nitrogen to NO, or greater thermal NO formation. Larger carpet waste charges will likely result in lower NO emissions due to reduced conversion of carpet nitrogen content, but may also result in pockets of unburned gas due to rapid volatilization of the carpet.

Rapid volatilization of the waste carpet could lead to transient puffs formation, however was not observed in this study. Incomplete combustion products including CO, THCs, VOCs and PAHs were increased only slightly when waste carpet was co-fired with natural gas, and no statistically significant relationships were observed between these measurements and combustion conditions. CO concentration was increased an average of 1.4 ppm and PAH concentration was increased by 2.5 mg/m^3.The only VOC increase observed in benzene concentration with small increment.

Emission of mercury, a potential contaminant in post-consumer carpet waste, was not detected above a level of 1–2 mg/m^3.

2.8.4.4 Spent aluminium pot liner (SPL)

SPL is a carbon-based waste from the electrolytic cells that convert alumina to aluminium (CIF, 2009). It is a valuable fuel replacement for coal, and its silica and aluminium content are needed for making clinker. It is really made up of two layers, a conductive carbon layer and a non-conductive insulation layer. Most aluminum manufacturers split these layers into the first cut (the carbon layer) and the second cut. In the 1980's a couple of cement kilns successfully utilized the first cut material as fuel feeding it in with the coal into coal mills. Unfortunately, the first cut SPL is a very hard material which the normal coal mill is not designed to handle and more over it was classified as hazardous material by environmental authorities. However, the renewed interests by the aluminum industry in placing SPL at cement kilns getting more popular.

The heat content of the first cut of SPL will be in the 14-18.6 MJ/kg range. The first cut contains a small amount of cyanide and a few heavy metals, primarily lead and chromium, as well as considerable sodium and fluoride. The cyanides are present as complex inorganic salts with concentrations may range from 0.03% to 0.6% (Appendix 2). However, the second cut SPL is non-hazardous but does not contain appreciable fuel value, though it does contain alumina, silica, calcium, sodium and fluoride a known mineralizer or fluxing agent (Constans, 1998). Another disadvantage property of SPL is highly water reactive generating ammonia, methane, hydrogen and heat on contact with as little water as can be found in humid air. There have been fires and explosions in enclosed shipping containers. The finer the material is ground the greater the potential for hazardous gas release. Extra precautions are needed when handling this material. However, the process for rendering hazardous waste SPL to non-hazardous has been developed and patented by an Australian company called Regain Services Pty Ltd (Gossman, 2006).

The SPL is ground and fed to the kiln like any other solid powdered fuel.

Stack emissions testing conducted at that time indicates that the cyanides were destroyed and very little of the fluoride was emitted. Fluoride concentrations were barely above background levels in the stack gases. The majority of the fluoride ended up in the clinker (Constans, 1998).

3 Plant description - Norcem Brevik

3.1 Cement manufacturing process: general overview

In 1824, Joseph Aspdin, a British stone mason was patented for portland cement invention and then by end of the 19th century, it had become a highly appreciated construction material throughout the Europe (CEMBUREAU, 1997). The basic process for cement manufacture is the same in all cases, although the details of the process can vary greatly. A central process step during the manufacturing of cement is the production of the intermediate product clinker.

The first stage of cement manufacturing is extraction of prime raw materials. Generally, raw materials consisting of combinations of limestone, shells or chalk which provide mainly calcium and shale, clay, sand, bauxite or iron ore which provide silicon, aluminium, iron and other elements (Tokheim, 1999). These are extracted from open quarries or underground mines. The raw materials which are quarried or mined are transferred to the manufacturing facility via trucks or by trains. The materials are crushed and then mixed with other components in order to achieve specific combination, depending upon the type of cement desired. Then the grounded fine powder called raw meal or raw mix is sent for the clinker production. A series of chemical reactions in pyroprocessing cause the materials to fuse and create cement clinker. A schematic representation of cement production unit is shown in figure 3.1 and the numbers are referred to description in the table below. The top part of the diagram is relevant to a dry process and bottom part is relevant to wet process. These processes are described in next sub chapter.

No.	Description	No.	Description
1	Quarry	10	Cooler
2	Drill	11	Clinker storage
3	Dumper	12	Place for additions
4	Crusher	13	Cement grinder
5	Pre homogenizer	14	Cement silos
6	Grinder	15	Wet grinder
7	Filter	16	Homogenizer
8	Preheater	17	Filter
9	Rotary kiln	18	Rotary kiln

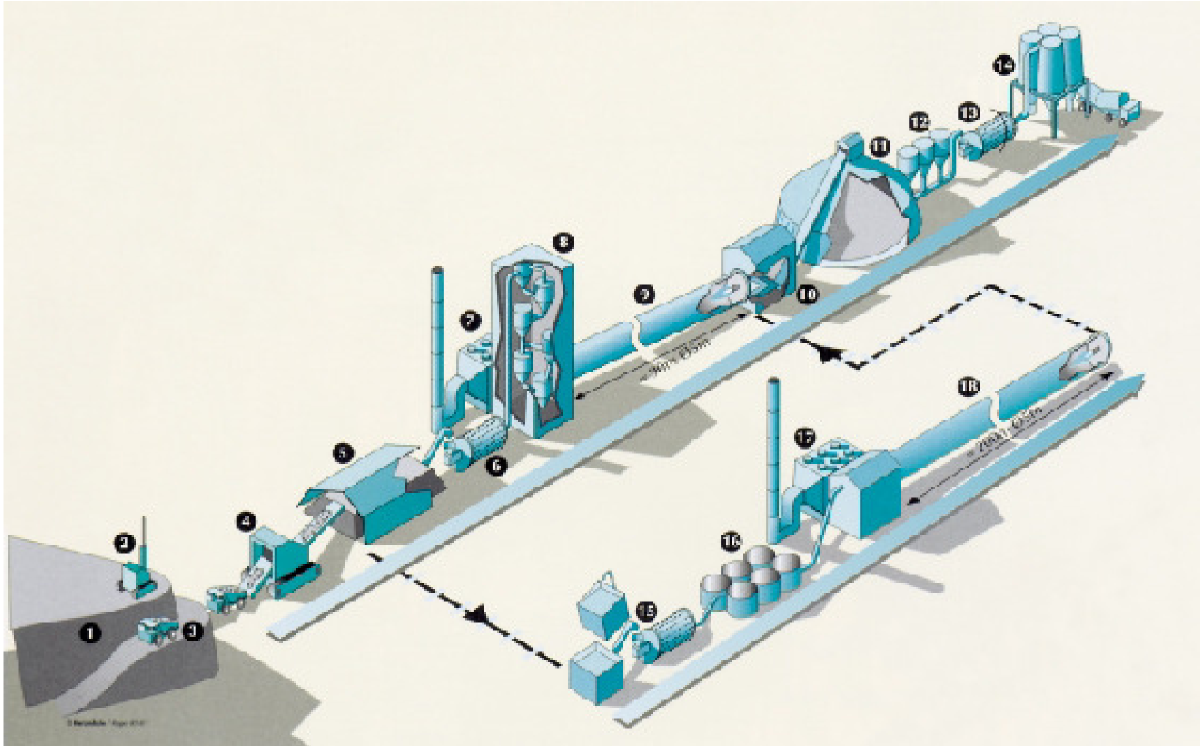


Figure 3.1: A schematic representation of cement production unit (CEMBUREAU, 1997)

The main components of clinker are the oxides of calcium, silicon, aluminium and iron. The following table presents the typical composition of major components in clinker.

Table 3.1: The primary components of clinker (Huntzinger & Eatmon, 2009)

Componenet	**% by mass**
CaO	60-67
SiO_2	17-25
Al_2O_3	2-8
Fe_2O_3	0-6

The water in the raw meal is driven off in three steps; first the free water is up to 200 °C and then adsorbed water at the temperature range of 100-400 °C and finally the chemically combined water around 400-750 °C. In the final step, the kaolinite is dehydrated and metakaolinite is formed.

$$H_2O_{(l)} \rightarrow H_2O_{(g)} \tag{3.1}$$

$$Al_4\left[(OH)_8 Si_4O_{10}\right] \rightarrow 2\left(Al_2O_3 \cdot 2SiO_2\right) + 4H_2O \tag{3.2}$$

Again, the metakaolinite is dissociated to alumina and silica at 600-900 °C. The most important reaction, the decomposition of calcium carbonate ($CaCO_3$) takes place around 900 °C. The $MgCO_3$ is dissociated in the same pattern but in low temperatures like 600- 900 °C.

$$Al_2O_3 \cdot 2SiO_2 \rightarrow Al_2O_3 + 2SiO_2 \tag{3.3}$$

$$CaCO_3 \rightarrow CaO + CO_2 \tag{3.4}$$

$$MgCO_3 \rightarrow MgO + CO_2 \tag{3.5}$$

In addition, any organic carbon present is oxidized to CO_2.

$$C + O_2 \rightarrow CO_2 \tag{3.6}$$

In the same time the solids undergo solid–solid reactions as they move forward and rapid neutralization of free lime occurs.

$$CaO + Al_2O_3 \rightarrow CaO \cdot Al_2O_3 \tag{3.7}$$

$$CaO + SiO_2 \rightarrow CaO \cdot SiO_2 \tag{3.8}$$

Following the above reactions, the formed oxides are further reacted with CaO to form clinker phases above 800 °C.

$$CaO \cdot Al_2O_3 + 2CaO \rightarrow 3CaO \cdot Al_2O_3 \tag{3.9}$$

$$CaO \cdot Al_2O_3 + 3CaO + Fe_2O_3 \rightarrow 4CaO \cdot Al_2O_3 \cdot Fe_2O_3 \tag{3.10}$$

$$CaO \cdot SiO_2 + CaO \rightarrow 2CaO \cdot SiO_2 \tag{3.11}$$

Above 1250 °C a liquid phase appears and this promotes the reaction called sintering which is very slow reaction between belite and free lime to form alite.

$$2CaO \cdot SiO_2 + CaO \rightarrow 3CaO \cdot SiO_2 \tag{3.12}$$

(Tokheim, 1999)

At approximately 1450 °C the mixture fuses into balls of 0.3 to 2.5 cm diameter clinker (Dalton et al., 2004). The major mineral phases found in the clinker (Gossman, 1992),

- Tricalcium Silicate: $3CaO\ SiO_2$ (Alite, C_3S)
- Dicalcium Silicate: $2CaO\ SiO_2$ (Belite, C_2S)
- Tricalcium Aluminate: $3CaO\ Al_2O_3$ (C_3A)
- Tetracalcium Aluminoferrite: $4CaO\ Al_2O_3\ Fe_2O_3$ (C_4AF)

The mineral phases formed are determined by the raw materials, residence time, and temperatures employed. The most important are alite and belite, which are most abundant in the clinker and make the greatest contribution to compressive strength (Dalton et al., 2004).

Next, the clinker is cooled and then ground with a small amount of gypsum to control the setting time and hydration process of the finished cement. During the cooling stage the molten phase forms C_3A and if the cooling is slow alite may dissolve back into the liquid phase and appear as secondary belite (Kääntee et al., 2002). Other additives can be included during grinding to make the wide variety of cement types. Finished cement is dispatched in bags or bulk.

Different types of portland cement are manufactured to meet various physical and chemical requirements. The American Society for Testing and Materials (ASTM) Specification C-150 provides classification about eight types of portland cement. The European cement association (CEMBUREAU) has also defined a classification for cement types; portland cement with 95-100% clinker, portland-composite cement with 65-95% clinker, blastfurnace slag cement with 5-64% clinker, pozzolana cement with 45-89% clinker, composite cement with 20-64% clinker (Lorea, 2006).

3.2 Kiln process

Rotary kiln is one of the key equipment in a cement industry used to convert calcineous raw meal to cement clinkers. Rotary kilns consist of a longer and wider drum oriented horizontally and at a slight incline on bearings, with raw material entering at the higher end and traveling as the kiln rotates towards the lower end, where fuel is blown into the kiln. Depending on how the raw material is handled before being fed to the kiln, basically four different types of rotary kiln processes can be distinguished: the dry, semi-dry, semi wet and wet processes. The wet process has a higher energy requirement than the dry process, making it more expensive to operate. As reported by CEMBUREAU (1997), about 78% of Europe's cement production is from dry process kilns, a further 16% of production is accounted for by semi-dry and semi-wet process kilns, and about 6% of European production now comes from wet process kilns due to lack of suitable raw materials for other processes.

- Dry process kilns: In this process the moisture in the raw materials is partly driven off in the initial processing stage, possibly during the grinding itself, when the meal becomes a flowable powder. There are 3 classifications for dry process. A long dry kiln, where the whole process as outlined above takes place in the same kiln, is used less frequently. Second, the kiln systems comprise a tower of heat exchange cyclones in which the dry raw material feed is preheated (‘‘suspension preheater kiln’’) by the rotary kiln’s hot exit gases prior to entering the kiln. Third, rotary kilns which use precalciners to calcine the raw materials after they have passed through the preheater but before they enter the rotary kiln. The heat input requirement for three methods are 4.8, 4.0 and 3.5 MJ/kg clinker respectively (Tokheim, 1999). In addition to improved heat economy, the additional benefits of latter two categories are the higher production capacity and shorter kiln requirement respect to long kilns.
- Semi-dry process kilns: In this process, the dry meal has water added up to 10-15% and is pelletized. Then pellets of feed material are loaded onto a traveling grate where they are preheated by the rotary kiln’s hot exit gases. By the time the feed material reaches the kiln entrance the water has evaporated and calcination has begun.
- Wet process kilns: In the wet process, the feed material is grinded with water (usually “soft” materials like chalk and clay, which have a relatively high natural moisture content is used in this process) and the resulting slurry, typically containing 30–40% water, is fed either directly into the upper end of the inclined kiln or first to a slurry drier (Karstensen, 2008).
- Semi-wet process kilns: Wet slurry is dewatered in a filter press and takes the form of pellets. These can be fed either to a grate preheater or a filter cake drier for raw meal production (Twigger et al., 2001).

3.3 Plant Introduction-Norcem Brevik

Since 1999, Norcem is member of the Heidelberg Cement Group, and the sole producer of cement in Norway. Norcem operates two modern cement plants, one is located at Brevik which is in southern Norway and another is at Kjøpsvik which is in northern Norway. The Brevik plant has an annual production capacity of about 1.3 million tons clinker and cement, and produces 7 cement products through 3 clinker types. Around 230 working staff is engaged with the production and Norcem-Brevik has 85% market share in Norway.

The main raw material, limestone is quarried both from an open quarry at Bjørntvet (70% $CaCO_3$) and from an underground mine at Dalen (90% $CaCO_3$) and it is transported via trains and trucks respectively. Three types of raw meals are produced; OPC (Ordinary Portland Cement), LA (Low alkaline) and oil well (G type- According to standards of American Petroleum Institute). To obtain the proper composition of the raw mix, quartz, iron ore, bauxite / serox are added as corrective ingredients.

(Tokheim, 2004)

The following sub chapters will mainly describe the kiln and alternative fuel systems in Norcem-Brevik cement plant.

3.4 The precalciner cement kiln at Norcem-Brevik

In 1989, the kiln system of Norcem-Brevik was modernized by introduction of the precalcination technology. In this modernization project, Kiln 6 was equipped with an additional 4-stage cyclone preheater string and a Pyroclone Low-NO_x calciner, supplied by KHD (Tokheim, 1999). However, by 2004 the old kiln system was again modified due to some combustion and flow related limitations and high chlorine input. The figure 3.2 reveals that the hot meal quality respect to Cl and SO_3 content was not much promising before the modification. Therefore, it was supposed to modify the calciner to increase the waste fuel utilization in the calciner up to 90% and install a bypass system for chlorine related issues (Tokheim, 2004). A special feature of the newly installed burning chamber of the calciner is the high temperature of the flame typically reaching 1200 °C (Tokheim, 2005).

The kiln no.6 at Norcem-Brevik is a four-stage dry-process suspension preheater kiln with precalciner ("Pyrotop" from KHD) and the grate cooler (Figure 3.3). The calciner is RSP/CLE type "hot spot" calciner (Tokheim, 2004). There are two points for introduction of fuels, the rotary kiln and the pre-calciner. The system is divided into two strings, denoted 1 and 2 and there is raw meal mill is located in string 2 which provides raw material to the both strings. The raw meal is fed first cyclone stage of the preheater.

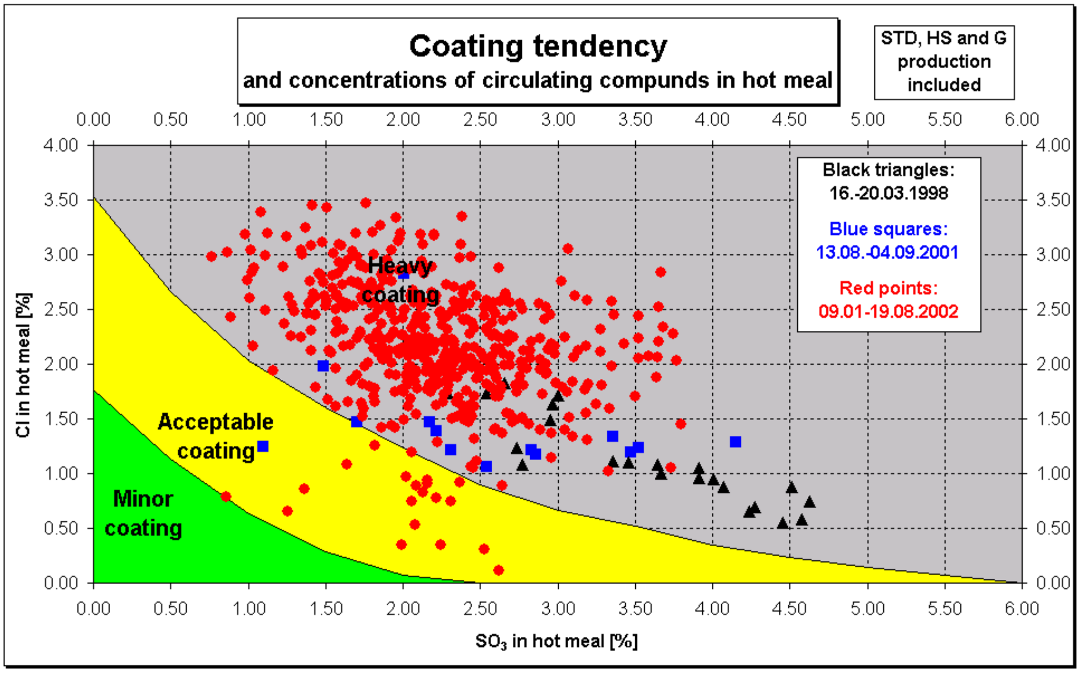


Figure 3.2: Hot meal quality with SO_3 and Cl content (Tokheim, 2004)

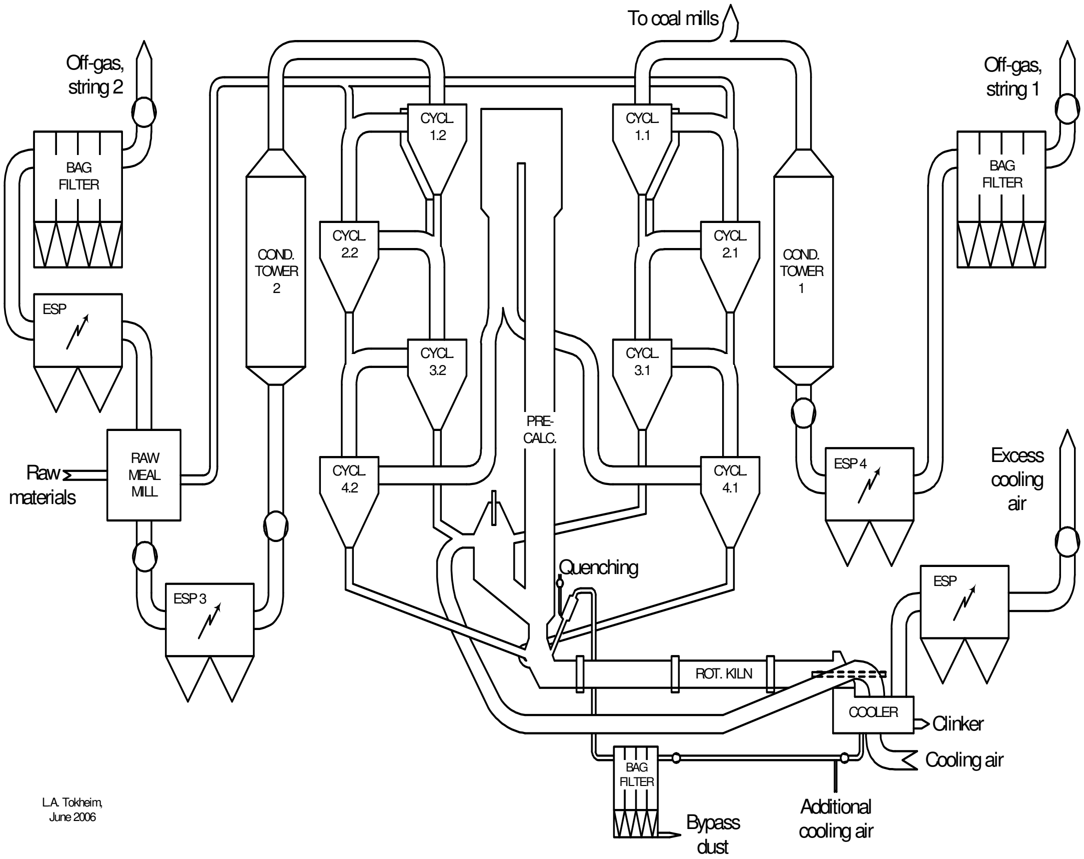


Figure 3.3: The kiln system at Norcem-Brevik (Tokheim, 2006)

As figure 3.3 shows, the coal in the coal mills is dried using small fraction (about 10%) of off gas from string 1. The off gases from both strings flow through separate conditioning towers, where water is evaporated in order to reduce the temperature of the gas. The conditioning tower downstream temperature of the gas is around 160 °C and 230-270 °C for string 1 and 2 respectively. The conditioning towers are followed by ESPs (electro static precipitators) in both strings. The cleaned gas of string 1 is then released to the surroundings through the bag filter and then main stack of string 1 at a temperature of about 140 °C. However, the downstream of ESP 3 is not directly released to the environment, the gas is used for drying the raw materials in the raw meal mill, but a fraction may bypass the mill (this is not shown in figure 3.3). Then string 2 also follows the similar path as string 1, passes another ESP in order to remove most of the dust coming from the mill and release to environment through bag filter and next through the stack (Tokheim, 1999).

Furthermore, around 5% of kiln gas is bypassed to reduce the recirculation of chlorine through out the system. The bypass gas is cooled down to the temperature around 300 °C in the quenching chamber by means of air and then it is passed through a bag filter where the chlorine contained dust is retained. The downstream of the bag filter which might contain dioxins, NO_x, heavy metals is further cooled down to a final temperature around 50-100 °C using air and it is fed to the cooler for cooling purposes instead of releasing to the stack since now the bypass gas has been enriched with around 90% O_2 which could reduce the air demand of the cooler. Although this slightly reduces the cooler efficiency due to less cooling capacity (i.e. high temperature than ambient air), it has been found to be acceptable (Tokheim, 2006).

The figure 3.4 and description explain more details about the kiln process.

The cold raw meal which enters to the preheater section is dried, dehydrated and decomposed while traveling the preheater section by the direct contact of countercurrent gas flow. Also, the organic compounds in the raw meal are oxidized and $MgCO_3$ is decomposed in this section. The raw meal is heated around up to 700 °C and the gas temperature is reduced from 900 °C to about 350 °C in the preheater section.

Then the preheated raw meal enters to the precalciner where the 90% of calcination process undergoes at 900 °C. The part of air required for the combustion in precalciner is drawn by part of the cooler exit air which is called “tertiary air” at around temperature 800 °C. Further more, a part of tertiary air (15%) is directly fed to the precalciner burner to control flame temperature by means of a flow control valve at precalciner. This air supply is called "quaternary air". Additionally there is also a primary air supply to cool down the burner of the calciner. Precalciner kiln 6 in Brevik is a so called "air separate system" which means the tertiary air is supplied through separate duct. Also this is an "in-line calciner" because the kiln gas led through the calciner. The typical gas retention time in precalciner is about 5 s (Tokheim, 2005). 80% out of the total energy requirement at the precalciner is supplied by alternative fuels and rest is from blend of coal mixture (Norcem, 2009).

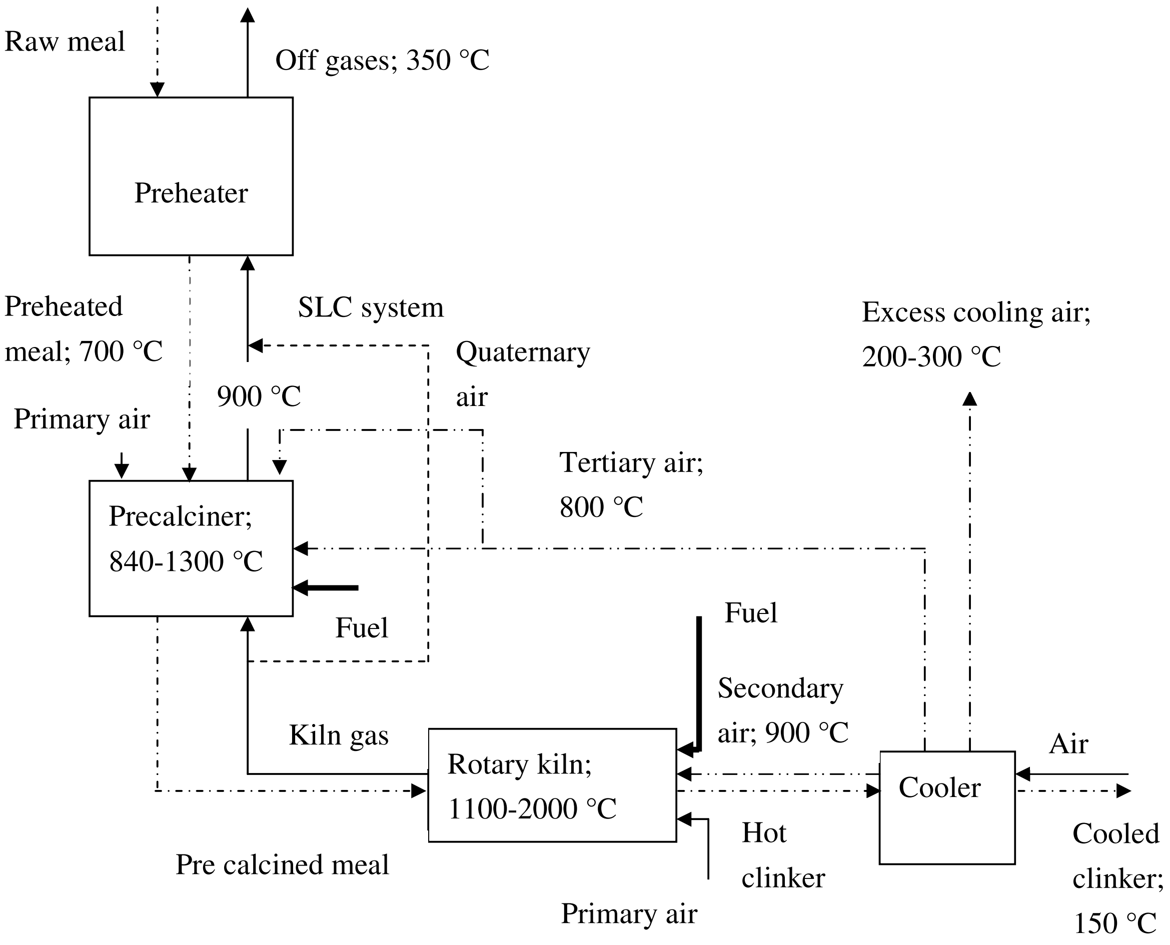


Figure 3.4: Principle drawing of precalciner kiln system (Tokheim, 1999)

Next the precalcined meal enters the kiln which has 68 m length and 4.4 m diameter. The inclination 2.5% and rotation typically around 2.5 rev/min (which depends on applied feed rate) cause the meal to move toward the lower or hot end of the kiln. The precalcined meal is completely calcined and at the lower end of the kiln the clinker is produced (> 1250 °C) by means of combustion gas with maximum temperature is about 2000 °C. The mean kiln gas velocity is 25 m/s prior to the supply of meal and fuels. The typical solid retention time in the kiln is 30 minutes. A part of cooling air which is called secondary air at 900 °C is used as part of combustion air required in the primary burning zone (Tokheim, 1999). The rest of air (10%) is provided through primary air which consists with pneumatic conveying air (with coal), swirl air and jet air (Figure 3.5). The energy required for the process in the rotary kiln is provided mainly by a blend of coal mixture and 20% by means of other alternative fuels (Norcem, 2009).

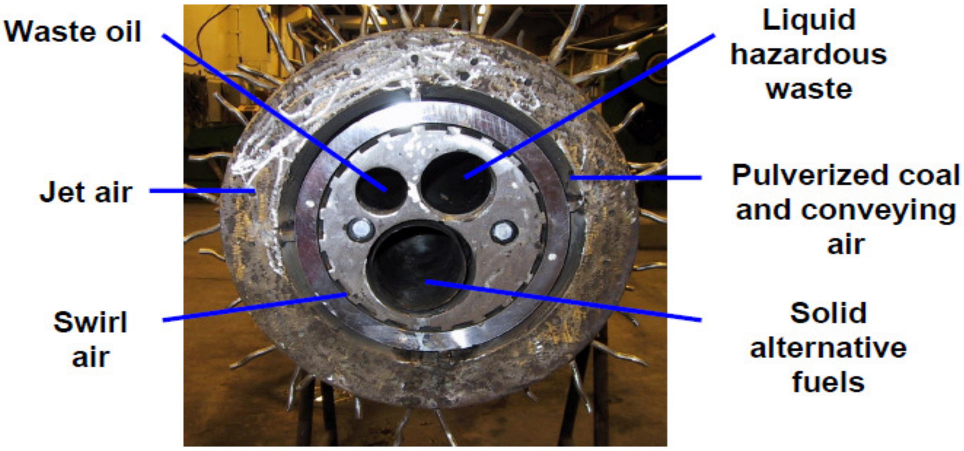


Figure 3.5: Kiln burner (Tokheim, 2004)

There are four types of clinker coolers used in the cement industry, namely rotary, planetary, grate and shaft cooler. At Norcem-Brevik, a grate cooler is used where the air is used in counter current flow to cool down the clinker to approximately 150 °C (Axelsen, 2002). The clinker residence time in the cooler is around 15 minutes. After using secondary and tertiary air from the cooler, the rest of the cooling air called "excess cooling air" at around 200-300 °C is released to the surroundings (Tokheim, 1999).

Some characteristics of the kiln system at Norcem-Brevik are presented in table 3.2.

Table 3.2: Kiln system characteristics (Tokheim, 2005)

Parameter	**Value**	**Unit**
Rotary kiln length	68	m
Rotary kiln (outer) diameter	4.4	m
Clinker production capacity	3300	t/d
Typical specific fuel consumption	3400	kJ/kg_cli
Representative temperature interval in the rotary kiln	1100-2000	°C
Representative temperature interval in the precalciner	840-1300	°C
Typical gas residence time in the rotary kiln	5	s
Typical gas residence time in the precalciner	5	s
Typical O_2 concentration in rotary kiln exhaust gas	3.5	%
Typical O_2 concentration in precalciner exhaust gas	4	%

3.5 Alternative fuel system at Norcem-Brevik

3.5.1 Brief description of the current system

Norcem-Brevik started utilization of alternative fuels in 1987 with liquid hazardous waste (LHW). With continuous growing of utilization of alternative fuels, by 1994 combustion of SHW was introduced to the plant (Tokheim, 2000). At present, Norcem-Brevik is one of the leading cement manufacturers in Europe since the plant has achieved their targets through continuous modifications and optimizations of the system and has gained financial and environmental benefits especially in the area of CO_2 reduction by proper utilization of alternative fuels in cement production process. The figure 3.6 shows the improvement of alternative fuel utilization at the plant from 1992-2007. Out of total energy requirement for the kiln process, 60% of fossil energy has been replaced by alternative fuels. 80% of energy required by precalciner is provided by solid hazardous waste and RDF which mainly contains paper, wood, soft and rigid plastic and some other waste materials. 20% of energy required by main burner is provided by burning liquid hazardous waste and animal meal. Waste oil is used for start up of burning in main burner.

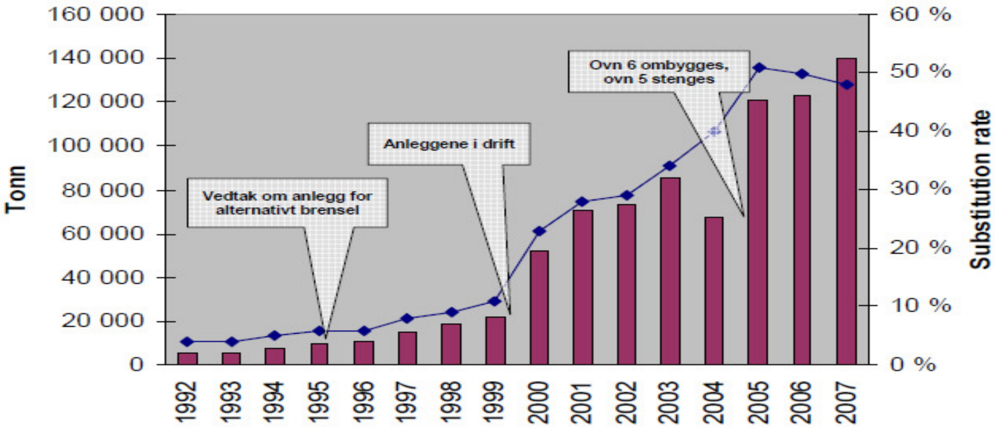


Figure 3.6: Fuel substitution rate by alternative fuels (Norcem, 2009)

The collection, sorting and preparation of RDF, SHW and LHW are done by external companies. The SHW and RDF are pretreated by shredding and sieving until particle size lower than 50 mm and 30 mm respectively. The animal meal is sterilized, ground (particle diameter < 1 mm) and homogenized prior to receiving to the plant. The received materials are stored in three separate bins (figure 3.7). Then the RDF and SHW are discharged to Sicon 2 conveyor at two loading points by means of first push flow dischargers (Figure 3.8) and then screw conveyors. The homogenization of fuel mix is almost completed within the conveyor. Sicon 2 delivers waste mix to 70 m^3 circular Saxlund silo at 6th floor which has a rotor with two hydraulically controlled arms to prevent bridging of the materials in the silo. Next, the fuel mix passes sequentially through two screw conveyors, a hopper mounted on "Schenck" weigh feeder, a hopper again and finally sharply inclined screw conveyor downwards to ensure trouble-free conveying of the fuel. Hence, the fuel particles enter the chamber by gravity forces through a chute. The level of the second hopper is controlled according to the weight measurement by the weighing belt and the speed of the first screw conveyor is controlled by the level of the second hopper.

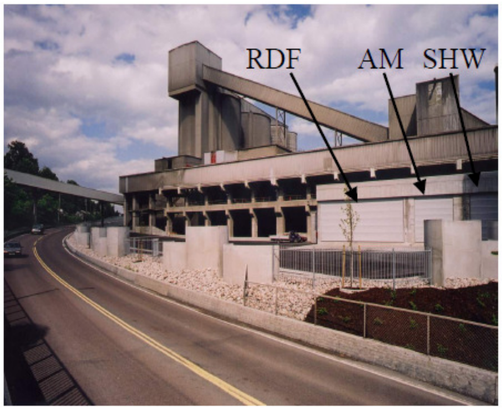


Figure 3.7: Alternative fuel reception bins (Tokheim, 2004)

Figure 3.8: Push floor dischargers

The proximate analysis and heating values of some fuels are presented in table 3.3. The analysis is presented in "as received" basis. The analysis for coal, RDF and animal meal is taken from laboratory report; Renor, 2005. The rest of data is from Axelsen, 2002.

Table 3.3: Proximate analysis and heating values of some fuels (Renor, 2005)

	Moisture (wt %)	Volatile matter (wt %)	Fixed carbon (wt %)	Ash (wt %)	LHV (MJ/kg)
Coal	0.90	29.51	55.9	13.60	29.56
RDF	21.02	58.37	4.03	16.58	13.35
Animal meal	5.32	64.39	8.30	21.99	16.70
SHW	10.70	46.30	7.70	35.30	15.75
LHW	45.70	54.30	0.00	0.00	17.88
Waste oil	0.00	100.00	0.00	0.00	41.60

However, the alternative fuel utilization in the plant is still being increasing and optimizing. The plant has planned two stepped strategy to achieve 65.2% fossil fuel substitution in total energy required by main burner and precalciner (i.e. 171200 t/yr of total alternative fuels). As shown in figure 3.9, by end of 2009, the annual coal usage will be reduced to 42500 t/yr and animal meal and RDF consumption will be increased by 10000 t/yr and 9500 t/yr respectively. In addition to that, plastics are going to be introduced to the main burner. A portion of solid hazardous waste which is currently fed to the precalciner will be fed to the main burner and then the RDF consumption at precalciner will be increased instead. The animal meal, pre shredded plastic and a portion of SHW will be introduced to the main burner through a new feeder system called "Pfister feeder". More detail about this new feeder will be addressed in next sub chapter.

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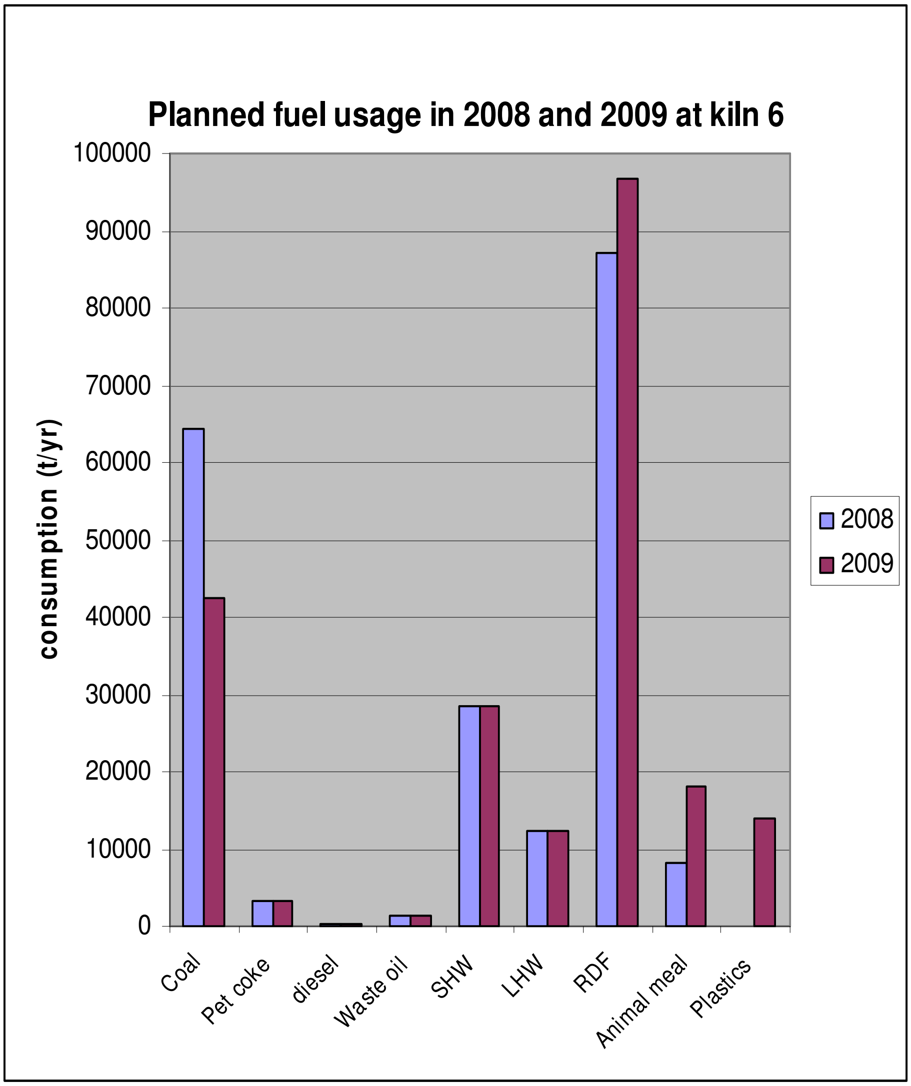


Figure 3.9: Planned fuel usage in 2008 & 2009 (Norcem, 2009)

3.5.2 New Pfister feeder system at main burner

The Pfister feeder (Figure 3.10) is a modern device which can be used for the constant mass feeding of solid secondary fuels. The system is designed to handle fuel material densities from 0.05-1.50 t/m^3 and the recommended particle size, water content, temperature and other characteristics for the system depend on the fuel type. More detail about the system is discussed in the following section. The numeric figures were taken either from Jon Sigmond, Norcem (Personal communication, 27.04.2009) or from Pfister, 2009.

Figure 3.10: Pfister feeder system

By the time of writing this report, the Pfister feeder system in Norcem-Brevik is used only for animal meal feeding to the main burner.A simple flow chart of animal meal feeding is shown in figure 3.11.

The received animal meal is stored in a reception bin (Figure 3.7) which has a capacity of 500 m^3. Then it is fed to a 310 m long closed conveying belt, Sicon 1 (Figure 3.12) by means of push floor dischargers (Figure 3.8) and then two screws (Figure 3.13) which have maximum speeds of 175 rpm and 32 rpm respectively. Sicon 1 has maximum conveying capacity 85 m^3/hr. There is a special sensor (Figure 3.14) is located at the end of Sicon 1 to sense the malfunctions of conveying belt. The material in Sicon 1 is then directly conveyed to a prehopper which is also called calibration bin or homogenization-bin (Figure 3.17) of the Pfister feeder through a gravity chute (Figure 3.15). However, the size and design of supply conveyor has to be selected to ensure that the rotor weighfeeder system including homogenization bin is provided with sufficient supply of bulk material with at least 120% of the maximum feed rate.

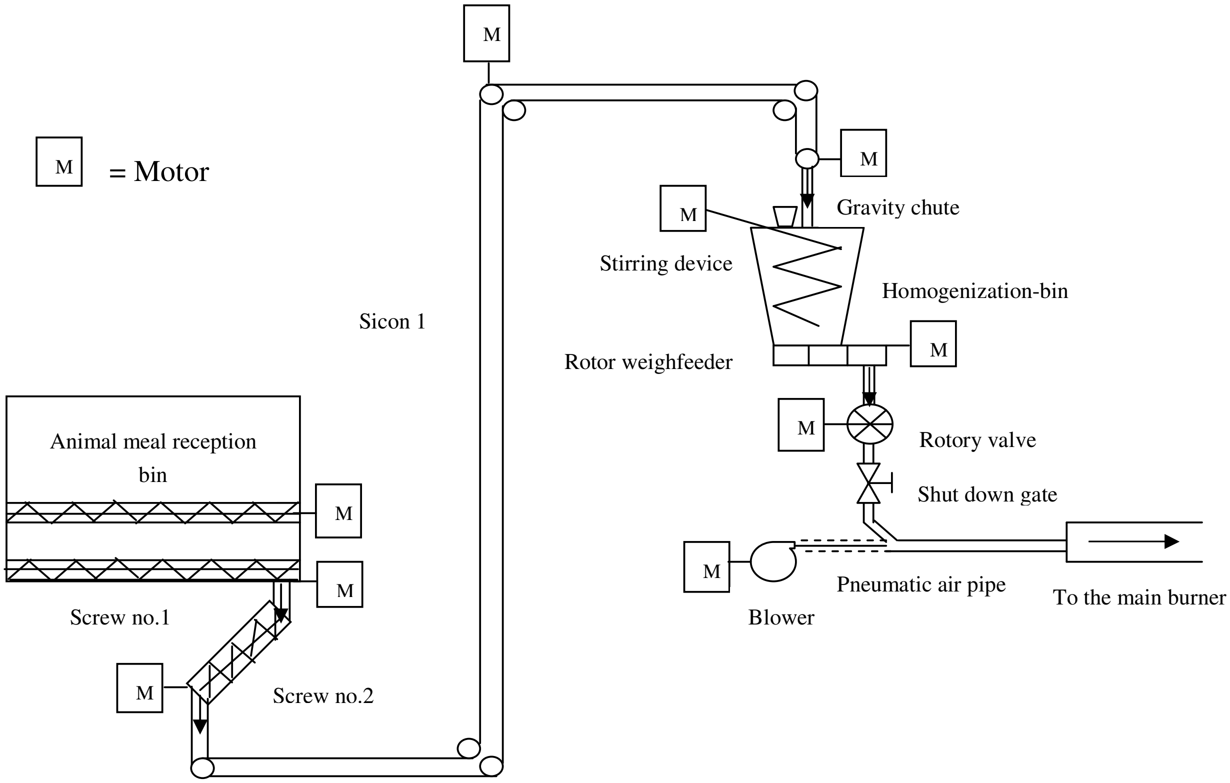


Figure 3.11: Process & Instrumentation Diagram for animal meal feeding to the main burner

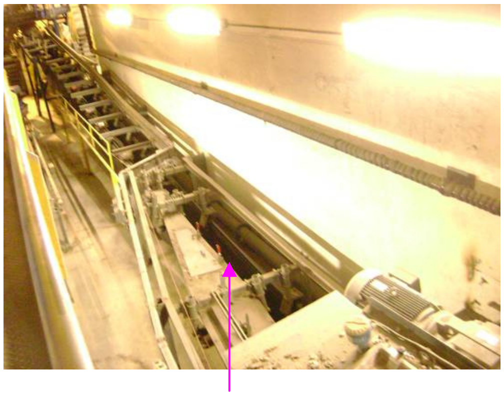


Figure 3.12: Sicon 1

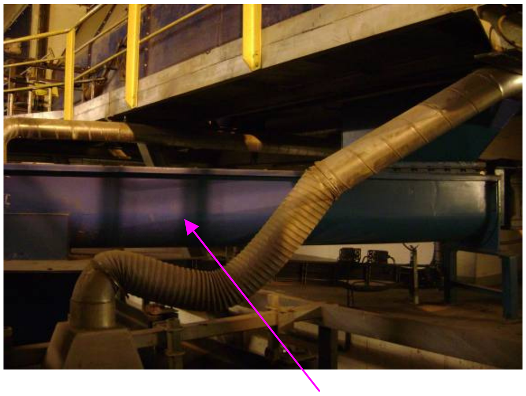


Figure 3.13: Screw no.2

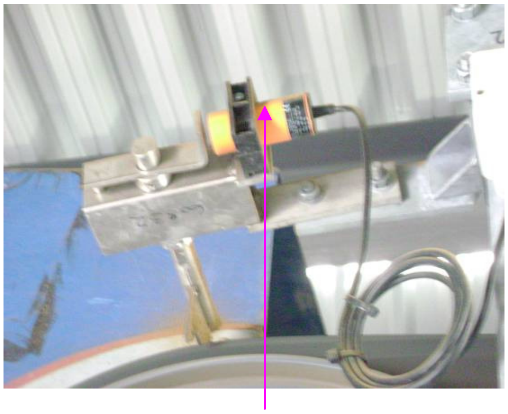


Figure 3.14: Sensor for the Sicon

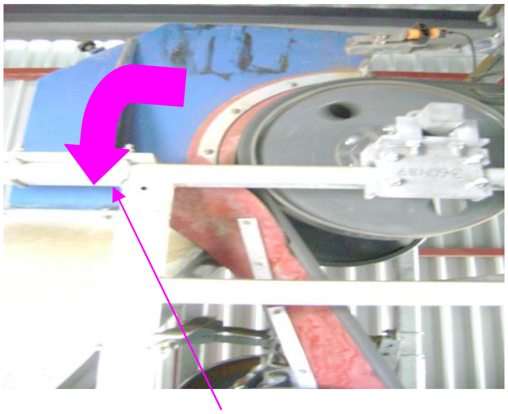
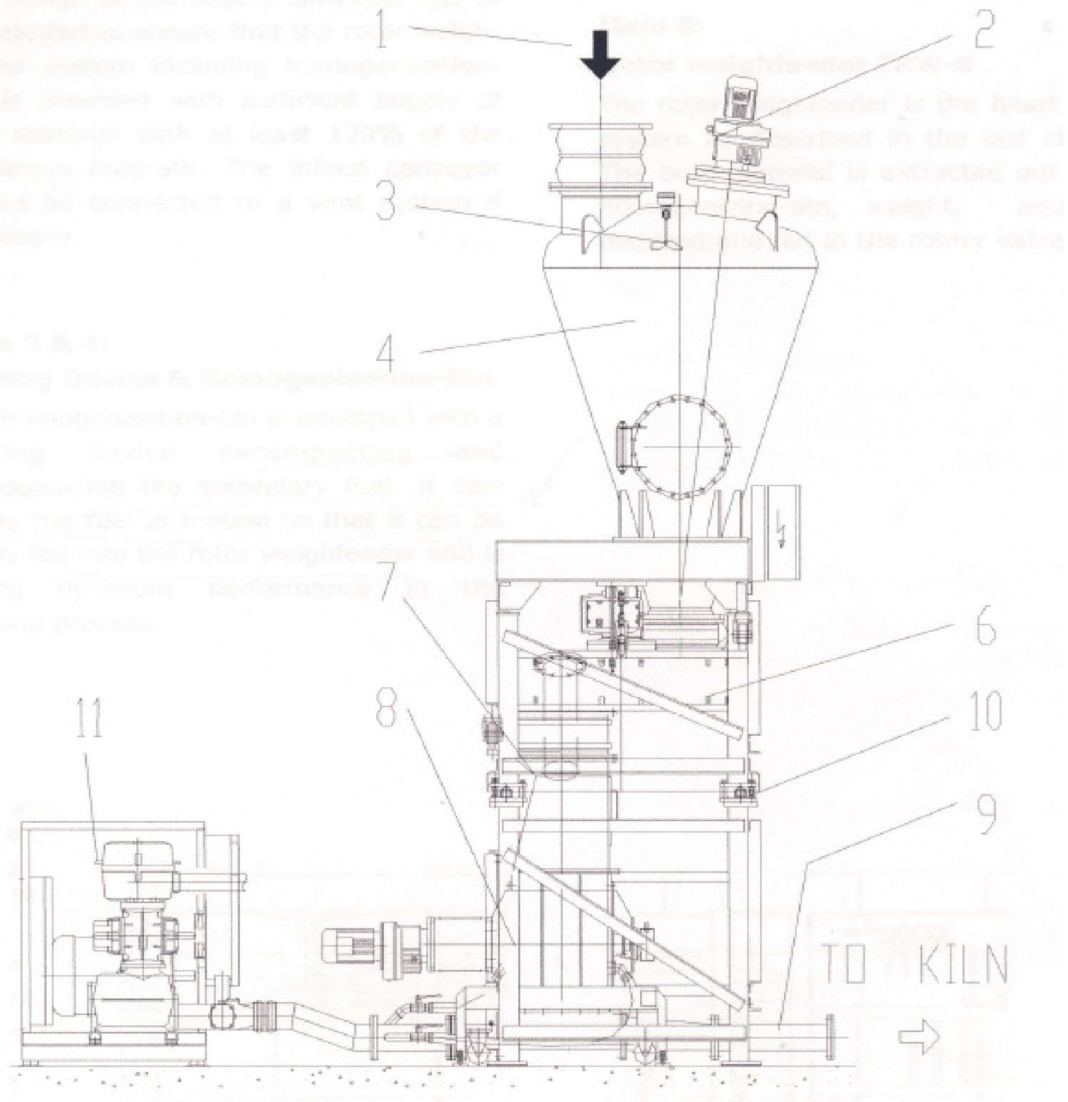


Figure 3.15: Animal meal entering to a gravity



Pfister Secondary-Fuel Dosing System

1: infeed, 2: stirring device, 3: level limit switch, 4: homogenisation-bin,
6: rotor weighfeeder TRW-S/D, 7: ventilation box with ventilation pipe,
8: rotary valve, 9: blower fitting, 10: load cells, 11: blower

Figure 3.16: Sketch of Pfister secondary fuel dosing system (Pfister, 2009)

The homogenization-bin of the Pfister has 7 m^3 capacity and the filling start level and filling stop level inside the prehopper have found to be 600kg and 1200 kg respectively for animal meal feeding in current situation. Moreover, the homogenization-bin is equipped with a stirring device along with 3kW geared motor (Figure 3.18) decompacting and homogenizing the material to give a steady fuel-quality. It also keeps the fuel in motion and ensures a steady loading of the rotor weighfeeder even if there is an interruption of material supply. Additionally, there is a level limit switch (Figure 3.19) on the top of the homogenization-bin to detect whether the homogenization-bin is full.

Figure 3.17: Homogenization-bin

Figure 3.18: Motor for the stirring device

Figure 3.19: Level limit switch

The material then enters to the rotor weighfeeder TRW-S (Figure 3.20) which is considered as the heart of the whole system. The rotor is rotated by means of 3kW motor (Figure 3.21) located on the top of the weighfeeder. The rotor weighfeeder which has been installed in Norcem-Brevik has a capacity of 7 T/hr (maximum 80 m^3/hr). The dimensions of rotor diameter and height are 1.4 m and 0.3 m respectively.

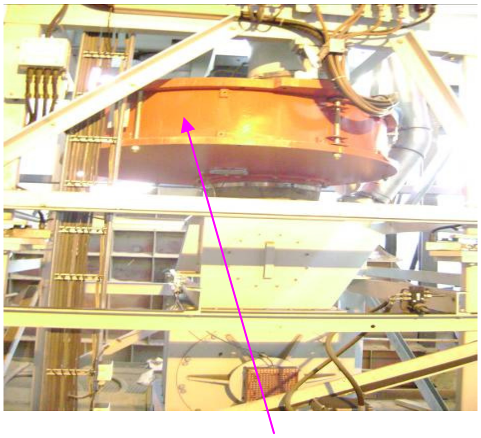


Figure 3.20: Rotor weighfeeder TRW-S

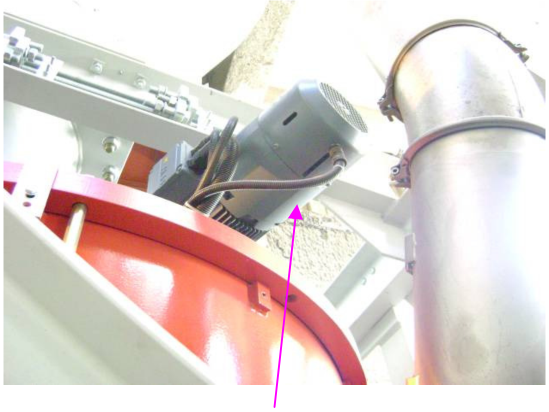


Figure 3.21: Motor of rotor weighfeeder

The rotor weighfeeder utilizes the operating principle of a gravimetric, horizontal chain conveyor transporting in a circular way, with radial scrapers and circulating trough walls.

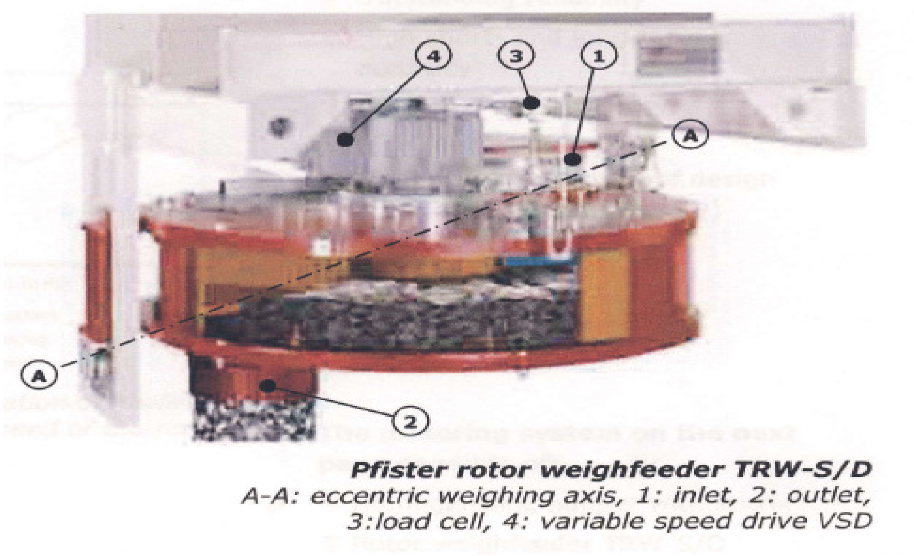


Figure 3.22: Pfister rotor weighfeeder TRW-S/D (Pfister, 2009)

As shown in figure 3.22, the material which is transported in the rotor from the inlet (1) to the outlet (2) produces a momentum around the weighing axis. This weighing axis is eccentric to the rotor-shaft but through the middle of both inlet (1) and outlet (2). This produced momentum is measured by the load cell device and this information is stored by sector in the weighing electronics together with the associated angular position. From the preset metering output and the stored mass of bulk material, the weighing electronics calculate the rotor angular speed of the motor (4) required for the moment when the material is discharged into the process. The Pfister rotor weighfeeder TRW-S is dosing with a high accuracy with maximum deviation of the actual-feed and set-feed rate of ±0.5%.

The rotor weighfeeder and homogenization bin are mounted together on four load cells (Figure 3.23) with accuracy class of 0.02%.

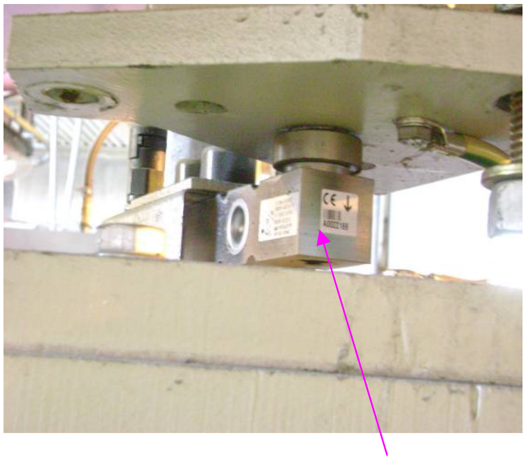


Figure 3.23: Load cell

The rotary valve (Figure 3.24) provides virtually pressure-tight infeed of the bulk material (with special sealing system) from rotor weighfeeder into the pneumatic feed line.The rotary valve is run by a 5.5 kW motor (Figure 3.25) which has the speed range from 0-17 rpm. The material is discharged (Figure 3.28) and conveyed by means of pneumatic air which comes through 127 mm inner diameter pipe (Figure 3.26). The blower (Figure 3.27) capacity is 1400 Nm^3/hr. Additionally there is a pneumatically operated automatic valve (Figure 3.29) for the immediate interlock of the system when any malfunction occurs.

Figure 3.24: Rotory valve with air sluice

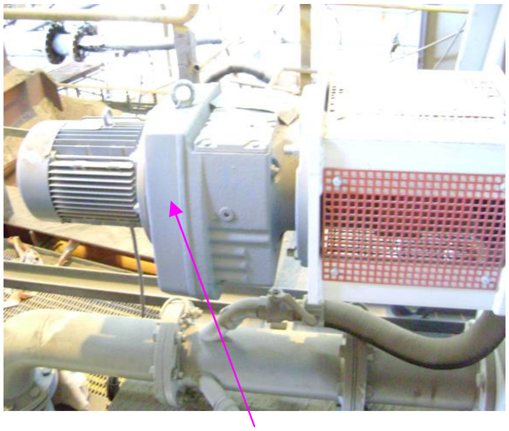


Figure 3.25: Motor for rotary valve

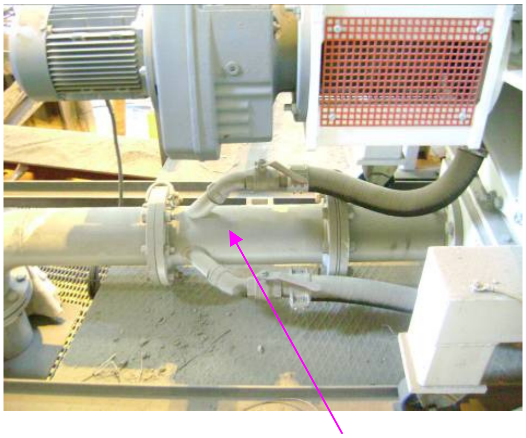


Figure 3.26: Pneumatic air pipe

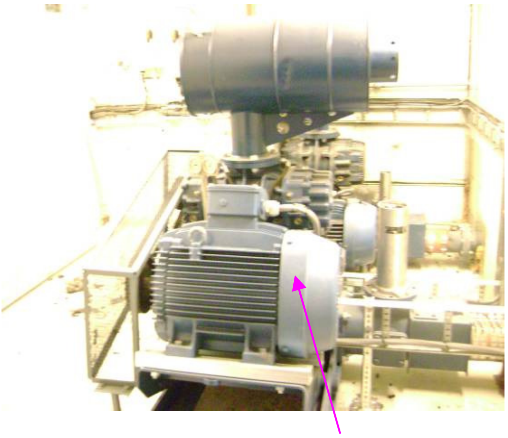


Figure 3.27: Blower

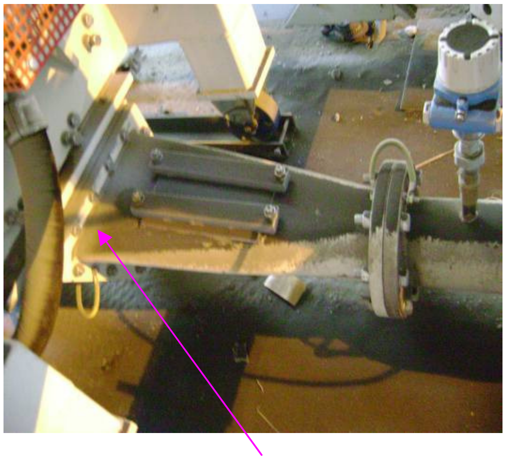


Figure 3.28: Material outlet from Pfister feeder

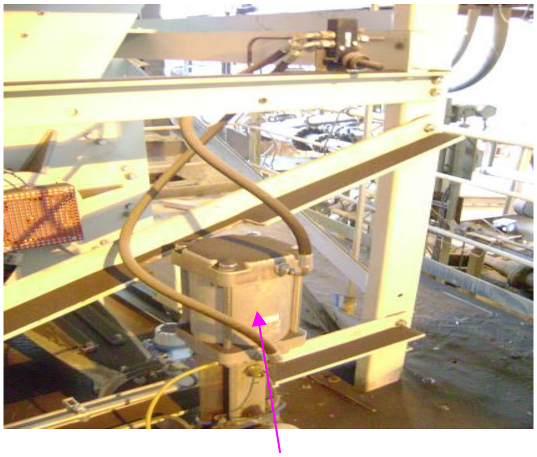


Figure 3.29: Shut down gate

A pressure gauge (Figure 3.30) which is located near by feeder outlet is used to measure the pressure of animal meal conveying line to the main burner. After all the material is conveyed to the main burner inlet (Figure 3.31). Main burner has three separate inlets for animal meal, LHW and waste oil.

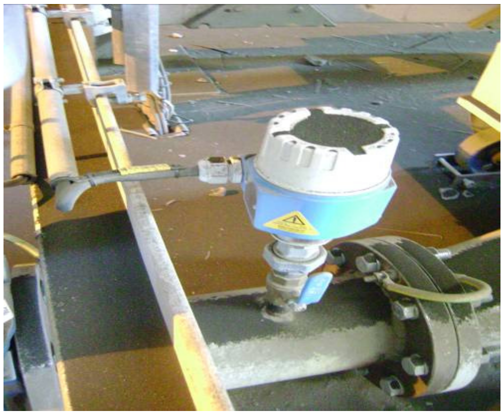


Figure 3.30: Pressure gauge

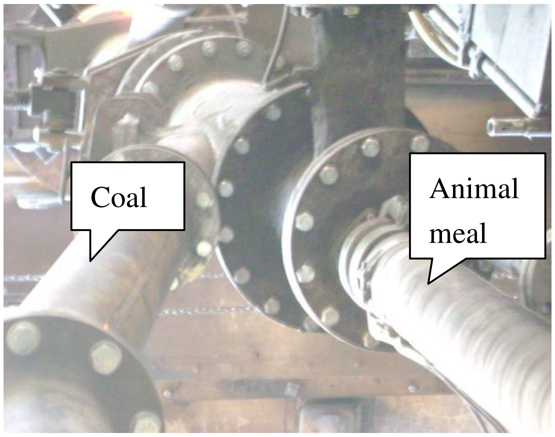


Figure 3.31: Main burner inlet

4 RDF characterization

In this study, the characterization of RDF is discussed in more details. There are several reasons for selecting RDF for further consideration.

- RDF is presently the most important and highly utilized alternative fuel at Norcem around 80000 T/yr and expecting more in future
- RDF sampling and characterization is very difficult due to heterogeneous nature of material
- The analyzed data found from the literature may not be applicable in other scenarios since the properties are highly dependent on the RDF production route and MSW feed which depends on local factors such as location, consumer behavior, climate, etc.
- Representative sampling and characterization is however required in order to report RDF characteristics specially when reporting stack emissions which should be clearly represented for regulatory authorities

Among all other properties of RDF, the biomass and non-biomass content is more important property since it is very useful for determination of net CO_2 emissions from the cement kiln when use RDF as alternative fuel and hence necessary for evaluations in the field of carbon trading.

4.1 The methods available for the determination of biomass content of RDF

According to the technical specification CEN/TS 15440:2006, three methods are recommended for the determination of biomass content in solid recovered fuels; selective dissolution in sulfuric acid, the manual sorting method and the informative reductionistic method. Nevertheless, all three methods are still not validated and even there are some general limitations when applying above three methods in determination of biomass content of SRF. They are not applicable for,

- Pure fractions of waste, products and by-products classified as CO_2 neutral biomass
- Char coal, peat and solid fossil fuels like hard coal, coke, brown coal and lignite and to mixtures of these and SRFs
- SRFs that contain more than 10% of natural and/or synthetic rubber residues

- SRFs that contain a combination of more than 5% by weight of ;
    - Nylon, polyurethane or other polymers containing molecular amino groups
    - Biodegradable plastics of fossil origin
- SRFs that contain a combination of more than 5% by weight of ;
    - Wool or viscose
    - Non-biodegradable plastics of biogenic origin
    - Oil or fat present as a constituent of biomass

Since most of municipal and assimilated waste is within the above limits for certain materials, there will be no issue of applying them on typical RDF analysis.

The fraction of biomass can either be expressed by weight or by energy content or by carbon content. However, for SRFs exceeding biomass content by weight of 95%, it is assumed that biomass content in percent by weight equals the biomass content in percent by total carbon content. In addition to above three methods, an alternative method “C-14 method” can be used for biomass content determination by carbon content however it is still in its early stages of development. The limitations of three methods are addressed in table 4.1.

In general, the solid recovered fuels comprising of a mix of biomass and non-biomass materials, the selective dissolution method is rather reliable, but within the biomass range of 10-90% by weight. The other reason for selecting this method is the quantitative implications of the sources of error are difficult to predict specially in manual sorting method. In the present study, the selective dissolution method is practiced and a test trial for manual sorting method is also carried out.

Table 4.1: Limitations and disadvantages of three methods

Selective dissolution in sulfuric acid	• Not better for samples with biomass content >95 wt% and minimum particle size>1 cm • Rely on the basic assumption of complete degradation of biomass materials and no biodegradation at-all of non-biomass materials however not always true practically e.g. Nylon has non-biomass origin but 97 wt% is biodegradable Wool, Viscose are biomasses but only 83 wt% biodegradable • Outside the concentration range 10% to 90%, the relative reliability of results decreases for some materials • Correction is also impossible due to complexity and diversity of substances present in SRF • Method has not been validated • Time consuming
Manual sorting method	• Not better for samples with biomass content <95 wt% • Not applicable for SRF with minimum particle size<1cm without a microscope • The potential presence of mixed materials that are not feasible to separate manually • The contamination from other materials are not taken into account, hence reduced accuracy • The presence of materials which mimic the physical appearance or properties of the complementary material class, e.g. biodegradable plastics • The sorting precision is calculated using selective dissolution test which is again not validated yet • Method has not been validated • Time consuming • More labour intensive
Informative reductionistic method	• Not applicable for SRF with biomass content > 80 wt% and <20 wt% • Not applicable for SRF with a significant amount of fat present in the SRF • Based on the assumption of stable net calorific value of biomass and non-biomass fractions • Highly rely upon available measured and fixed variables and mass and energy balances • Applicable only for internal control and specific agreements • Method has not been validated

4.2 Determination of biomass content of RDF by weight and by energy content from selective dissolution method

The experiment was followed according to technical specification CEN/TS 15440:2006. Though, for more accurate results, the primary sampling of RDF should be done according to the method described in technical specification; CEN/TS 15442:2006 and the laboratory samples should be prepared according to technical specification; CEN/TS 15443:2006 (the test portions with nominal top size of 1 mm), those specifications were not followed in the present study due to time and resource limitations.

4.2.1 Material

The RDF which is used as an alternative fuel at Norcem was selected for the analysis. The material was supplied from Renor. The sample has been received by Renor on February, 2009 for certain analyses. The figure 4.1 shows the nature of the sample. It is predried (60 °C) and shredded version of fuel RDF used at Norcem. No any special pre-treatment was done for the received material prior to all analyses exception of calorific value determination. Accordance with instrument manual, the tablets were made from dried sample for latter case (Figure 4.2). However, the received sample was mixed before taking portions for the analysis.

Figure 4.1: Pre-dried and shredded RDF fuel sample

Figure 4.2: Tablets made for HHV determination

4.2.2 Apparatus and chemicals

The moisture content was analyzed by drying the sample in a normal electric oven until having the constant weight. The ash analysis was carried out in a muffle furnace accordance with CEN/TS 15403:2006. 0.5-1 g of sample which was dried at 105 °C was used for the determination of higher calorific value (GCV or HHV) in Leco AC-350 automatic calorimeter and the ash correction was done separately whenever the method requires the net or gross calorific value in dry and ash free basis. An electronic balance which has minimum measurement of 0.1 mg was used for weighing purposes.

Commercially available 35% (g/g) H_2O_2 was provided and available 96% (g/g) H_2SO_4 solution was diluted to make 78% (g/g) H_2SO_4 solution which was needed for dissolution of the sample.

4.2.3 Procedure

The experimental procedures were followed according to Annexes B and D of particular technical specification (CEN/TS 15440:2006).

The crucibles were cleaned and dried before each analysis. 3 g of original RDF portion (portion A) was pre-dried in each experiment for the analysis of ash and HHV. For the ash analysis, the dried sample was kept in the muffle furnace at 250 °C for around 2 hrs and then at 550 °C for 20 hrs (It is not required necessarily 20 hrs. Minimum 3 hrs is enough).

In the present study, a portion of residue which was going to be analysed for ash, was taken for the calorific value analysis of the residue instead of making separate residue for HHV analysis (except test B4[*]). Since enough dissolution residue was needed for the ash and calorific value analysis, 20g of wet sample was taken as portion B and the volumes for dissolution were scaled up proportionately i.e. 600 ml of 78% (g/g) H_2SO_4 and 120 ml of 35% (g/g) H_2O_2. The pre-dried RDF sample (Figure 4.3) which was taken for the dissolution was carefully weighed and then dissolved first in 600 ml of 78% (g/g) H_2SO_4 (Figure 4.18) and secondly in 120 ml of 35% (g/g) H_2O_2. After each addition of H_2SO_4 and H_2O_2, the mixture was thoroughly stirred by glass rod and placed away in a fume cupboard around 16 hrs and 5 hrs respectively. After all, the mixture was diluted with 300 ml of demineralized water and filtered over a weighed, pre-dried GF6 grade filter paper (ø 10 cm) in a Buchner funnel (Figure 4.4). It was careful to take all the mixture from mixing flask since the heavy materials tend to retain in the bottom of the flask (Figure 4.5). Then the residue was rinsed with more

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[*] B4 was carried out with two dissolutions for each CV and ash analyses of residue and the procedure described here is for first three tests.

50 ml doses of demineralised water until the last filtrated volume gets a pH of at least 3 in order to make sure the total removal of H_2SO_4 from the residue (Figure 4.6).

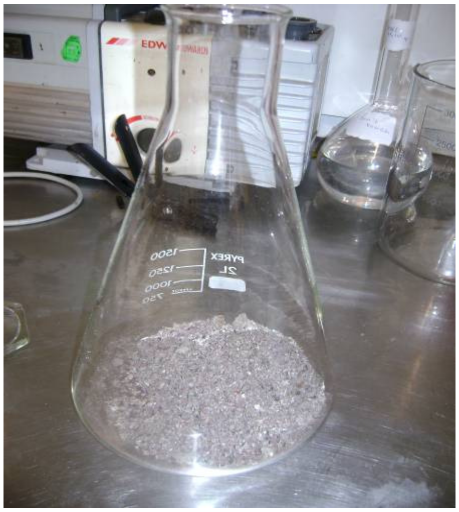

Figure 4.3: Pre-dried sample for dissolution

Figure 4.4: Mixture filtering through Buchner funnel

Figure 4.5: Heavy materials retained in the bottom

Figure 4.6: Residue after rinsing

The residue including filter was carefully taken out from the Buchner funnel without wasting any of the residue and placed in a dried and pre-weighed crucible (Figure 4.7). The residue was dried and then weighed after achieving constant weight (Figure 4.8).

Figure 4.7: Residue before drying

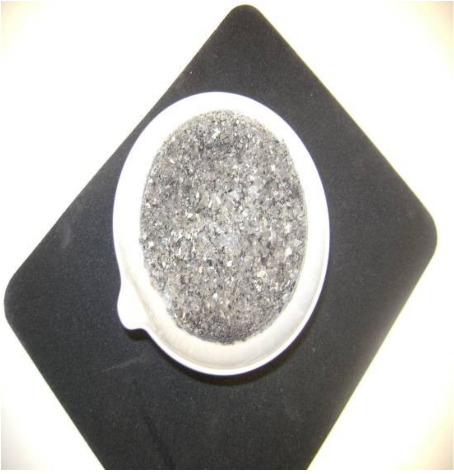

Figure 4.8: Residue after drying

Since a representative dried residue portion should be taken for the HHV analysis, the residue was carefully scraped (as much as possible) from the filter paper without damaging to filter paper (Figures 4.9 & 4.10).

Figure 4.9: Scraping the filter

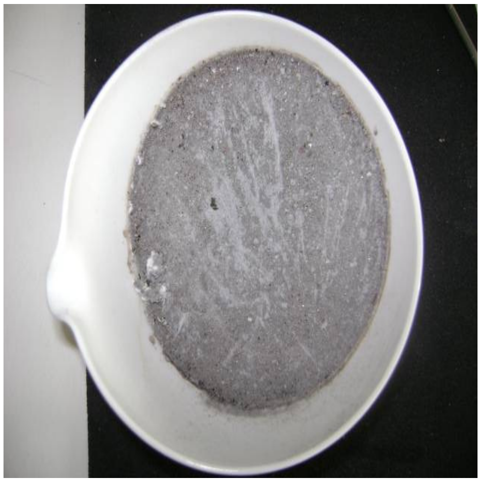

Figure 4.10: Scraped filter

The residue taken out from the filter paper was well mixed (Figure 4.11) and put into a row as shown in figure 4.12. A total sample was taken (not only the top layer but bottom layer as well, since heavy materials have settled down in the bottom) from a particular cross section of the row using sharp-wide pincette (Figure 4.13). However, it is important to have well representative residue for HHV analysis. The rest of the residue was placed back on the filter paper plus crucible and carried out the ash analysis similar to portion A.

Figure 4.11: Mixing scraped residue

Figure 4.12: Sampling residue for HHV analysis

Figure 4.13: Take off everything in certain cross section

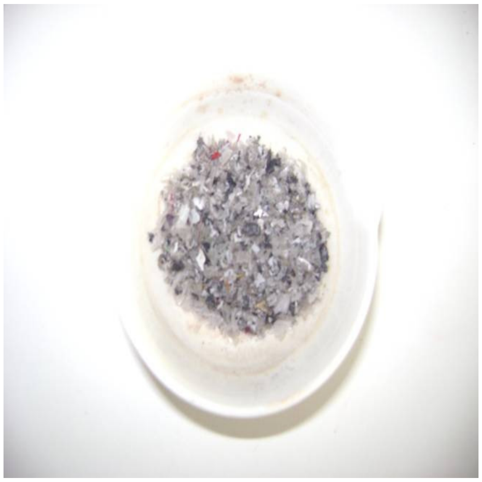

Figure 4.14: Residue for HHV analysis

The ash after igniting the residue in a muffle furnace is shown in figure 4.15. Since the GF grade filter papers are totally made from glass fibres, the mass of filter paper would not be changed while igniting in fact retained as ash.

Figure 4.15: Ash after igniting the residue

Figure 4.16: Two dissolutions for test B4

4.2.4 Experimental details

Portion A is referred to the RDF sample as received and portion B is referred to the dissolution residue of RDF. Three trials per each test (sample no. A1, A2 & A3) were carried out for the analysis of moisture and ash content for portion A. A TGA experiment (sample no. A4) was also carried out for further verification of the results. The sample taken for the TGA experiment was 5.481 mg. Also, one calorific value analysis was carried out for portion A. The results are shown in table 4.3. However, the average values of portion A (when more than one test was carried out) are used in calculations of each four experiment of portion B.

At the same time, four dissolution tests were carried out for portion B (B1, B2, B3 & B4). Four CV analyses and ash analyses were carried out for the dissolution residues and all other required parameters were found (Table 4.4). In first three tests, a portion of dried residue was taken for CV analysis and in final test, separate dissolutions were carried out for each CV analysis and ash analysis of residue (Figure 4.16). In test B4, 5 g of original RDF was taken in each dissolution.

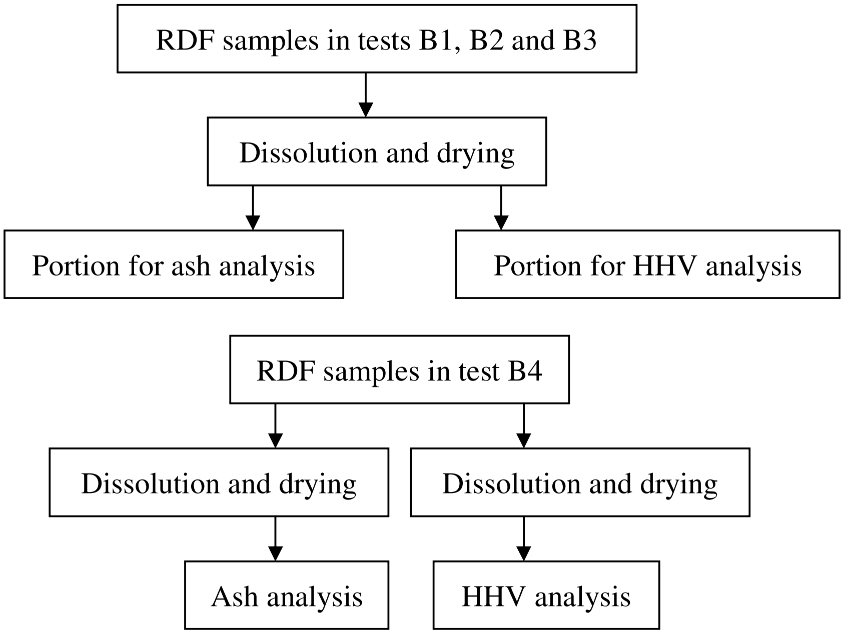

Figure 4.17: The test procedures for portion B

4.2.5 Special observations & typical time consumption for the experiment

After adding H_2SO_4 and stirring, the system heated up little bit and a dark blackish brown colour could be observed (Figure 4.18). After keeping the mixture for 16 hrs, the top layer became as sludge like material (Figure 4.19).

Figure 4.18: After addition of H_2SO_4

Figure 4.19: After leaving for 16 hrs

The following observations could be experienced after adding H_2O_2 and stirring it for couple of minutes.

- Formation of lot of bubbles and foam (Figure 4.20)

Figure 4.20: After adding H_2O_2 and stirred for couple of minutes

- The colour of mixture turned to pale green (Figure 4.21) and then more brownish (Figure 4.22)
- Clear phase separation of liquid and solid particles (Figures 4.21 & 4.22)

Figure 4.21: Pale green & clear separation

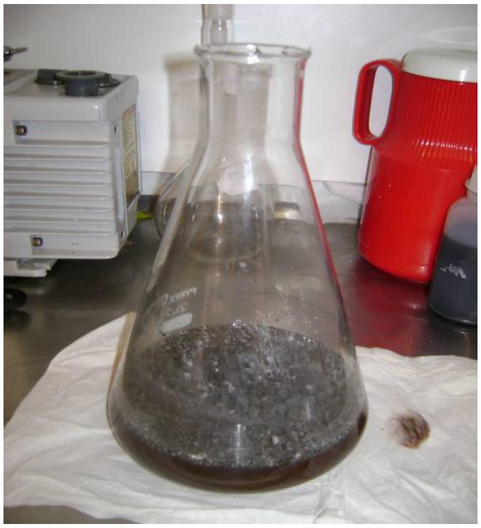

Figure 4.22: More brownish

- Rapidly heated up due to highly exothermic reaction
- Strong odour

A typical minimum time required by an experiment for determination of the biomass content of RDF in percent by calorific value is discussed below. It is assumed that required samples, apparatus, utilities, chemicals and reagents are available within the lab facility. In addition to below mentioned activities, the time should be allocated for laboratory sample preparation and sampling of laboratory sample for the test. It should be noted that the time consumption for moisture determination (or simply for drying) of a sample in an oven highly depends upon the sample weight. Also, additional time should be allocated if separate residue would be prepared for the CV analysis of residue instead of taking portion from dried residue which is going to be analysed for ash content (test B4).

Table 4.2: Time consumption for one experiment

Portion	Activity	Labour-minutes	minutes
A (3g initial sample)	Crucible drying		60
	Cooling the crucible in a desiccator		15
	Sample drying		240
	Cooling the dried sample in a desiccator		15
	Dried sample ignition in a muffle furnace		290
	Cooling the sample on thick metal plate & then desiccator		20
	Taking the weight measurements in above activities	20	20
	Sample preparation for HHV analysis in bomb calorimeter	15	15
	HHV analysis	45	45
B (20g initial sample)	Drying & cooling glass fibre filter + crucible		60
	Sample drying		240
	Cooling the dried sample in a desiccator		15
	Sample mixing with H_2SO_4 by hand	15	15
	Keeping the H_2SO_4 mixed sample in a fume cupboard		960±120
	Sample mixing with H_2O_2 by hand	15	15
	Keeping the H_2O_2 mixed sample in a fume cupboard		300±60
	Rinse the diluted mixture over the GF filter in a Buchner funnel	90	90
	Drying the residue		240
	Cooling the dried residue in a desiccator		15
	Take a representative residue for HHV analysis	15	15
	Dried residue ignition in a muffle furnace		290
	Cooling the residue ash on thick metal plate & then desiccator		20
	Taking the weight measurements in above activities	20	20
	Sample preparation for HHV analysis in bomb calorimeter	15	15
	HHV analysis	45	45
	Total time	**295**	**3075**

4.2.6 Calculation

A sample calculation of tests A1 and B1 is presented below.

4.2.6.1 Determination of parameters

Portion A (RDF-Test A1)

- *Moisture & ash determination*

The wt. of empty crucible after heating at 550 °C = 137.0660 g

The wt. of (empty crucible + sample) = 147.2305 g

The wt. of (empty crucible + sample) after drying at 105 °C = 145.1305 g

The moisture content in RDF sample $= \frac{(147.2305 - 145.1305)}{(147.2305 - 137.0660)}$

$= 20.7\%$

The wt. of (empty crucible + dried sample) = 145.1305 g

The wt. of (empty crucible + sample) after burning at 550 °C = 140.6995 g

The ash content in RDF sample in dry basis $= \frac{(140.6995 - 137.0660)}{(145.1305 - 137.0660)}$

$= 45.1\%$

- *Calorific value determination*

The wt. of dried sample taken = 0.78 g

The HHV in dry basis = 14753 kJ/kg

The results for all tests are shown in table 4.3.

Portion B (Dissolution residue-Test B1)

- *Weights and ash determination*

The wt. of (empty crucible + dried sample) = 112.5282 g

The wt. of crucible after emptying the sample to dissolution flask = 96.8430 g

The wt. of dried sample taken for the dissolution ($m_{SRF,\,1}$) = 112.5282-96.8430

= 15.6852 g

The wt. of filter paper (f.p.) after drying = 0.5997 g

The wt. of empty crucible after drying = 103.0338 g

After dissolving in H_2SO_4, H_2O_2 and filtering,

The wt. of (residue + f.p. + crucible) after drying at 105 °C = 111.9530 g

$$m_{residue\text{-}fp,1} = 111.9530 - 0.5997 - 103.0338 = 8.3195 \text{ g}$$

It should be noted that in the present calculation for test B1, a portion of dissolved and dried sample was taken for the calorific value analysis of residue. i.e. not all the residue was ignited for the ash analysis of residue. Therefore, it should be careful when using the parameters in the equations mentioned in the technical specification. Otherwise, the same dissolution procedure should be carried out to get a residue for calorific value analysis (test B4).

After taking portion of dried residue for CV analysis,

The wt. of dried (residue + f.p. + crucible) taken for ash analysis of residue = 111.2146 g

$$m_{residue\text{-}fp} = 111.2146 - 0.5997 - 103.0338 = 7.5811 \text{ g}$$

Also, $m_{residue} = 111.2146 - 103.0338 = 8.1808$ g

The wt. of (residue + f.p. + crucible) after burning at 550 °C = 109.3268 g

$$m_{residue\text{-}ash} = 109.3268 - 103.0338 = 6.2930 \text{ g}$$

Also, $m_{residue\text{-}ash\text{-}fp} = 109.3268 - 0.5997 - 103.0338 = 5.6933$ g

For the equation 4.3, the above mentioned $m_{SRF,\,1}$ is not valid any more since a portion of residue has been taken for CV analysis. Therefore, the real m_{SRF} (which one really originated $m_{residue}$ *and* $m_{residue\text{-}ash}$) is back calculated using available data.

$$\frac{m_{residue-fp,1}}{m_{SRF,1}} = \frac{m_{residue-fp}}{m_{SRF}} \tag{4.1}$$

$$m_{SRF} = 7.5811 \cdot 15.6852/8.3195$$

$$= 14.2931 \text{ g}$$

The ash content of residue in dry basis ($A_{residue}$) $= \dfrac{m_{residue-ash-fp}}{m_{residue-fp}} \cdot 100$ (4.2)

$= 5.6933 \cdot 100/7.5811$

$= 75.1$ %

- *Calorific value determination*

The wt. of dried residue taken = 0.656 g

The HHV of residue in dry basis ($q_{residue}$) = 35404 kJ/kg

The HHV of the residue in this particular experiment (B1) represents only the combustible part of the residue (More details are discussed in sub chapter 4.2.7). In fact, it represents HHV in dry and ash free basis and not only in dry basis. Therefore only in this particular test (B1), the analysed HHV is not required to convert into ash-free basis as it is already analysed as ash free basis. In the other cases, i.e. if representative residue sample could be taken for the CV analysis; the dry basis HHV should be converted to dry and ash free basis using equation 4.5.

In this experiment, q_{NB} = 35404 kJ/kg

4.2.6.2 Determination of biomass content

Using above evaluated values and the following equations, the combustible part of biomass fraction content is determined. For the calculations in all four experiments, the A_{SRF} value (41.6 wt%, dry) is taken from the average of ash analyses in A1, A2 and A3 tests and the q_{SRF} is considered as 14753 kJ/kg in all experiments.

x_B = The biomass content on a dry basis, expressed as a percentage by weight

x_{NB} = The non-biomass content on a dry basis, expressed as a percentage by weight

$m_{residue}$ = The remaining dry mass (including filter) after dissolution and filtering, g

$m_{residue-fp}$ = The remaining dry mass (excluding filter) after dissolution and filtering, g

$m_{residue-ash}$ = Mass of the ash of dissolution residue (including filter) in dry basis, g

$m_{residue-ash-fp}$ = Mass of the ash of dissolution residue (excluding filter) in dry basis, g

m_{SRF} = The mass of dry SRF test portion used for dissolution, g

A_{SRF} = The ash content of SRF sample in dry basis, wt %

x_B^{cal} = The biomass content on a dry basis, expressed as a percentage by CV

x_{NB}^{cal} = The non-biomass content on a dry basis, expressed as a percentage by CV

q_B = The CV of the biomass fraction on a dry and ash-free basis; MJ/kg

q_{NB} = The CV of the non-biomass fraction on a dry and ash-free basis; MJ/kg

q_{SRF} = The CV of the SRF sample in dry basis; MJ/kg

$q_{residue}$ = The CV of the non-biomass fraction (excluding filter) on a dry basis; MJ/kg

$A_{residue}$ = The ash content of non-biomass fraction (excluding filter) on a dry basis, wt %

By weight;

$$x_B = \left[1 - \left\{\frac{m_{residue} - m_{residue-ash}}{m_{SRF}} + \frac{A_{SRF}}{100}\right\}\right] \cdot 100 \tag{4.3}$$

$$x_B = \left[1 - \left\{\frac{8.1808 - 6.2930}{14.2931} + \frac{41.6}{100}\right\}\right] \cdot 100$$

$$x_B = 45.2 \text{ dry wt \%}$$

$$x_{NB} = 100 - x_B - A_{SRF} \tag{4.4}$$

$$x_{NB} = 100 - 45.2 - 41.6$$

$$= 13.2 \text{ dry wt \%}$$

By calorific value;

$$q_{NB} = \frac{q_{residue}}{1 - A_{residue}/100} \tag{4.5}$$

$$q_B = \frac{q_{SRF} - (x_{NB}/100) \cdot q_{NB}}{1 - x_{NB}/100 - A_{SRF}/100} \tag{4.6}$$

$$q_B = \frac{14.753 - (13.2/100) \cdot 35.404}{1 - 13.2/100 - 41.6/100}$$

$$q_B = 22.300 \text{ MJ/kg}$$

$$x_B^{cal} = \frac{x_B \cdot q_B}{q_{SRF}} \tag{4.7}$$

$$= 45.2 \cdot 22.3/14.753 = 68.3 \text{ \%}$$

$$x_{NB}^{cal} = 100 - x_B^{cal} \tag{4.8}$$

$$= 100 - 68.3 = 31.7 \text{ \%}$$

4.2.7 Results & discussion

Table 4.3: Results of test runs for portion A

Sample no. (Test no.)	Moisture wt %	Ash; A_{SRF} wt % (dry basis)	Ash wt % (wet basis)	HHV; q_{SRF} MJ/kg (dry basis)	HHV; MJ/kg (dry & ash free basis)
A1	20.7	45.1	35.8	14.753	26.872
A2	19.6	42.6	34.2		
A3	19.5	37.1	29.9		
Average		**41.6**		**14.753**	
A4 (TGA)	6.2	31.4	29.4		

The moisture, ash (dry basis) and the low calorific content (dry basis) of the original RDF sample given by Renor (Sample name: Veolia miljøgjenvinning Larvik, Sample date: 20/02/2009) are 18.6%, 40.2% and 13916 kJ/kg respectively and when the average result of the present study compare with those analyses, it could be observed that 19.9% of moisture, 41.6% of ash (dry basis) and 14753 kJ/kg of high calorific value (dry basis) are easily acceptable. However, it should be noted that this RDF sample has much higher ash content than the typical RDF fuel used at Norcem. However, the ash content analysed using TGA instrument shows little bit less ash content than real situation and it might be due to volume limitation of the sample pan of the instrument which restricts using sufficiently enough samples for representative analysis, especially for a heterogeneous material like RDF.

Table 4.4: The results of measurements and calculations for four experiments

Experiment & data type	B1	B2	B3	B4	Measured/ Calculated
$m_{SRF,\,1}$ (g, dry)	15.6852	19.2824	17.5760	-	Measured
$m_{residue\text{-}fp,1}$ (g, dry)	8.3195	10.8098	9.7076	-	Measured & calculated
$m_{residue}$ (g, dry)	8.1808	9.7808	9.0108	3.2602	Measured
$m_{residue\text{-}fp}$ (g, dry)	7.5811	9.1482	8.3220	2.6269	Calculated
m_{SRF} (g, dry)	14.2931	16.3185	15.0673	4.4314	Calculated
A_{SRF} (% by wt, dry)	41.6	41.6	41.6	41.6	Measured
$m_{residue\text{-}ash}$ (g, dry)	6.2930	7.2958	6.7548	2.5858	Measured
$m_{residue\text{-}ash\text{-}fp}$ (g, dry)	5.6933	6.6632	6.0660	1.9525	Calculated
x_B (% by wt, dry)	**45.2**	**43.2**	**43.4**	**43.2**	Calculated
x_{NB} (% by wt, dry)	**13.2**	**15.2**	**15.0**	**15.2**	Calculated
$A_{residue}$ (% by wt, dry)	75.1	72.8	72.9	74.3	Calculated
$q_{residue}$ (MJ/kg, dry)	8.816*	16.746	17.528	15.401	Measured
q_{NB} (MJ/kg, dry & ash free)	35.404	61.566	64.679	59.926	Calculated
q_{SRF} (MJ/kg, dry)	14.753	14.753	14.753	14.753	Measured
x_B^{cal} q_B (MJ/kg, dry & ash free)	22.300	12.488	11.639	13.065	Calculated
x_{NB}^{cal} **(% by CV, dry)**	**68.3**	**36.6**	**34.2**	**38.3**	Calculated
(% by CV, dry)	**31.7**	**63.4**	**65.8**	**61.7**	Calculated

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* This is back calculated from q_{NB}

As shown in table 4.4, the average biomass and non-biomass content of RDF by weight were 43.75% (dry basis) and 14.65% (dry basis), respectively (Figure 4.23). A very small standard deviation (1.92%) reveals the reliability of experimental results. However, it is observed that 10g of original sample would be enough for the dissolution instead of 20 g sample which was used for the experiments B1, B2 and B3.

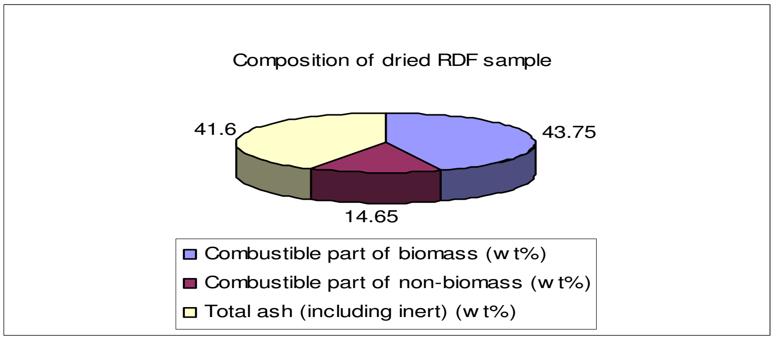

Figure 4.23: The biomass and non-biomass content in dried RDF sample

The analysed calorific value for residue in test B1 was considered as ash free basis, since only the top layer of the residue was taken for the CV analysis and hence it was assumed that the ash and inert part was left on the filter paper. However, when it is compared with the CV analyses of the rest of the tests, it can be concluded that the residue taken for the CV analysis in test B1 might also have contained some ash. Therefore when taking averages in next analyses, the calorific value of test B1 is not taken into consideration.

The test B4 was carried out to check whether there is an error occurs with sampling of dried residue for ash and CV analyses. However, there is no big difference between the results of ash and CV analyses of residues in B2 and B3 compared to B4. However, the calorific value analysis result of test B4 shows a better result than B2 and B3.

Some unlikely values were found when determining the biomass content of RDF by calorific value. Practically, the calorific value of non-biomass fraction in dry and ash free basis could not be high as 62.057 MJ/kg. Therefore the error might be either encountered with the ash content of residue or the calorific value of residue. According to the experimental results, the average ash content of the residue is 73.78% (dry basis) and the average calorific value of the residue is 16.558 MJ/kg (dry basis).

Let’s try to analyse this theoretical result with a real situation.

Consider the following box as 100 kg of dried RDF sample. In the following equations *m* stands for weight (dry basis) and *E* stands for energy (which relevant to HHV) and *q* stands for HHV (dry basis).

Biomass combustible (a)	Non-biomass combustible (b)	Inert (e)
Ash: biomass (c)	Ash: non-biomass (d)	

Theoretically,

For original RDF sample;

$$\frac{m_a}{m_a+m_b+m_c+m_d+m_e}\cdot\frac{E_a}{m_a}+\frac{m_b}{m_a+m_b+m_c+m_d+m_e}\cdot\frac{E_b}{m_b}=1\cdot\frac{E_{a+b+c+d+e}}{m_a+m_b+m_c+m_d+m_e} \tag{4.9}$$

For residue;

$$\frac{m_b}{m_b+m_c+m_d+m_e}\cdot\frac{E_b}{m_b}=1\cdot\frac{E_{b+c+d+e}}{m_b+m_c+m_d+m_e}=q_{residue} \tag{4.10}$$

(Ash does not contribute any energy value for the fuel)

Substituting the experimental results in (4.9) and (4.10),

$$\frac{43.75}{100}\cdot\frac{E_a}{m_a}+\frac{14.65}{100}\cdot\frac{E_b}{m_b}=14.753 \tag{4.11}$$

$$\frac{26.22}{100}\cdot\frac{E_b}{m_b}=q_{residue} \tag{4.12}$$

Let's assume that the biomass has 17 MJ/kg (dry basis) of HHV and 14% (dry basis) of ash in reality (The highest biomass fraction contained in RDF is paper/ cardboard; see sub chapter 4.3.1).

i.e.

$$\frac{E_a}{m_a+m_c}=17 \quad \text{MJ/kg}$$

$$\frac{m_c}{m_a+m_c}=0.14$$

$$\frac{E_a}{m_a} = \frac{17}{1-0.14} = 19.767 \quad \text{MJ/kg}$$

Then, from (4.11), $\frac{E_b}{m_b} = 41.672$ MJ/kg

From (4.12), $q_{residue} = 10.926$ MJ/kg

This value is 4.5 MJ/kg lower than the experimentally found minimum HHV.

Let's check whether the ash content of non-biomass fraction is realistic.

Assume non-biomass fraction has plastic with HHV of 40 MJ/kg in dry basis.

$$\frac{m_d}{m_b + m_d} = \left(1 - \frac{40}{41.672}\right) \cdot 100 = 4\%$$

The ash content of non-biomass fraction is 4% which is practically possible.

In this actual case the composition of RDF sample;

The combustible part of biomass content = 43.75%

The combustible part of non-biomass content = 14.65%

The ash part of biomass content = 7.12%

The ash part of non-biomass content = 0.61%

The inert part = 33.87%

Since the heating values and ash contents of biomass and non-biomass fractions occur in a fixed range (i.e. E_a/m_a and E_b/m_b are within a fixed range), the values of $q_{residue}$ and $A_{residue}$ might be unrealistic in the present test results. To obtain an acceptable solution, either the HHV of residue should be around 11 MJ/kg (dry basis) with 73.78% (dry basis) ash or the ash content of residue should be around 60% (dry basis) with 16.558 MJ/kg (dry basis) or the intermediate values of both ash and HHV. This discrepancy might be due to some experimental errors encountered with following activities.

- There might be some combustibles are left even after igniting the residue at 550 °C and hence give high ash content but not the ash in reality
- Taking the representative laboratory sample of RDF for each experiment (B4)
- Taking the representative sample of residue for ash and calorific value analysis (B1, B2 and B3)

- The nominal top size was not exactly less than 1 mm (might have influenced on dissolution)
- Typical human errors while taking weight measurements and when exchanging material (minor errors)

As a further investigation of above mentioned first point, already ignited ash sample (at 550 °C) was again ignited at 900 °C for 20 hrs in the same muffle furnace. When observe the result, it could be found that only 2.5 wt% of ash material has been lost while further igniting. If this is taken into consideration, the $A_{residue}$ in B2, B3 and B4 are 70.98 wt% (dry), 71.08 wt% (dry) and 72.44 wt% (dry) respectively which are not significantly different from previous analyses.

The second and third points might be critical in this experimental series, since the RDF sample contains very high amount of ash which is not typical for a RDF fuel at all. In fact most of this ash can be considered as inert (glass, metal, sand, etc) which has not come from either biomass or non biomass (Figure 4.24). The technical specification does not have any explanation to distinguish the ash fraction of biomass, ash fraction of non-biomass and inert. It is described by a common term "ash" which is not more explanatory. Moreover, the technical specification simply defines x_B and x_{NB} as "biomass" and "non-biomass" fractions of RDF, nevertheless those should be defined as the weight percentage of "combustible part of biomass" and "combustible part of non-biomass" fractions respectively unless the ash of those fractions is dissolved in acid solution.

Figure 4.24: High inert content of sample

When considering the time requirement to perform this experiment, it takes around three days, but the labour hour requirement is around 5 hrs for one experiment. However, intermediate involvement of personnel is needed through out all three days.

It can be concluded that even though this method seems reliable for RDF characterization, the method and accuracy should be more validated. Also, more explanatory details are needed in some areas like when differentiating inert and other ash material which comes from biomass and non-biomass fractions. There might be a high possibility to have an inaccuracy of the final result of this test since it depends on lot of experimentally determined parameters.

4.3 Test trial for manual sorting

A grab sample of RDF was collected from the conveyor belt Sicon 2 at Norcem. It was sorted manually and the different fractions were weighed. The weight fractions are presented in table 4.5. The fractions are categorized according to the technical specification CEN/TS 15440:2006; Annex C. Simply, organic, fossil and inorganic fractions are categorized as biomass, non-biomass and inert respectively.

4.3.1 Results & discussion

The figures below show the sorted materials.

Figure 4.25: Wood

Figure 4.26: Paper/cardboard

Figure 4.27: Fabric

Figure 4.28: Rigid plastic

Figure 4.29: Soft plastic

Figure 4.30: Biological waste

Figure 4.31: Glass

Figure 4.32: Ceramic

Figure 4.33: Metals

Figure 4.34: Rubber

Figure 4.35: Mixed waste

Figure 4.36: Fines

Table 4.5: Characterization of RDF by manual sorting method

Fraction	Wet weight (g)	Weight fraction (%)	Category
Wood	215.4	10.03	Biomass
Paper/cardboard	336.2	15.66	Biomass
Fabric	92.0	4.28	Biomass
Rigid plastic	127.0	5.91	Non-biomass
Soft plastic	149.4	6.96	Non-biomass
Biological waste	46.5	2.17	Biomass
Glass	12.5	0.58	Inert
Ceramic	18.6	0.87	Inert
Iron	0.7	0.03	Inert
Nonferrous metals (Al)	6.5	0.30	Inert
Rubber	3.0	0.14	Biomass
Mixed waste (plastic & metal together)	10.7	0.50	-
Fines	1128.9	52.57	Inert
Total	**2147.4**	**100.00**	

Biomass content of RDF by weight (as received) =10.03+15.66+4.28+2.17+0.14

= 32.28 wt%

Non-biomass content of RDF by weight (as received) = 5.91+6.96

= 12.87 wt%

Inert content of RDF by weight (as received) = 0.58+0.87+0.03+0.3+52.57

= 54.35 wt%

It is hard to make a conclusion here, since the sample is not a real RDF sample and in fact it contains SHW as well. The higher portion of the fines should have come from the SHW but not from RDF fuel. By neglecting 90% of fines and considering the rest of the fractions as RDF, the following numeric figures can be obtained.

Table 4.6: Characterization of RDF by manual sorting method neglecting 90% fines

Fraction	Wet weight (g)	Weight fraction (%)	Category
Wood	215.4	19.04	Biomass
Paper/cardboard	336.2	29.72	Biomass
Fabric	92.0	8.13	Biomass
Rigid plastic	127.0	11.22	Non-biomass
Soft plastic	149.4	13.20	Non-biomass
Biological waste	46.5	4.11	Biomass
Glass	12.5	1.10	Inert
Ceramic	18.6	1.64	Inert
Iron	0.7	0.06	Inert
Nonferrous metals (Al)	6.5	0.58	Inert
Rubber	3.0	0.27	Biomass
Mixed waste (plastic & metal together)	10.7	0.95	-
Fines	112.89	9.98	Inert
Total	**1131.39**	**100.00**	

Biomass content of RDF by weight (as received) = 61.27 wt%

Non-biomass content of RDF by weight (as received) = 24.42 wt%

Inert content of RDF by weight (as received) = 13.36 wt%

This analysis can not be compared with selective dissolution results since,

- Not the same sample is used
- At least not a real RDF sample in latter case (RDF+SHW)
- The potential presence of mixed materials that is not feasible to catogerize into one category e.g. mixed waste
- The presence of materials which mimic the physical appearance or properties of the complementary material class, e.g. biodegradable plastics
- Not applicable for SRF with minimum particle size<1cm without a microscope
- Fines were separated out manually not by means of sieve, therefore fines can contain not only inert but biomass and non-biomass as well
- The calculations were performed without considering sorting precisions

It can be concluded that in general, the major part of the RDF (by weight in as received basis) is paper and cardboard followed by wood. Then the soft and rigid plastics take place. However, the difference would be higher when it is taken into dry basis.

The manual sorting method is also a time and labour intensive process which typically takes around 3 labour-hrs only for sorting and weighing. In addition to that the time should be allocated for sampling of RDF, pre-preparation (sieving) and for drying of materials after sorting.

5 TGA Experiments for RDF characterization

5.1 Material selection

RDF was selected for the characterization experiments in TGA instrument, since it is used in large quantities in Norcem-Brevik cement plant as an alternative fuel and it is very heterogeneous by nature. The sample which was collected for the test run in determination of biomass content by manual sorting method (sub chapter 4.3) has already been sorted out into the several fractions and out of these sorted fractions, the highest weight fraction categories were selected for the analysis in TGA instrument. Although the fines were available in the highest fraction, it was not thermally analyzed since it is easily burnt in the burner without giving any burning issue and also it is very hard to take well-homogenized sample for the analysis. And most of the fine part has been come from solid hazardous waste since the RDF sample for the sorting was taken from the mixed stream of RDF and hot mix (solid hazardous waste). The following figures show the selected materials for TGA analysis. A pen has been located for the visual indication of the size of the material. Rigid and soft plastics including LDPE and PS, wood, paper and fabric fractions were separately analyzed in TGA instrument.

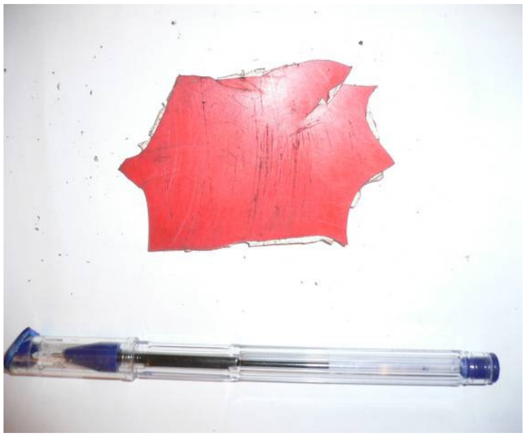

Figure 5.1: Rigid plastic 1

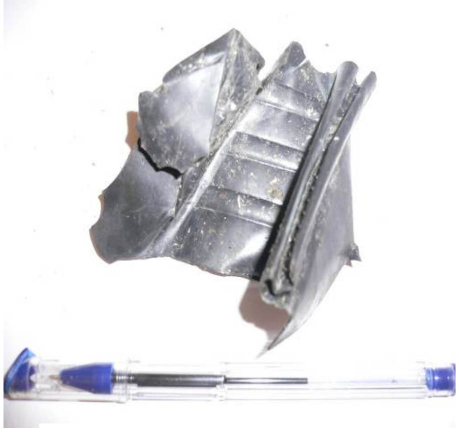

Figure 5.2: Rigid plastic 2

Figure 5.3: Low Density Polyethylene (LDPE)

Figure 5.4: Polystyrene

Figure 5.5: Wood

Figure 5.6: Paper

Figure 5.7: Fabric

5.2 Material preparation

Among the above materials shown in the pictures, rigid plastic 1 and 2, LDPE and wood materials were cleaned with pure water and left it for open drying for 4-5 hours. A small piece was cut from the inner part of the polystyrene sample to avoid contaminated surface. A normal copy paper and fabric piece were used instead of paper and fabric found in RDF sample. Otherwise, it would be difficult to analyze the TGA results if waste materials are used as it is, because it has been contaminated with several unknown contaminants. In addition to above materials, a piece from a gloves packing box (cardboard) was analyzed as it is probable to appear it in typical RDF fuel sample. Each material was tested as small cut pieces without any physical treatments except size reduction which is essentially required by the small sample pan in TGA instrument.

5.3 TGA experiments for RDF analysis

TGA equipment from Perkin-Elmer was used for the experiments. The instrument consists with Thermogravimetric analyser; TGA 7, Thermal analysis controller; TGA 7/DX, Thermal analysis gas station; TAGS and soft ware; Pyris (Arvoh & Ariyaratne, 2008). The designed maximum temperature of the TGA 7 furnace is 1000 °C. The TGA 7 microbalance has 1300 mg maximum capacity and can detect even 0.1 µg changes in the weight (Tokheim, 1999). The same temperature programme was used for all 8 material samples[*] for easy analysis of the results (Table 5.2 & figure 5.8). Nitrogen was used to make a reducing atmosphere and air was employed to create oxidising atmosphere. The experimental procedure was followed according to the TGA user manual (Haugen, 2009).

The table 5.1 lists the experimental series.

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[*] Only for cardboard the maximum isothermal temperature used was 800 °C and paper was kept 5 minutes more at isothermal temperature 750 °C

Table 5.1: TGA runs

Experiment no.	TGA sample ID	Material tested	Sample weight (mg)
1	361	Rigid plastic 1	4.612
2	369	Rigid plastic 2	5.816
3	368	LDPE	4.771
4	370	Polystyrene	1.140
5	363	Wood	5.432
6	371	Paper	13.435
7	362	Cardboard	8.651
8	364	Fabric	7.837

Table 5.2: Temperature programme

Step No:	Descr-iption	Sample purge	Tempera-ture (°C)	Duration (min)	Heating rate (°C/min)	Objective
1	Hold	Nitrogen	25	30	0	Sample purging
2	Heat	Nitrogen	25-110	1.7	50	Raise the temperature
3	Hold	Nitrogen	110	30	0	Removal of moisture
4	Heat	Nitrogen	110-750	64	10	Removal of volatiles
5	Hold	Nitrogen	750	5	0	Switch gas
6	Hold	Air	750	25	0	Removal of fixed carbon

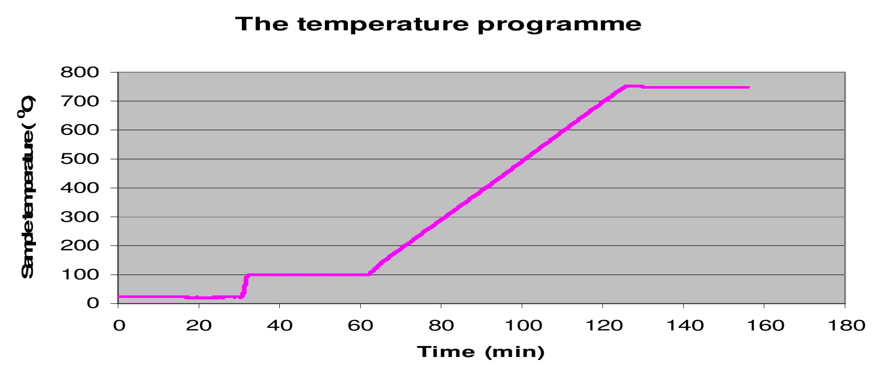


Figure 5.8: Temperature programme

5.4 Results and discussion

The following figures show the mass loss curves and time derivatives for above selected materials.

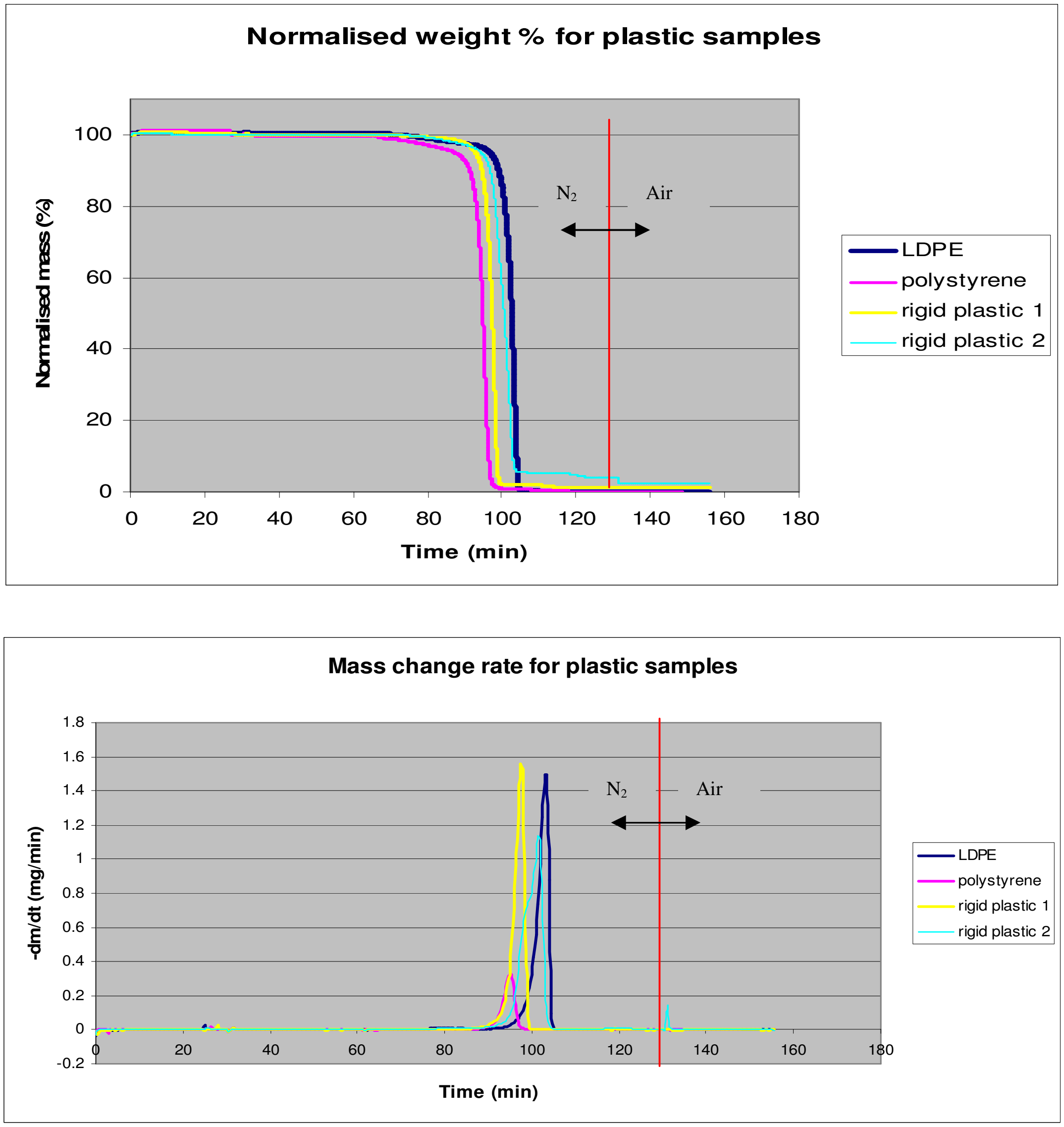


Figure 5.9: Mass loss curve and time derivative for plastic samples

The weight loss curves for plastics have almost the same trends (Figure 5.9); this indicates that they have the same pyrolysis behaviours due to similar chemical bonds in their molecular structures. The decomposition of the plastics starts at higher temperatures when compared to the lignocellulosic materials since they are thermally more stable. The weight losses show that degradation of plastic occurs almost totally in one-step process under reducing conditions which was described as first order reaction by Zhou, Luo & Huang (2009). As can be seen from the degradation curves, all plastic samples have very negligible amount of moisture. Very small amount of ash and fixed carbon could be observed only in the sample “rigid plastic 2” (Table 5.3).

In the case of polyethylene (LDPE), the thermal decomposition starts at approximately 251 °C and slight weight loss appears until 454 °C. However, the major weight loss, around 96%, is observed in the temperature region of 454-540 °C. The maximum rate of pyrolysis exhibits at 529 °C, whilst is followed from the evolution of paraffines and olefins (Grammelis et al., 2009). The experimental results are in accordance with the results of previous studies; Cozzani, Petarca & Tognotti (1995) & Galvagno et al. (2009). However, some literature figures out that the decomposition period for LDPE lies between 400-500 °C with the maximum decomposition around 475- 495 °C (Marcilla et al., 2008). An initial stage of polymer degradation is often accompanied by melting (or softening) around 440 °C followed by the start up of decomposition at 400 °C and then gone off the volatiles with further heating (Zhou et al., 2006). Saha, Reddy & Ghoshal (2008) reported that at initial stage, the thermal degradation can be controlled by the process of formation of a gas phase inside the polymer and by nucleation and nucleus growth in a heterogeneous medium. This was predicted through nucleation and growth model ($n = 2/3$). The reporters further mention that nucleation, growth and diffusion and chemical reaction mechanisms significantly control the decomposition phenomena. However, they’ve mentioned further investigations are needed to conclude the polymer degradation.

In the case of polystyrene, it is believed that, although the molecular weight of polystyrene drops between 200 and 300 °C, the volatile products are not given out since the products from cage disproportionation of polystyrene are stable up to 300 °C. Polystyrene degrades into a mixture of styrene (40%), toluene (2.4%), methyl styrene, etc. above 300 °C (Mathew, Packirisamy & Thomas 2001). The TGA curve for PS shows that PS is almost stable up to 200 °C and gentle drop (5.8%) has occurred within the temperature range of 200-400 °C. After that degradation occurs rapidly. The sharp degradation starts at about 400 °C and at 469 °C the degradation is complete. Above 469 °C no residue remains. The major peak in the DTG curve is at 446 °C which is minimum among tested plastics revealing lowest stability of the material. However, data reported by Mathew, Packirisamy & Thomas (2001) described that pure cross linked PS is degraded around 360 °C and this corresponds to the chain scission to give monomer along with some amount of dimer, trimer, tetramer and pentamer. A detailed study on the evolved gases during pyrolysis has revealed that the devolatilisation of PS differs from the ones of PE and PP (Grammelis et al., 2009).

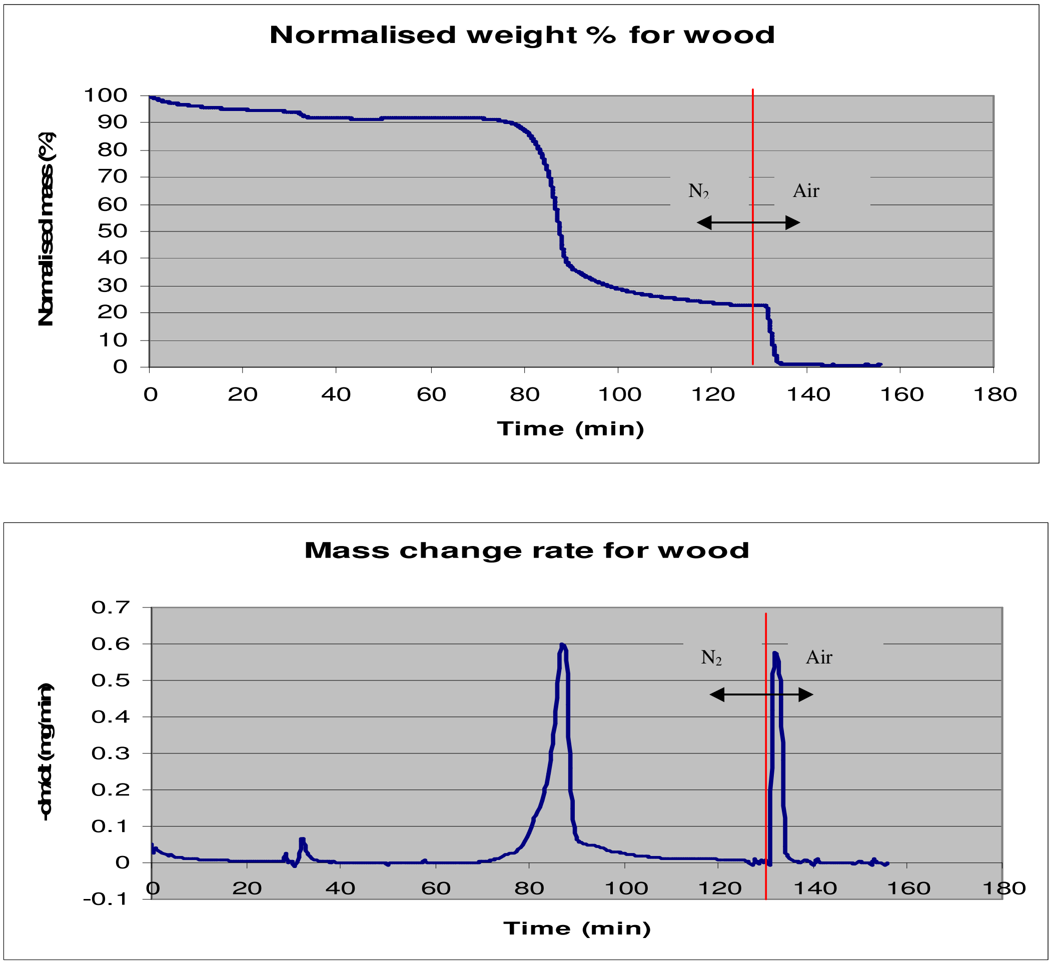


Figure 5.10: Mass loss curve and time derivative for wood

Under reducing conditions, while heating up to 110 °C and keeping at isothermal condition, a significant weight loss (8.4%) is noted indicating the surface and bound moisture content of the material (Figure 5.10). Betwen 200-280 °C, water vapor, carbon dioxide, formic and acetic acids, glyoxal, and perhaps a little carbon monoxide are evolved and additional vapors pass through and moreover the wood slowly becomes charred (Browne, 2009). The thermal decomposition of wood starts at approximately 280 °C and a major weight loss, around 51.6%, is observed in the temperature region of 220-370 °C indicating the hemicellulose and cellulose degradation. At a higher temperature range, 370–750 °C, around 17.5% weight loss is observed. As Browne (2009) reported, the active pyrolysis is going on around 280-500 °C while combustible gases and vapors notably carbon monoxide, methane, formaldehyde, formic and acetic acids, methanol, and later hydrogen; diluted with carbon dioxide and water vapor are produced. Above 500 °C, more vigorous secondary reactions occur and the gaseous products and tars are further pyrolyzed to more highly combustible products. For example, carbon dioxide and water vapor react with carbon to form carbon monoxide, hydrogen, and formaldehyde (Browne, 2009). According to Branca & Blasi (2003), the TGA results for wood with slow dynamics should show three main regimes of weight loss under reducing condition. The lower-temperature regime could be correlated with the decomposition of hemicellulose (225-325 °C), secondly cellulose (325-375 °C) and finally lignin (250-500 °C). According to the experimental results, two different regimes with different weight loss rates can be observed and the weight loss until 370 °C might be due to overlapping the decomposition of cellulose and hemicellulose and the initial stages of lignin decomposition. The higher-temperature regime (370-750 °C) can be mainly correlated with the later stages of lignin decomposition. However, Casu et al. (2005) reported that the decomposition of ligneous material occurs above 650 °C.

The oxidation of the wood material at 750 °C shows 21.7% of fixed carbon. Very less amount of materials (0.8%) is stable at 750 °C after the oxidation, indicating the presence of some inorganic materials in the wood.

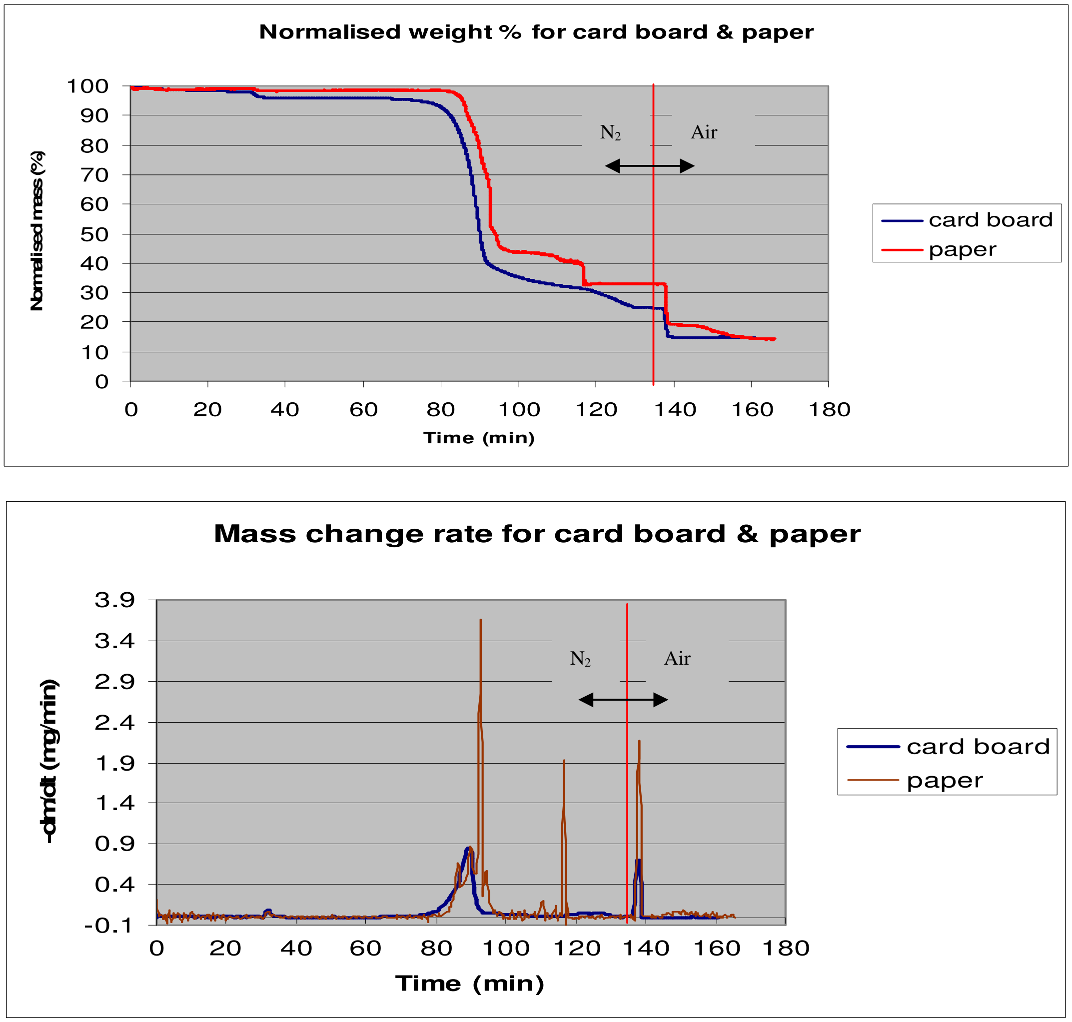


Figure 5.11: Mass loss curve and time derivative for cardboard and paper

The curves for both cardboard and paper show almost same thermal profiles indicating few exceptions (Figure 5.11). Cardboard, a significant weight loss, around 4.2% is observed up to 110 °C indicating higher moisture content compared to copy paper (1.6%). A major weight loss around 53% is noted for cardboard in the temperature range of 266- 417 °C while maximum pyrolysis rate can be observed in the range of 360- 400 °C which was similarly observed by Grammelis et al., 2009. For paper, it is in the range of 411-415 °C and the major loss, 44.3% is in between 347-418 °C. However, Cozzani, Petarca & Tognotti, 1995 has reported that the highest thermal degradation peak for paper pyrolysis is around 375 °C. The deviations of the peak heights in time derivative curves indicate the reactivity of the material. The DTG curves clearly indicate that the copy paper has comparatively high reactivity. It is also important to remark that both samples exhibit similar ash content around 15%. The fixed carbon content of the paper is twice higher than cardboard. The first shoulder around 250 °C reveals the degradation of the lignocellulosic compounds (Grammelis et al., 2009). The final section under reducing condition shows above 400- 450 °C corresponds to the degradation of lignin (Grammelis et al., 2009). However, the sudden weight loss observed in paper sample at 653 °C can be explained by thermal degradation of $CaCO_3$, widely used in the paper manufacturing process as an inorganic filler (Cozzani, Petarca & Tognotti, 1995).

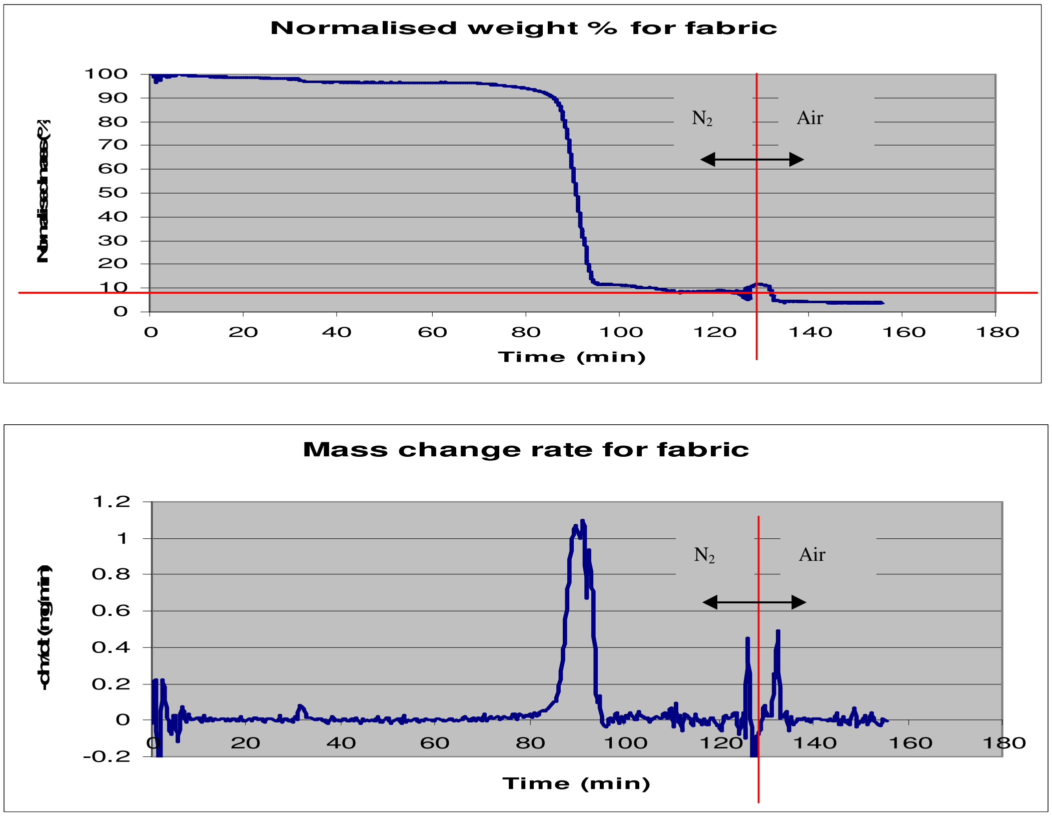


Figure 5.12: Mass loss curve and time derivative for fabric

A little moisture content (3.2%) could be observed (Figure 5.12). A major weight loss around 82.5% is noted for fabric in the temperature range of 282- 430 °C. The graph shown in the Appendix 3 shows 3 peaks under reducing condition at the temperatures around 391, 406 and 421 °C. Miranda et al. (2007) has reported 3 stages for textile waste pyrolysis which are in the temperature ranges in 115-284 °C, 284-390 °C, 395-474 °C with corresponding peaks at 264 °C, 374 °C and 433 °C. However, the degradation of waste textile which might have been associated with contaminants can be slightly differed from normal fabric decomposition. Also some peaks might have been overlapped and are not clearly separated under applied heating rate. The degradation below 380 °C could be associated with decomposition of the hemicellulose and cellulose or with different processes of cellulose decomposition. According to the literature, the main, fast and significant weight loss occurs in the temperature range of 300-380 °C and in this region, pyrolysis takes place in crystalline regions of cellulose fibres. The gentle decrease of weight after 430 °C is defined as pyrolitic char formation of fabric sample. During this stage, dehydration and decarboxylation occurs, releasing water and carbon dioxide and produces double bond, carboxyl and carbonyl products as the main products (Miranda et al., 2007). A reasonable explanation can not be given for the sudden increase of mass around 750 °C and it might be due to a malfunction of the instrument.

Table 5.3: Proximate analysis of tested materials

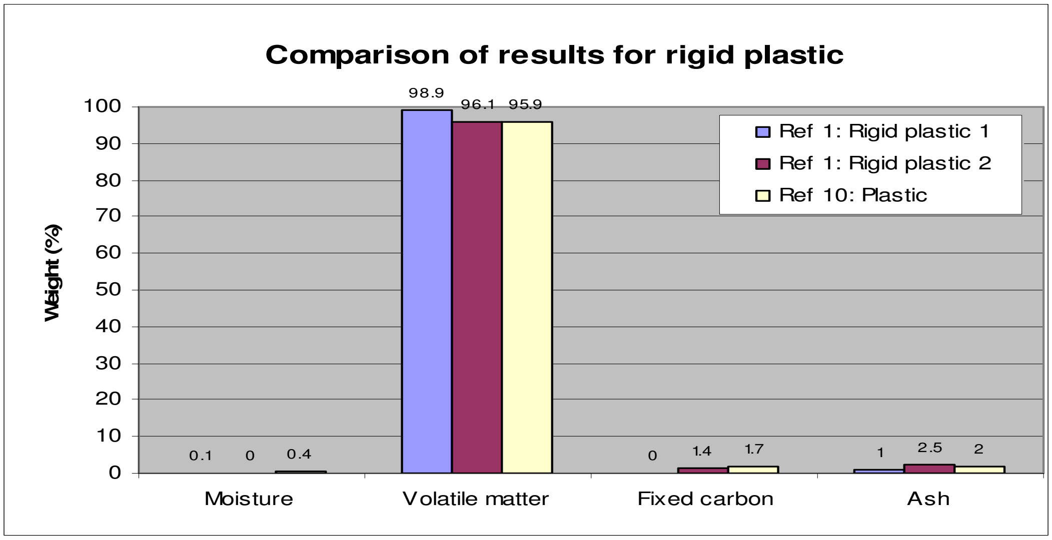
Material	Moisture (wt %)	Volatile matter (wt %)	Fixed carbon (wt %)	Ash (wt %)	**Total**
Rigid plastic 1	0.1	98.9	0.0	1.0	**100**
Rigid plastic 2	0.0	96.1	1.4	2.5	**100**
LDPE	0.0	100.0	0.0	0.0	**100**
Polystyrene	0.6	99.4	0.0	0.0	**100**
Wood	8.4	69.1	21.7	0.8	**100**
Paper	1.6	65.6	18.4	14.4	**100**
Cardboard	4.2	71.0	9.8	15.0	**100**
Fabric	3.2	88.6	4.3	3.9	**100**

5.5 A comparison of proximate analysis with previous studies

The following figures present the proximate analysis done by several researchers and the experimental result taken from this present study is compared with them. The corresponding references are described in table 5.4.

Table 5.4: Corresponding references

Ref no.	Description
1	Present study
2	Miranda et al., 2007
3	Grammelis et al., 2009
4	Cozzani, Petarca & Tognotti, 1995
5	Reina, Velo & Puigjaner, 1998
6	Demirbas, 2004
7	Aboulkas et al., 2008
8	Zhou, Luo & Huang, 2009
9	Zhou et al., 2006
10	Tokheim, 1999



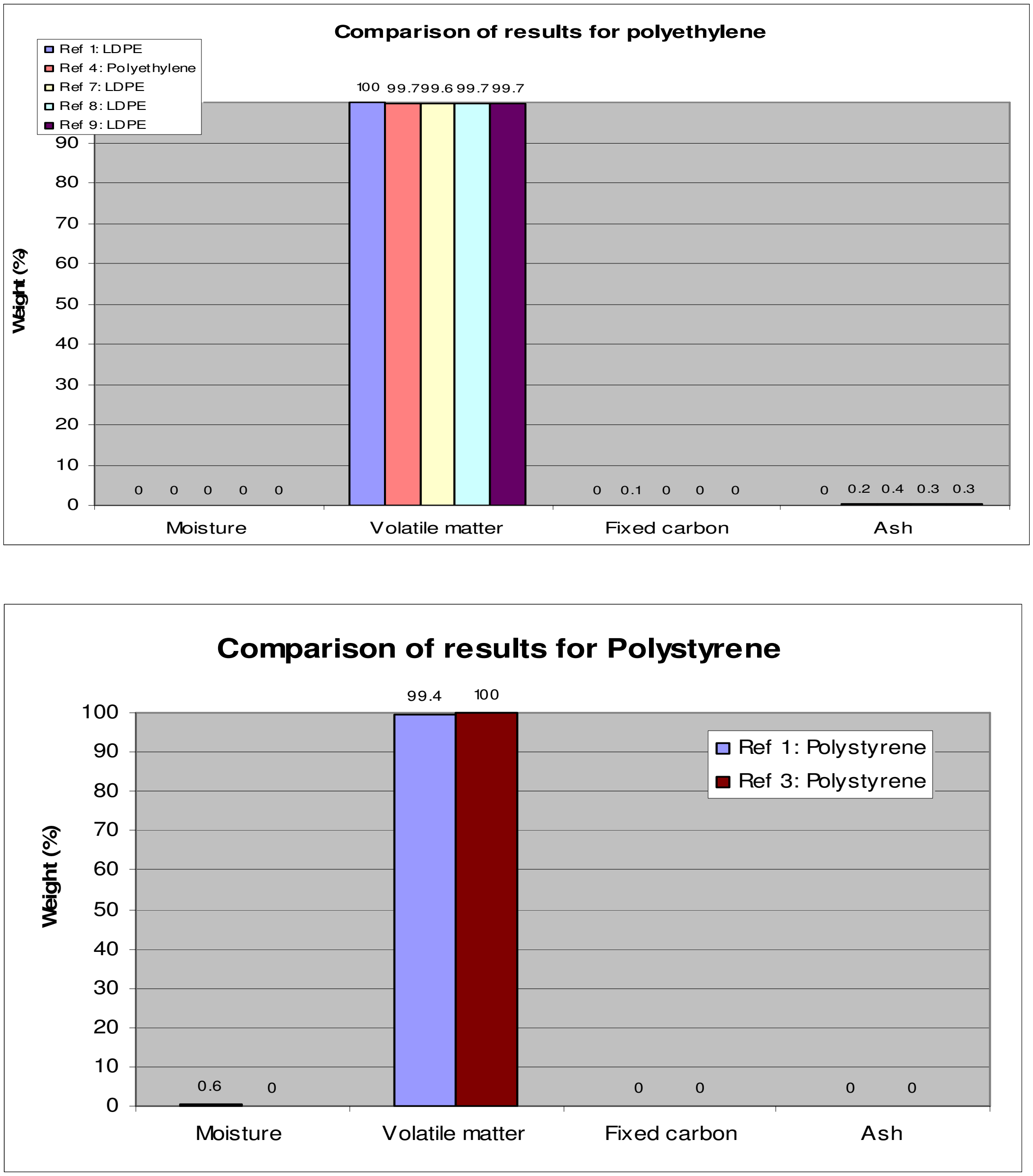


Figure 5.13: Comparison of results for plastic samples

The graphs of polyethylene and polystyrene reveal that the major constituent is volatile matter and almost similar results from literature could be observed (Figure 5.13). The analysis of rigid plastic 1 & 2 is compared with a mixture of plastic which contained polypropylene and polyethylene-terephthalate which should not necessarily be similar to our result since no any detailed information is known about the plastic category of rigid plastic 1 and 2.

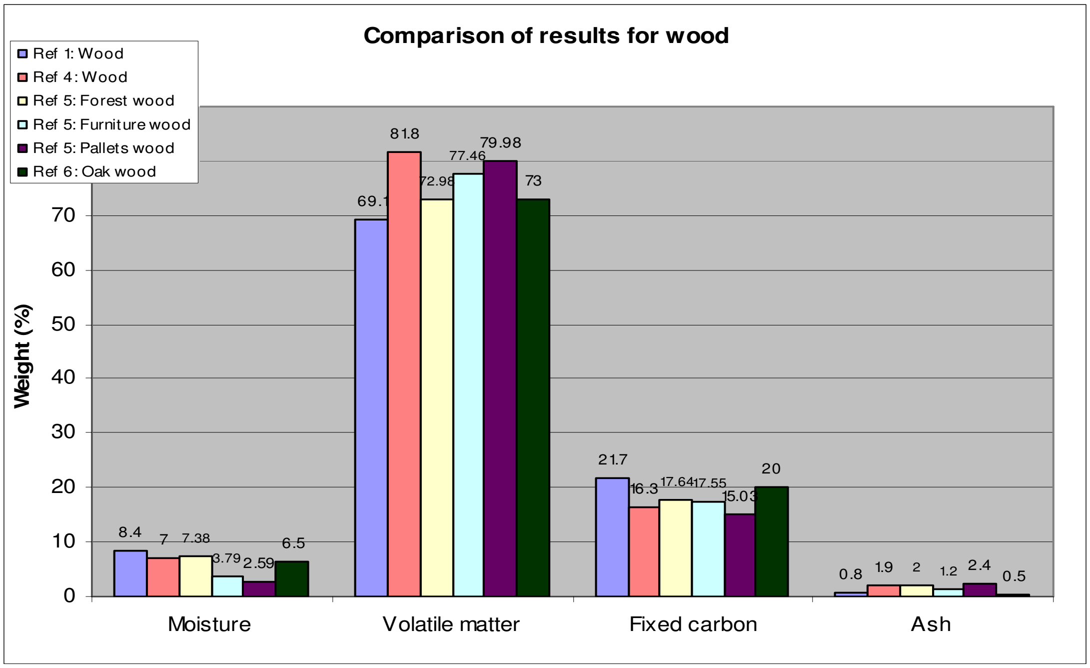
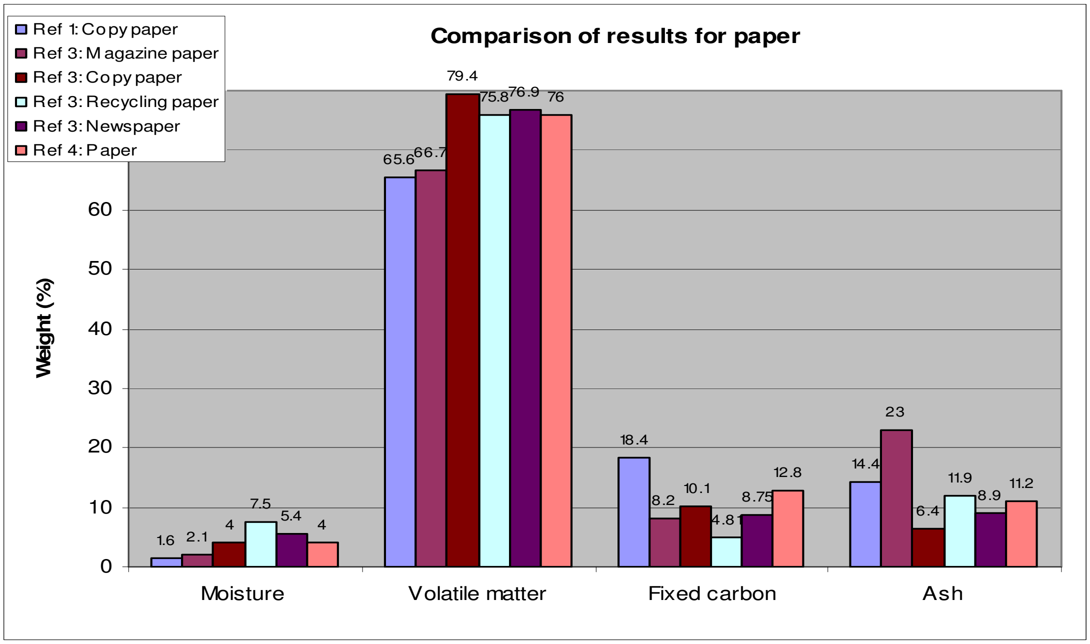


Figure 5.14: Comparison of results for wood

The figure 5.14 presents the comparison for wood. The previous studies have performed for different wood materials generated from different sources. It can be observed that the results of the analysis of wood sample is very much close with the results from oak wood. Since a cleaned wood sample used for present analysis, a reasonable agreement can be made, both wood materials are less contaminated compare to other samples. The other studies were carried out for waste or processed wood samples which might have been highly contaminated from dirt accompanied with other waste or additives used in wood processing. It is clearly proven by the ash fractions.



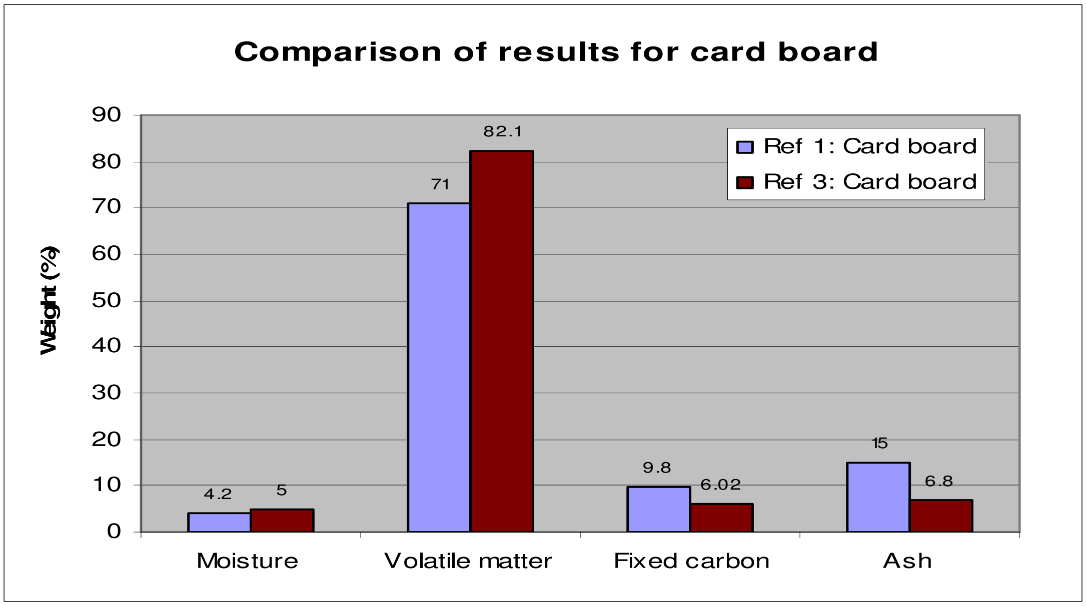


Figure 5.15: Comparison of results for paper and cardboard

The paper and cardboard are essentially wood based products which constitute with lingo cellulose materials. As shown in the figure 5.15, the copy paper tested by Grammelis et al. (2009) shows the highest volatile matter and the lowest inorganic content. In contrary, the present study for copy paper reveals lowest volatile and moisture and highest fixed carbon among the samples. Magazine paper has the highest ash content indicating poor contribution for better combustion.

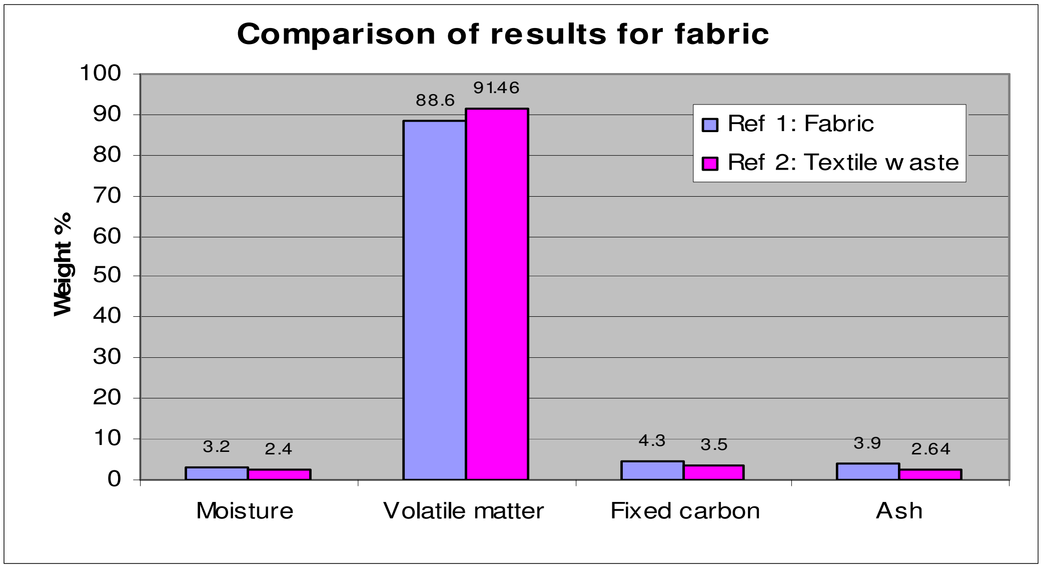


Figure 5.16: Comparison of results for fabric

Textiles may be either natural or synthetic fibres. Actual relative fractions of key components are somewhat uncertain, since it is not easy to find out to which of these components are attributed. If the pyrolysis behavior is similar to that of plastics, its major constituents are synthetic fibres. Otherwise it will be assimilated to that of cellulosic materials. In the present study, it can be concluded that it is not pure synthetic because of the considerable amount of fixed carbon and ash (Figure 5.16).

Generally, some differences in above graphs may be due to the material contamination level from the atmosphere and inaccuracy of numbers when reading the TGA graphs. Also it is difficult to make comparisons due to lack of information about the nature of the materials (the original source of the material, pretreatments done, level of contamination, etc) found in the literature.

5.6 Material characterization procedure using combined TGA/FTIR technique

Thermogravimetric Analysis (TGA) has proven to be a very useful technique for studying the thermal characteristic of a wide variety of solid and liquid samples. Basically, TGA measures sample weight as a function of temperature and it is useful in characterization and quantification of decomposition of the particular material of its decomposition steps. When TG analysis is coupled with evolved gas analysis, a great deal of additional information can be obtained as approach for solving specific analytical problems. As a method of evolved gas analysis (EGA), Fourier Transform Infra Red spectrometer (FTIR) is sensitive, fast, and can detect every type of molecule except homonuclear diatomics. The combination of the two techniques can give both qualitative and quantitative information about thermal decomposition and reaction mechanisms.

The following information is based on the TUC master project report, fall 2008 (Arvoh & Ariyaratne, 2008).

5.6.1 Procedure for gas bag transfer technique for evolved gas analysis

5.6.1.1 Apparatus and accessories

- TGA 7 instrument from Perkin-Elmer: Documentation 3.1.6 (Arvoh & Ariyaratne, 2008)

- Spectrum One FT-IR Spectrometer from Perkin-Elmer: Documentation 3.2.6 (Arvoh & Ariyaratne, 2008)
- Gas bags (Figure 5.17): Can be provided in different volumes according to the user requirement and these products can be taken from Atlantic Scientific Co. Inc and Calibrated Instruments Inc., USA. Because of the very low diffusion of the gas bags, the collected gas samples can be kept for a long time unless the gas bags are damaged
- Low diffusive tubes and connectors
- Syringe: 50-100 ml (according to the requirement)
- N_2 gas supply for cleaning

Figure 5.17: Gas bags (1.5L, 500 ml and 200 ml) supplier; Atlantic Scientific Co. Inc

5.6.1.2 Method

The sample should be prepared for the TGA experiment according to the physical nature of the material and requirements by the instrument. Then the steps are followed according to the description of the TGA user manual and the user's preference (e.g. the thermal programme can be defined by the user). Perhaps, the instrument should be cleaned and calibrated as described in user manual, before using (Haugen, 2009).

While carrying out the TGA experiment, the exhaust gas is collected for any period of time depending on the requirement by the user. It can either be collected through out the whole experiment or when undergoing oxidation or reducing conditions or when the maximum decomposition appears or when the graph starts to drop. It should be realised that this technique is not sophisticated enough for the continuous and dynamic analysis of evolved gas from the TGA. The exhaust gas is collected into cleaned-labelled gas bags via exhaust outlet of the TGA instrument (Figures 5.18 & 5.19). Prior to use, the gas bags should be cleaned as described in sub section 5.3.2 in the project report; Arvoh & Ariyaratne (2008). When collecting the exhaust, to avoid atmospheric contamination, it is better to fix the tube few seconds before of the collection. Then the gas bag should be connected to the tube and after that the valve of the bag should be opened. Similarly, when collection is completed, the valve of the gas bag should be closed before taken off. The collected exhaust sample is now ready for the analysis in FTIR spectrometer.

Figure 5.18: Exhaust outlet of TGA

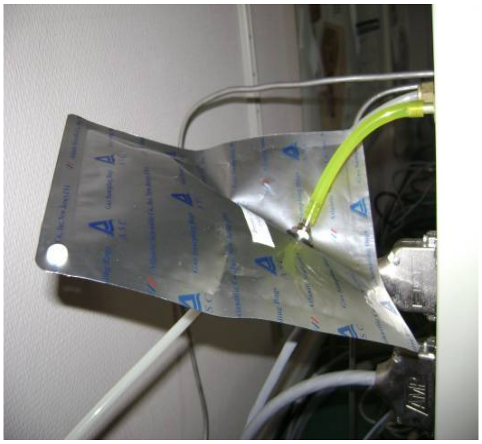


Figure 5.19: Exhaust collect in gas bags

Before the gas analysis, the FTIR spectrometer should be purged with pure nitrogen gas. There are two ports at the backside of the FTIR instrument while one for sample chamber purging and the other one for instrument purging to remove all the gases inside the instrument which can be detected by the beam when it passes through the instrument and possibly give wrong spectrum. Instrument is purged with nitrogen for 10 minutes before start the experiment. The gentle purging of sample chamber is continuing through out the experiment. The 10 cm gas cell is cleaned as described in sub section 5.3.3 (Arvoh & Ariyaratne, 2008) before the experiment. The special care is taken to switch off "CO_2/ Water compensation" option in the software, if CO_2 gas is going to be analysed. First the background spectrum should be taken either for evacuated gas cell or N_2 filled gas cell. Then the gas sample is filled into the 10 cm gas cell using a syringe with as less as possible contamination from the atmosphere (Figures 5.20 & 5.21). The experiment is carried out after entering the sample data, the number of scan, scan range, resolution. After having the spectrum for unknown sample, the qualitative analysis can be performed using reference spectra available in the software itself or from other literature and quantitative analysis can be carried out using Beer's law, only if the particular concentration level is less than 0.01 M and more over within other limitations of applying Beer's law (Skoog, Holler & Nieman, 1998). However, if the evolved gas is going to be analyzed quantitatively, volume fed to the gas cell should be known and calibration should be carried out for certain gases which are going to be analyzed quantitatively. The concentrations of certain gases inside the gas cell of the unknown sample can be read through calibration curves by considering the absorbance (corrected height) at particular wave lengths where calibration was carried out. It should be noted that the concentration read through the calibration curve is not the real concentration and it should be back calculated to find out the real concentration of the gas in unknown gas mixture assuming same temperature and pressure.

Figure 5.20: Gas taking from gas bags

Figure 5.21: Gas entering to the gas cell

5.6.1.3 Calibration of a certain gas for quantitative analysis

The calibration test is carried out using commercially available standard calibration gases which are having known composition. The 10 cm gas cell should be cleaned. The standard gas is analysed in the same way as the sample gas, but with known different volumes in several times to get the spectra for different concentrations. The method of calculating the concentrations for the calibration is presented in Appendix 4. The particular wave numbers which give the peaks for certain gases can be found from the Perkin-Elmer infra red bulletin (Zeller & Juszli, 1973). The absorbencies (corrected heights) of the peaks are recorded at certain wave lengths for several volumes. If it is complied with Beer's law the absorbance should be proportional to the concentration of the gas.

As an example, the figure 5.22 shows a part of a spectrum taken from exhaust gas analysis for diesel fuel combustion. The hypothetical figure 5.23 shows a calibration curve for CO_2 at 2361 cm^{-1} and both figures show how to interpret the CO_2 concentration inside the gas cell for diesel exhaust gas.

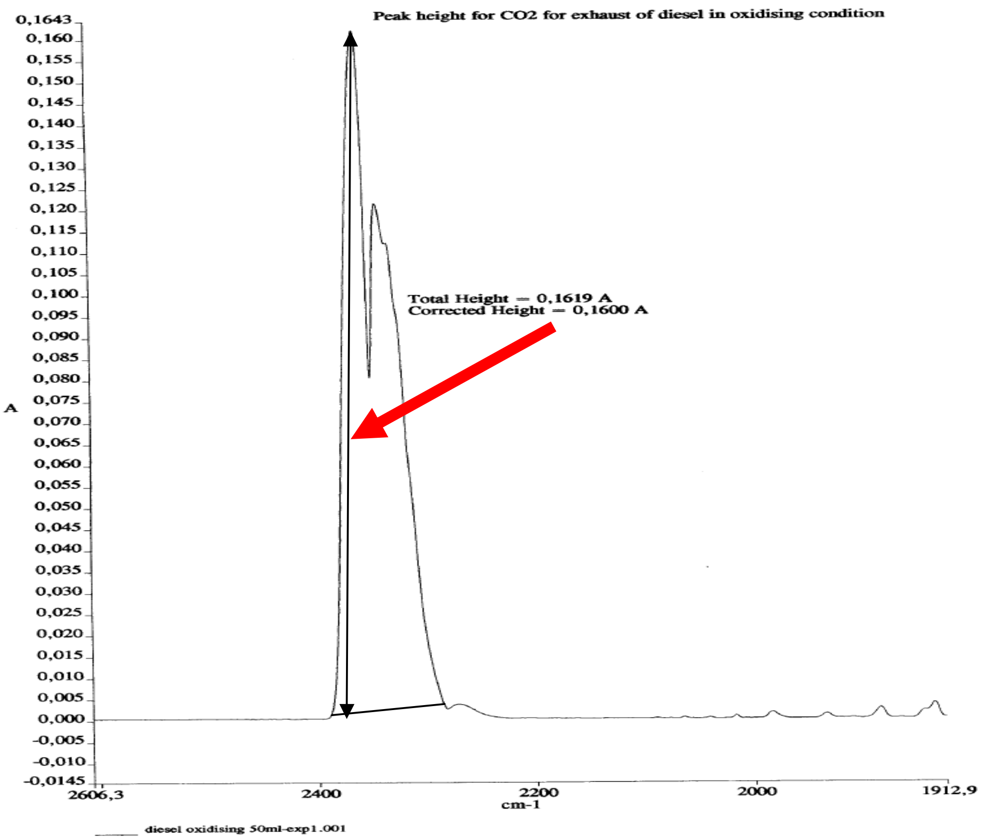


Figure 5.22: Part of spectrum for the exhaust gas form diesel combustion

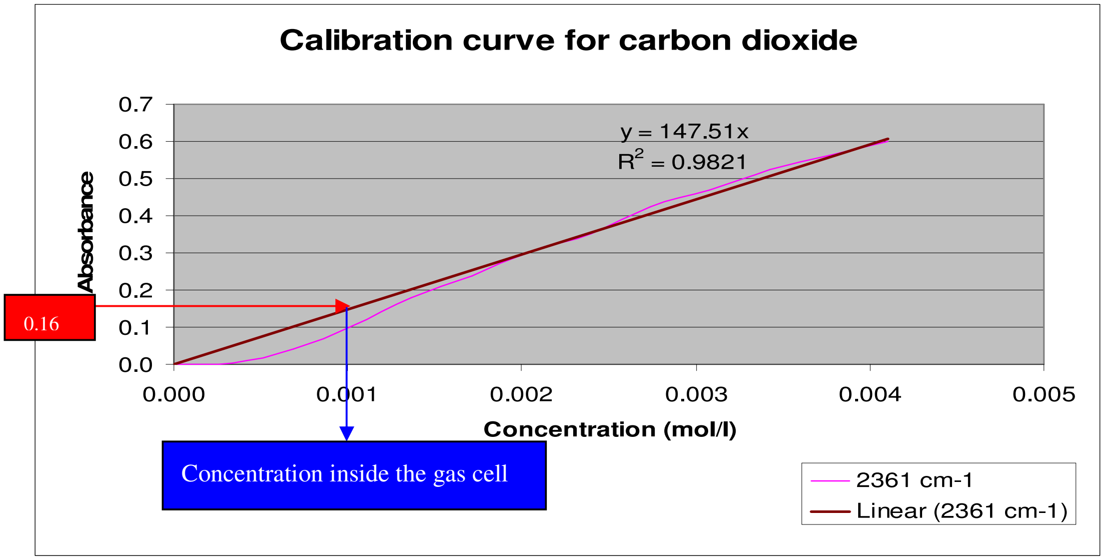


Figure 5.23: Hypothetical curve for CO_2 calibration and quantitative analysis of CO_2

6 Full scale combustion experiments

6.1 Introduction

As a recent improvement of alternative fuel system at Norcem-Brevik, a new Pfister system has been installed for feeding alternative solid fuels to the main burner. Norcem-Brevik has a long term strategic plan for increasing alternative fuel consumption at main burner replacing fossil fuels. Finding the optimum mixture of shredded plastic, animal meal and solid hazardous waste is the major challenge related to this improvement. To achieve this target, it is better to analyse the combustion and process characteristics with pure materials rather than a fuel mixture at once. Therefore, the capacity tests will be carried out in step wise and different characteristics will be analysed in each case with pure shredded plastic, pure animal meal, pure solid hazardous waste and next with a mixture of those materials. The optimization is considered in following areas.

- Maximize the alternative fuel usage – maximizing the revenue receiving for waste disposal
- Optimize of kiln system itself - avoiding operational issues
- Reduce emissions – to comply with environmental regulations
- Reduce CO_2 emissions – earn revenue from carbon trading
- Improve product quality – keep the product quality in the highest level
- Improve the feeding capacity of dosing systems – overcome restrictions with storage, discharge, conveying and dosing capacities

Two or three new reception bins will be constructed at the plant site and the Sicon 1 would be extended for new bins. The material would be fed to Sicon 1 through hoppers and weighing systems such that the feeding of one fuel followed by another fuel to have evenly distributed fuel mix (Equipment lay out is shown in Appendix 5).

Since Norcem-Brevik is already using the new Pfister feeder system with animal meal, this test would focus on carrying out animal meal capacity test of the new Pfister feeding system. In the present study, the optimization will be focused on the areas of maximization of alternative fuel usage with optimum kiln operation while keeping the product quality in a higher level. The emission reductions and the feeding system improvements will be investigated in future. Also, in the future, the similar optimization strategy will be followed for the above mentioned other fuel types.

6.2 Objectives

The purpose of the test is to find out the maximum possible feed rate of animal meal at the main burner using the Pfister feeder system. The effects on the process and on the clinker will also be analysed.

6.3 Test plan

The animal meal was fed to the main burner through Pfister feeder system as described in sub chapter 3.5.2. The clinker type produced was OPC (standard). The energy needed for the kiln was supplied through animal meal and the rest via coal. Very little amount of LHW and waste oil was used in addition to above fuel. The conditions at precalciner and kiln were almost kept stable through out the experiment. The total feed rate of RDF/SHW in the calciner and the average secondary coal feed rate were almost kept constant during the test around 15 t/hr and 3 t/hr respectively. The raw meal feed rate was 110 t/hr in each string and then it was totally 220 t/hr raw meal feed rate in both strings. However, total raw meal feed rate was reduced by 10 t/hr at 20.30; since the free lime content was started to going up than maximum limit with 7 t/hr of animal meal feeding. As a rule of thumb, the total clinker production rate could be calculated by dividing the total raw meal feed rate by a factor of 1.61 and it is around 137 t/hr.

The average process data was collected through PHD system in one minute interval during whole experiment. In addition to that, the clinker quality data was collected from the laboratory at Norcem. Among them, major emphasis was given for free lime content and P_2O_5 content of the clinker since those are the most critical parameters to sense the quality of clinker and the effect of phosphorous comes from animal meal. The oxides and P_2O_5 of clinker were analysed in 2 hrs interval and free lime and SO_3 content were analysed in 1 hr interval. The clinker samples were collected from the conveying belt after the cooler (Figure 6.1).

Figure 6.1: Clinker sampling

When it comes for the time of animal meal feed increment, the clinker sample was collected just before the increment taken place. Typically, the hot meal is analysed for SO_3, Cl content and degree of calcination once per day and in the present study it was collected only at 2.30 on 23/04/2009 and at 00.30 on 24/04/2009 but not during the testing period.

The following table indicates the test schedule.

Table 6.1: Test schedule

Date	Time interval	Animal meal feed rate (t/hr)	Coal feed rate at primary burner (t/hr)
23/04/2009	10.00-11.00	0	7.8
23/04/2009	11.00-13.00	2	6.5
23/04/2009	13.00-15.00	4	5.0-5.5
23/04/2009	15.00-17.00	5	4.2-4.3
23/04/2009	17.00-19.00	6	3.6
23/04/2009	19.00-21.00	7	3.0-3.4

6.4 Results and discussion

The thermal energy consumption in each step of animal meal feeding was calculated (Table 6.3) using average process data and average calorific values of the fuels (Table 6.2).

Table 6.2: The average heating values of fuels

Fuel	Heating value (kcal/kg)
Waste oil	9500
RDF	3446
SHW	3727
LHW	3956
Animal meal	4423
Coal	6689

Table 6.3: Thermal energy consumption

Time period	10.00-11.00	11.00-13.00	13.00-15.00	15.00-17.00	17.00-19.00	19.00-21.00
Thermal energy usage (kcal/kg clinker)	925	940	935	920	930	937
Thermal energy usage calciner (kcal/kg clinker)	543	554	544	550	560	545
Thermal energy usage calciner (%)	59	59	58	60	60	58
Thermal energy usage alternative fuels (kcal/kg clinker)	409	473	537	570	602	641
Thermal energy usage alternative fuels (%)	44	50	57	62	65	68
Thermal energy usage alternative fuels in calciner (%)	75	74	75	74	73	76

It can be seen that the specific thermal energy consumption is in the range of 920-940 kcal/kg clinker which is considerably higher than typical value (830 kcal/kg clinker). Total and alternative energy consumption at the precalciner is more or less constant which is a good indication of stable calciner operation. It is promising that the total alternative fuel contribution, 68% has been achieved at the final stage of the test, however it will be further analysed with process and laboratory data in following sections.

6.4.1 Laboratory analyses

In this sub chapter, the results of hot meal and clinker quality are discussed. The oxides of clinker were analysed in once per two hour, and the free lime, SO_3 and P_2O_5 content were analysed in once per hour. The hot meal quality was not analysed during the test, however the results which were taken after 4 hrs of the test is discussed here (since all SO_3 and Cl might not be flushed out for some hours after the test).

6.4.1.1 Hot meal (pre-calcined meal) properties

Table 6.4: The properties of hot meal before and after the test

	23/04/2009; 2.30	24/04/2009; 00.30
The degree of calcination (%)	98.9	96.1
SO_3 % in hot meal (%)	2.45	2.86
Chloride content of hot meal (%)	1.31	1.41

The figure 6.2 (which is also described in sub chapter 3.4) shows no any significant difference of SO_3 and Cl content for the hot meal before and after the test. If it is in the region of heavy coating (either high Cl or high SO_3 concentration), then the meal gets more sticky and gives melting problems inside the kiln causing operational and process issues. Here, it could be observed that the point is rather close to the limit of acceptable coating in both cases. However, these results are not decisive without the analyses during the test.

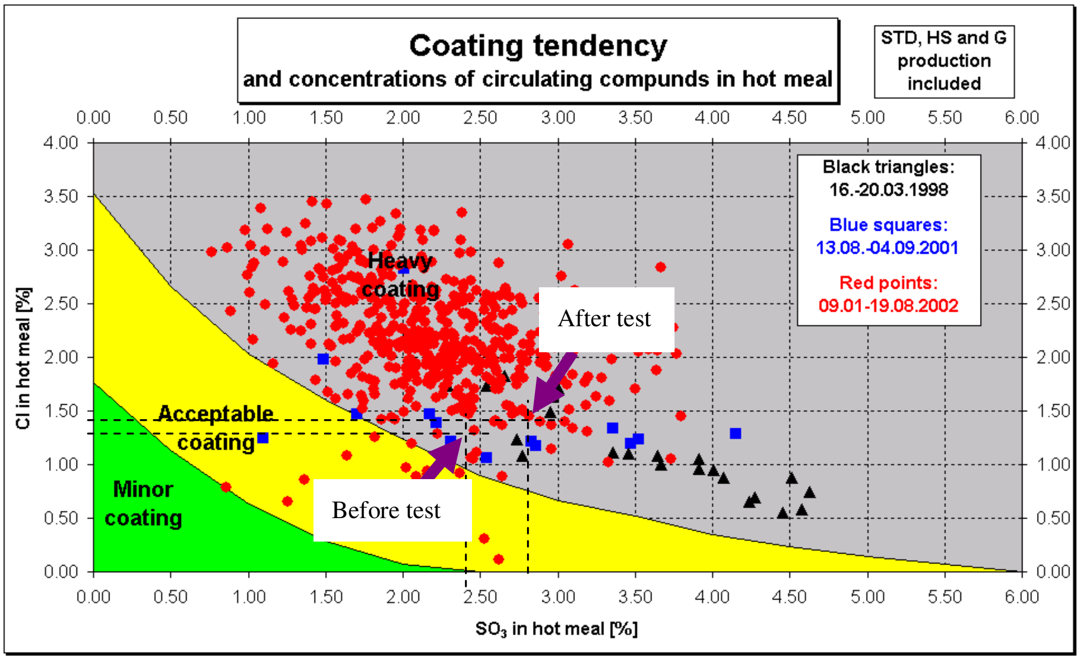


Figure 6.2: Hot meal quality with SO_3 and Cl content

6.4.1.2 Clinker properties

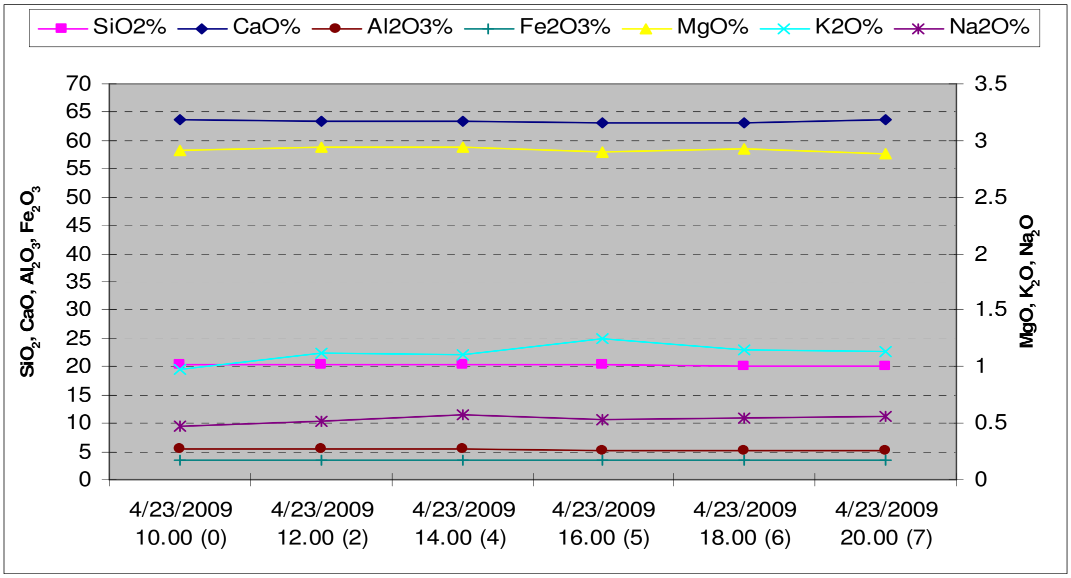


Figure 6.3: Oxides in clinker

Table 6.5: Comparison of oxide levels with typical values

Oxide	Typical value (%)	Present test (%)
CaO	66	63-64
SiO_2	21	20.0-20.5
Al_2O_3	5	5.0-5.5
Fe_2O_3	3	3-4
Other	5	4-6

The typical values for the oxides are taken from Tokheim (1999). It could be observed that there is no any significant difference of the oxide levels between typical values and values obtained from the test (Table 6.5).

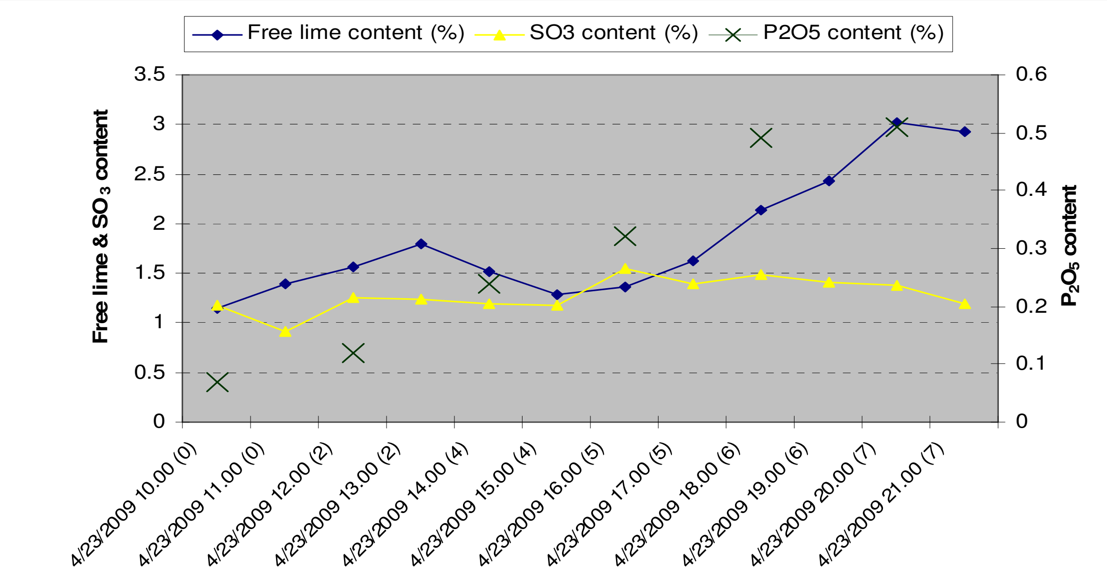


Figure 6.4: The free lime, SO_3 and P_2O_5 content of the clinker

Though there is no certain recommended limitation for P_2O_5 content in the clinker, the typical maximum limit is considered as 2%, higher values may give concrete expansions when the product is used. Even though animal meal has high phosphorous content compared to other fuel types, the P_2O_5 in the clinker is still acceptable with even the maximum feeding rate of 7 t/hr.

The SO_3 content is also in an acceptable range (less than 1.5%) for a standard clinker.

The main issue indicates here is the increasing of free lime content with increments of animal meal feeding. When the animal meal feeding rate is 6 t/hr in moderate clinker production rate (220 t/hr raw meal feed rate), the free lime content is slightly less than the maximum allowable limit, 2.5%. It is even higher (3%) when the animal meal feed rate is 7 t/hr, in fact the final slight decrement of free lime shown in the figure 6.4 (however, it is still above the recommended limit) is due to reduction of raw meal feed rate by 10 t/hr (i.e. raw meal feed rate is 210 t/hr) in the last half an hour (20.30-21.00) of the test. Therefore, it can be concluded that even with low clinker production rate, 7 t/hr animal meal feeding is not appreciable. The very high free lime content reveals improper burning of raw meal and bad quality of clinker. The one possible reason for increasing of free lime content with animal meal feeding is the introduction of extra calcium at the kiln outlet via a high calcium phosphate content in animal meal and then might accumulate and add to the clinker without proper burning since that calcium does not have enough residence time for complete reaction at kiln outlet.

This is further evaluated based on theoretical aspects. Respectively, the figures 6.5 and 6.6 indicate the maximum theoretical free lime content that could be added to the clinker via animal meal feed and the resulting total CaO in the clinker. It should be noted that the theoretical calculation was carried out only considering the reaction mechanisms behind the clinker production and it was assumed that all the CaO comes via animal meal ends up as free lime. The following information was considered for the theoretical calculations.

Clinker production rate: 137 t/hr

Ash added to the clinker via animal meal: 25%

The CaO content in ash of animal meal: 50%

Reference free lime: 1.27% (i.e. the average free lime content with 0 t/hr of animal meal feeding in the test)

Reference total CaO: 64% (i.e. the total CaO taken from oxides analysis of the clinker with 0 t/hr animal meal feed in the test)

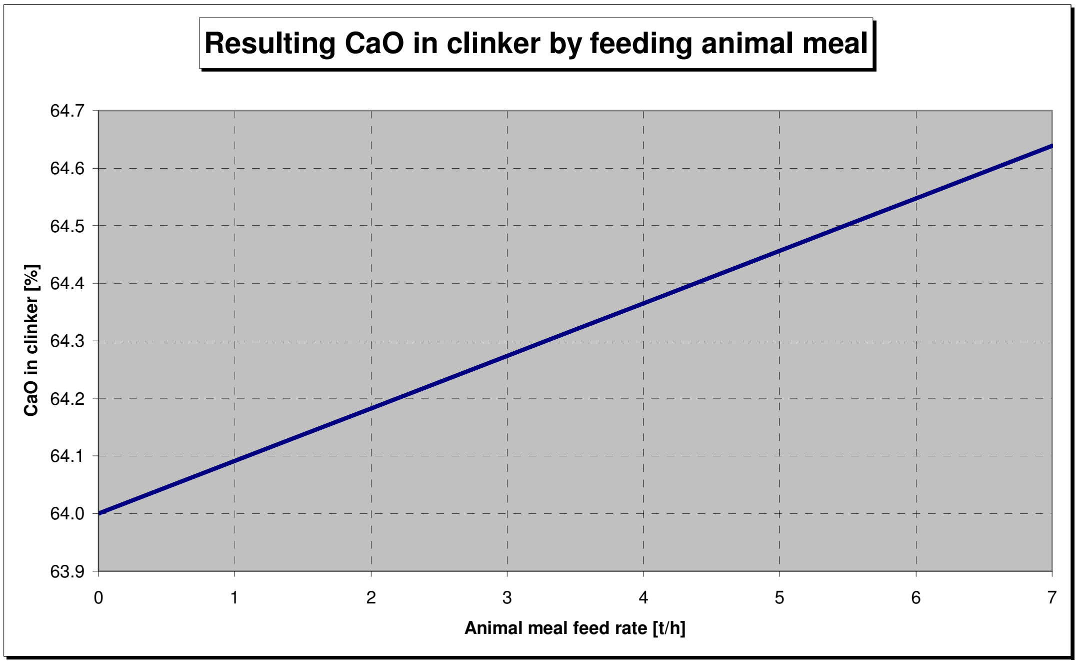


Figure 6.5: Resulting CaO in clinker by feeding animal meal

It could be observed that the total CaO content in the clinker has been only increased by 0.65% when the animal meal feed rate is in maximum level, 7 t/hr (Figure 6.5).

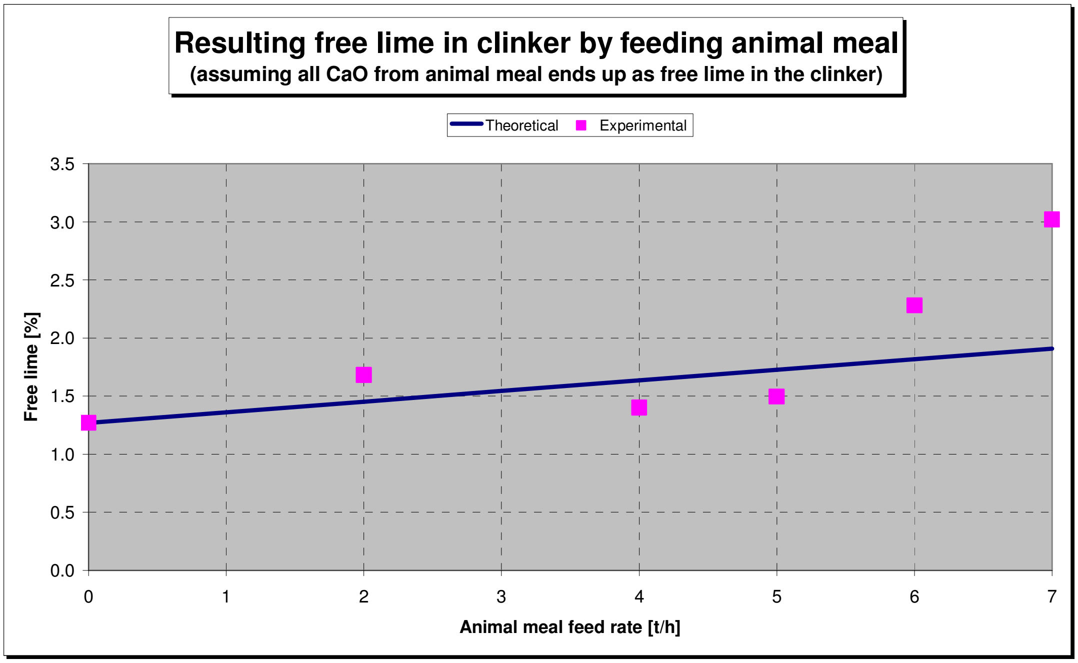


Figure 6.6: Resulting free lime in clinker by feeding animal meal

The results shown in figure 6.6 indicate that when animal meal feed is in higher rate, the experimental free lime content is higher than the maximum theoretical values which were estimated based on chemistry behind clinker reactions. Theoretically, this reason could contribute only around 37% for the increase of free lime content due to animal meal feeding at 7 t/hr. Therefore, there should be other phenomena which cause 67% of the increased free lime content at 7 t/hr animal meal feeding.

The other possibility can be described as the increase of alternative fuel consumption at main burner, which might reduce the flame temperature due to lower calorific value compared to coal and hence reduce proper burnability.

However, it should be pointed out that if the relatively short residence time of the animal meal in the kiln proves to be not a limiting factor for complete reactions to occur, the introduction of CaO via animal meal feeding could be an extra benefit in clinker production, since it must reduce the demand for high grade limestone in the production process.

6.4.2 Process data

Although the following graphs show the process data from 2.30 in the same day, the test was formally started at 10 o’clock due to emergency shut down of the kiln around 8 o’clock. However, by the time of 10 o’clock the stable operation had been achieved in the kiln and the calciner.

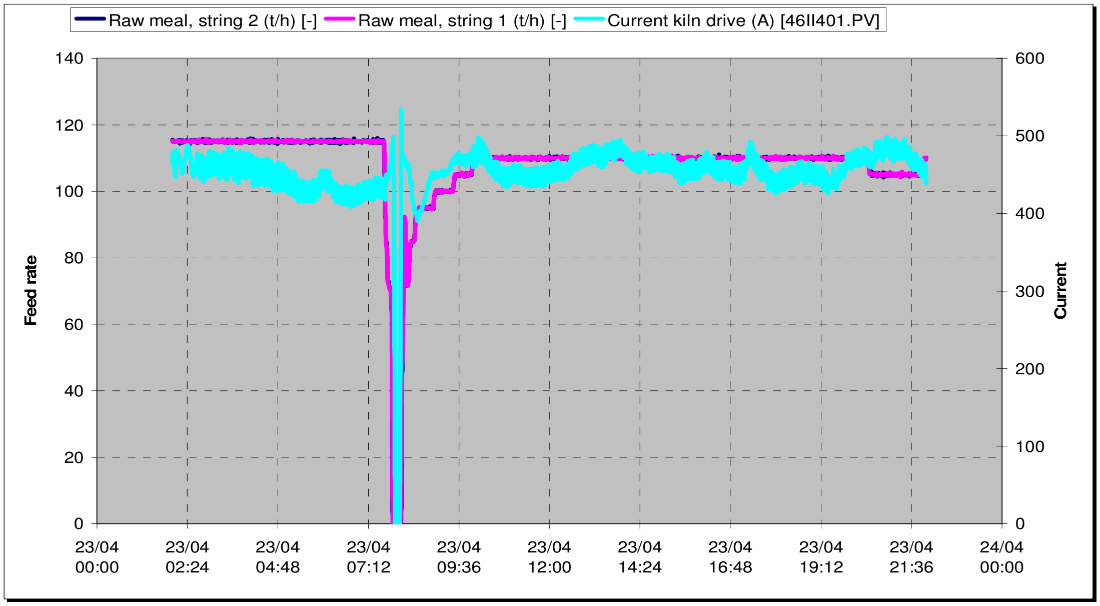


Figure 6.7: Raw meal feed rate and current of kiln drive

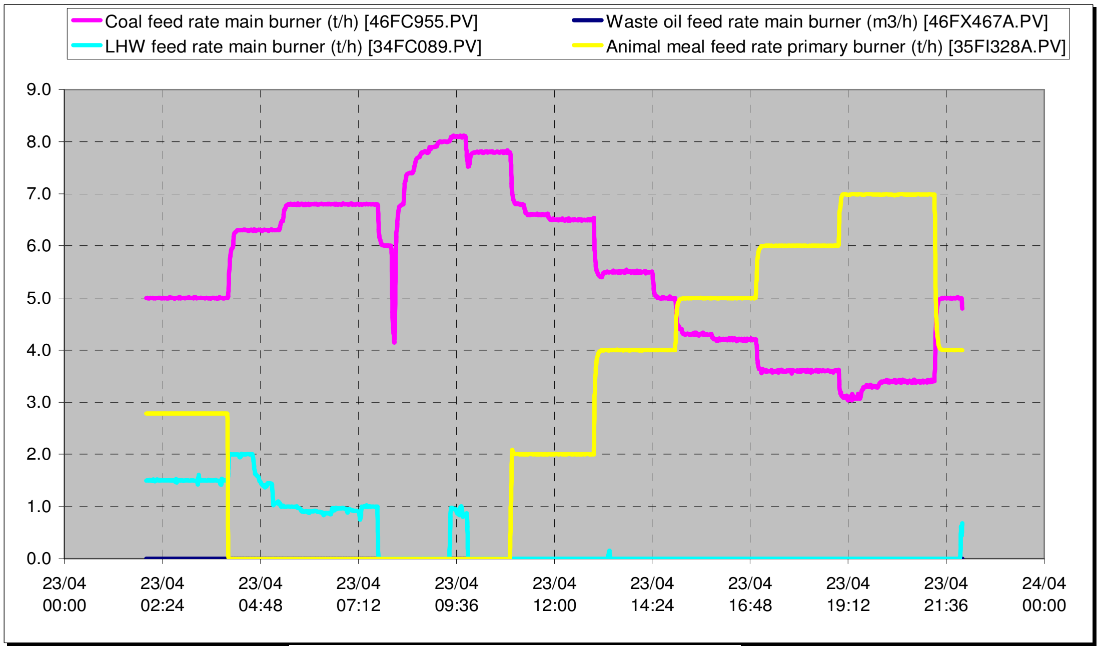


Figure 6.8: Primary fuel supply

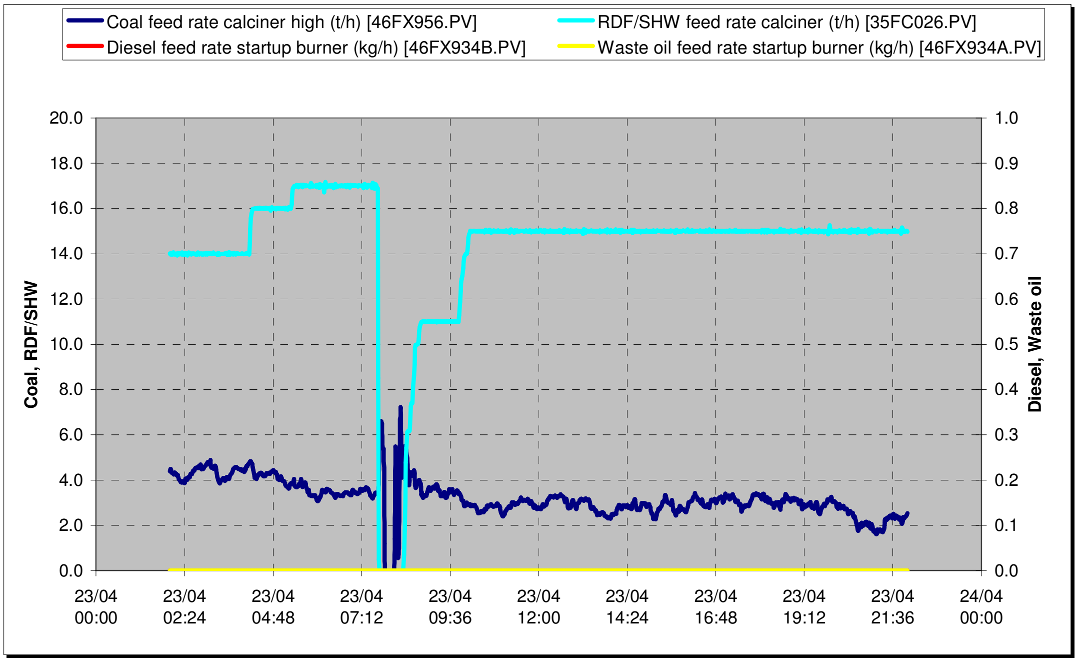


Figure 6.9: Secondary fuel supply

The raw meal feed rate is in a moderate level (110 t/hr in each string) during the experiment, however it is in low level (105 t/hr in each string) during the last half an hour to keep free lime content in required range with 7 t/hr animal meal feeding.

Kiln current drive shows typical range for smooth operation (400-500 A) for OPC type cement (Figure 6.7). The high value of kiln current poses more power requirement for the rotation of the kiln, because of properly melted clinker is attached to the kiln wall, hence better heat transfer.

The main burner is fed with increments of animal meal and decrements of coal proportionately (Figure 6.8). Waste oil has been used only for the start up.

The figure 6.9 shows a low rate of RDF/SHW feeding (15 t/hr) compared to typical rate (20-25 t/hr) and it might be due to the requirement of maintaining the smooth operation of calciner after the kiln shut down. However, the almost constant values of secondary coal feed rate (3 t/hr) and alternative fuel feed rate at calciner reveal stable operation of the calciner through out the experiment.

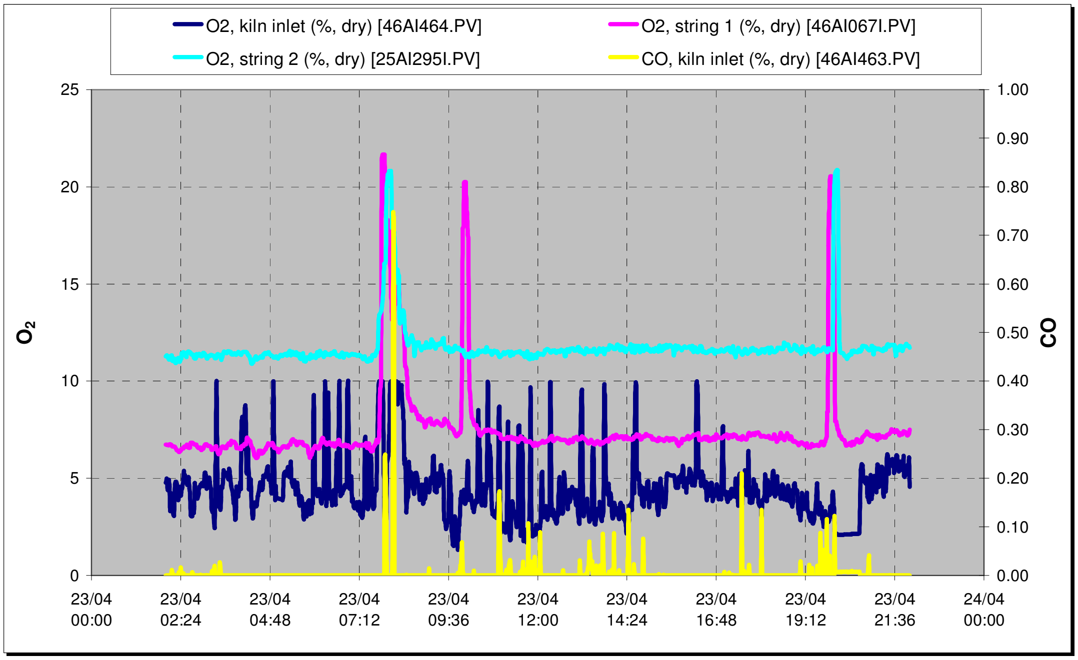


Figure 6.10: O_2 and CO concentrations

The typical O_2 concentration maintained in the kiln inlet is 3-4% (dry basis). The sudden peaks observed in the graph of O_2 (kiln inlet) in figure 6.10 are due to turbulent condition near by the sensor probe.

The O_2, string 1 and 2 are measured from the each stack after bag filter. Typically the O_2 concentration in string 2 is higher than string 1, since the gas stream in string 2 passes additional equipments (raw meal mill and extra ESP) allowing to add more air to the gas stream on the way of final emission.

A too high CO content in the kiln gas can be recognised by a brownish colour and it reveals bad quality of clinker due to incomplete solid reactions inside the kiln. Typically the CO concentration should be 0% at the kiln inlet but up to 0.1% is acceptable. It could be observed that the higher O_2 concentration at the kiln inlet causes less CO production, which is generally an obvious fact. In fact, the result shown in the figure 6.10 reveals the acceptable CO at kiln inlet.

The O_2 after ESP in string 2 (8%, dry) and O_2 before ESP in string 1 (9%, dry) are also quite typical for kiln 6 at Norcem-Brevik, but those are on the high side (Figure 6.11). However, it is far better when these values are low as possible, otherwise it will reduce the effectiveness of fans due to more energy consumption for removal of false air which is not the desired purpose of the fans.

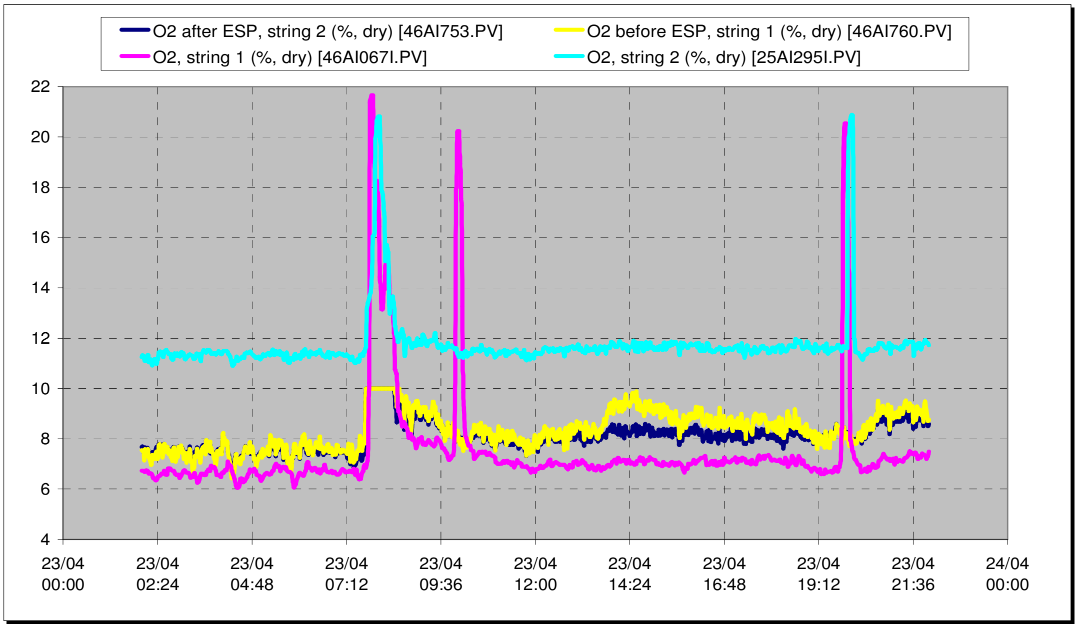


Figure 6.11: O_2 concentrations

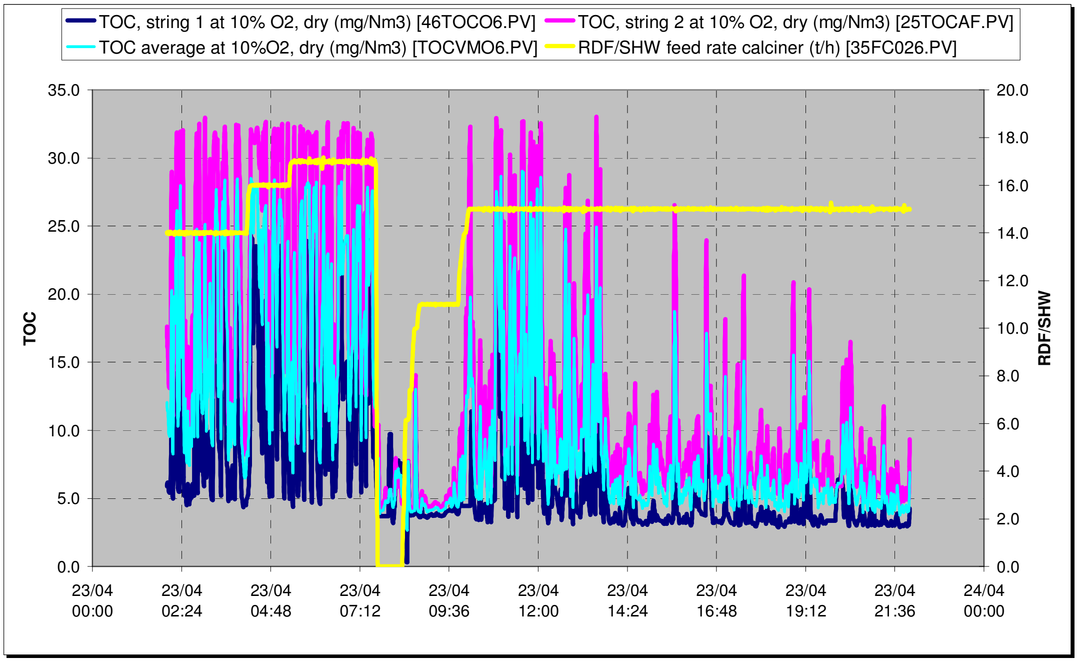


Figure 6.12: TOC and RDF/SHW feed rate

The allowable limit for the emission of TOC is 10 mg/Nm^3 at the reference O_2 10% (dry). In the present study, the average TOC in string 1 and 2 is around 5 mg/Nm^3 at reference condition; in fact the TOC at string 2 is slightly higher than string 1 (Figure 6.12). However, the lower rate of secondary alternative fuel feeding might have influenced for very low TOC emission.

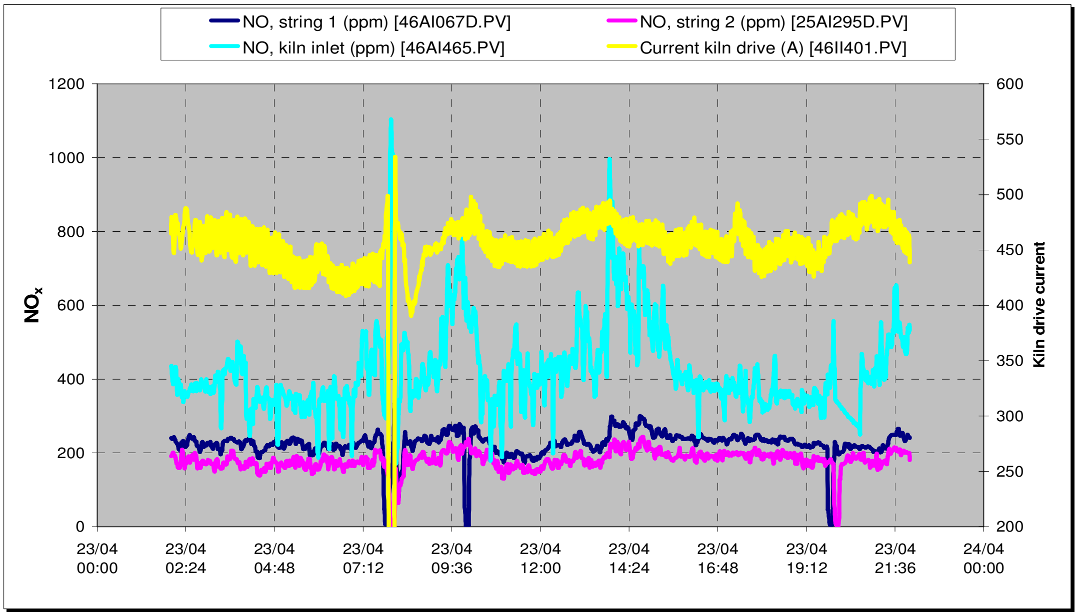


Figure 6.13: NO_x emission in real situation

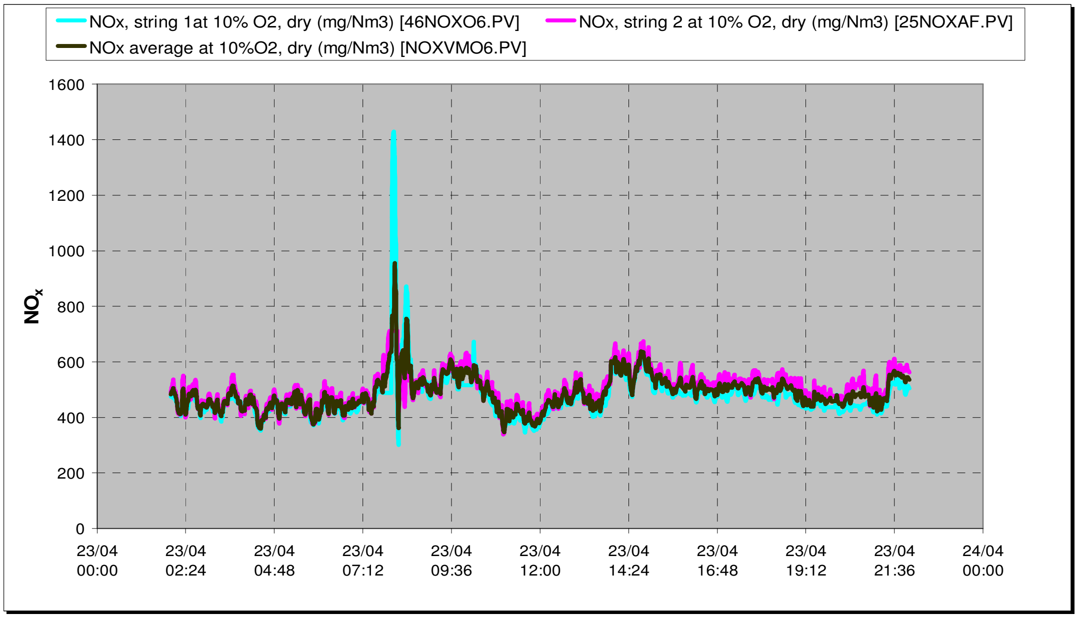


Figure 6.14: NO_x emission in reference condition

The plots of NO_x at kiln inlet and current kiln drive follow the same shape, conforming that the increase of temperature at the kiln inlet increases the current kiln drive. And also the high temperature at kiln inlet increases the thermal NO_x production as well. Also, the higher level of NO_x at kiln inlet where the temperature is very high compare to NO_x in strings where the temperature is low, verifies the effect of temperature for NO_x production (Figure 6.13).

However, the average NO_x emissions (500 mg/Nm^3 at reference condition, figure 6.14) are considerably lower than the allowable limit which is 800 mg/Nm^3 at the reference O_2 10% (dry).

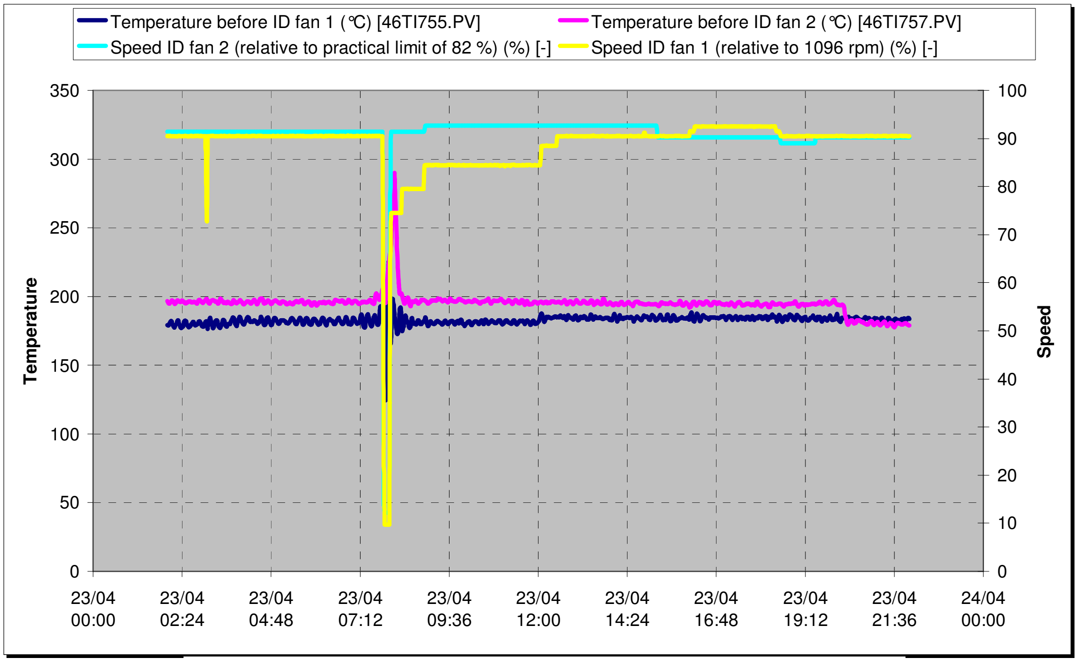


Figure 6.15: The temperature and speed of ID fans

The ID fan 1 and 2 are located in between conditioning tower and ESP in string 1 and 2 respectively. The temperature of gas stream before ID fan is typically around 180-200 °C, however it depends on the type of raw meal used. This temperature measurement controls the water flow inside the conditioning tower.

The ID fans typically operate around 90% of full capacity and similar operation could be observed here (Figure 6.15). Though more gas could be pulled out with high speed operation of fans, there is a risk that also the false air in leakage will increase, which could reduce the effectiveness of the fans. Also the fan bearings could be heated up and damaged easily when running in high speeds specially in summer time.

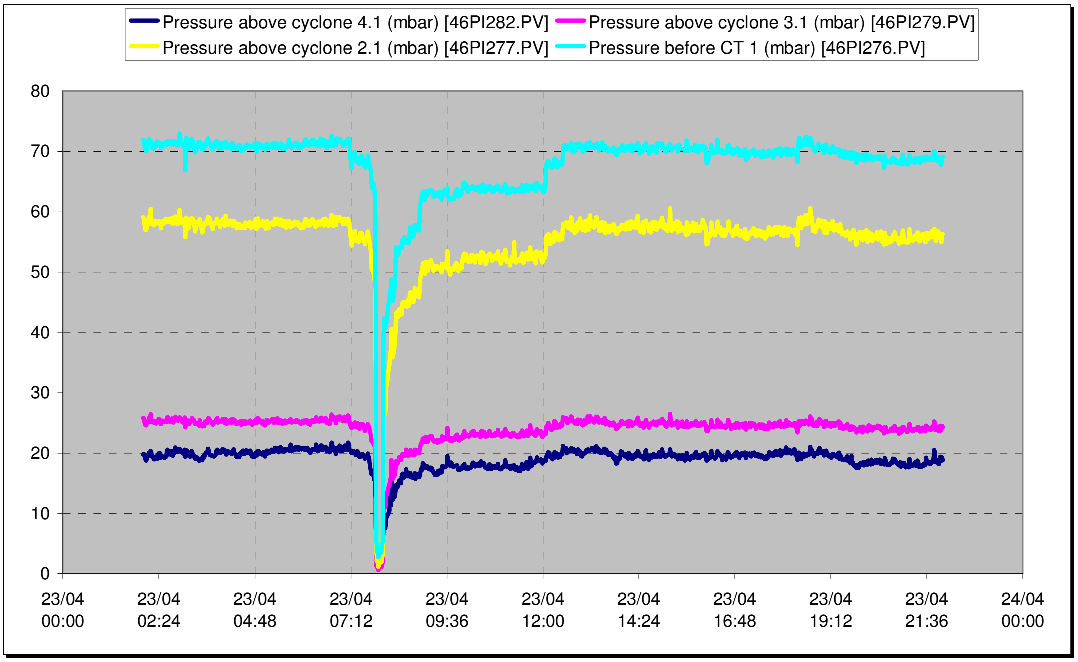


Figure 6.16: The pressure above cyclones in string 1

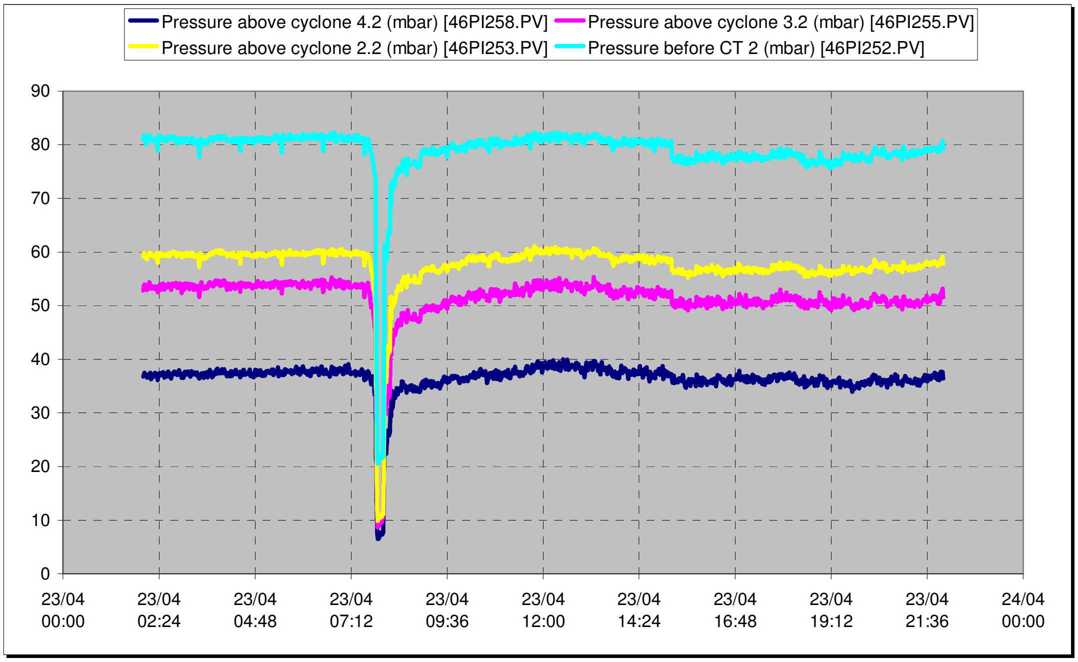


Figure 6.17: The pressure above cyclones in string 2

The pressure drop in string 2 is generally high, since the dimensions are smaller in tower 2 than tower 1.

Table 6.6: Comparison of pressures with typical values

Above cyclone	Typical value in string 1 (mbar)	Figure 6.16 (mbar)	Typical value in string 2 (mbar)	Figure 6.17 (mbar)
1	70-80	70	80-90	80
2	50-60	58	65-75	58
3	40	25	50	50
4	25-30	20	30-40	35

It could be observed that the measurements relevant to 3.1 and 2.2 are not acceptable. This deviation might be due to the sensor contamination with dust particles in those locations.

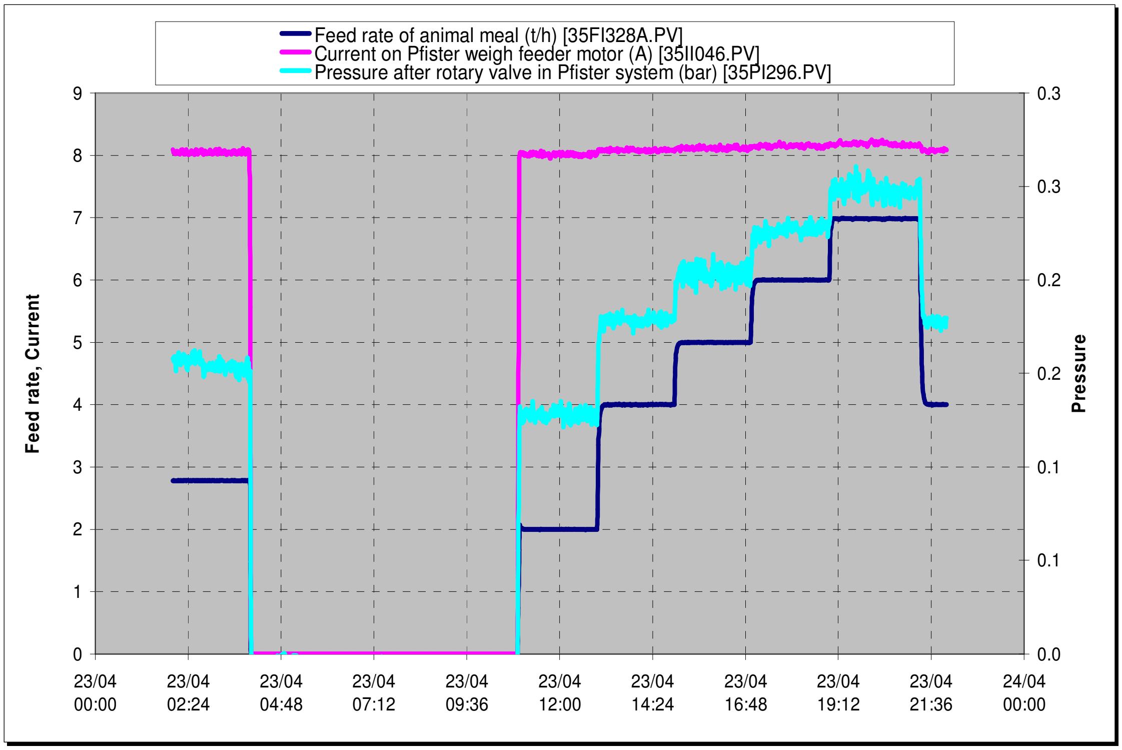


Figure 6.18: Current of Pfister weighfeeder and pressure variation after rotary valve with increase of animal meal feeding

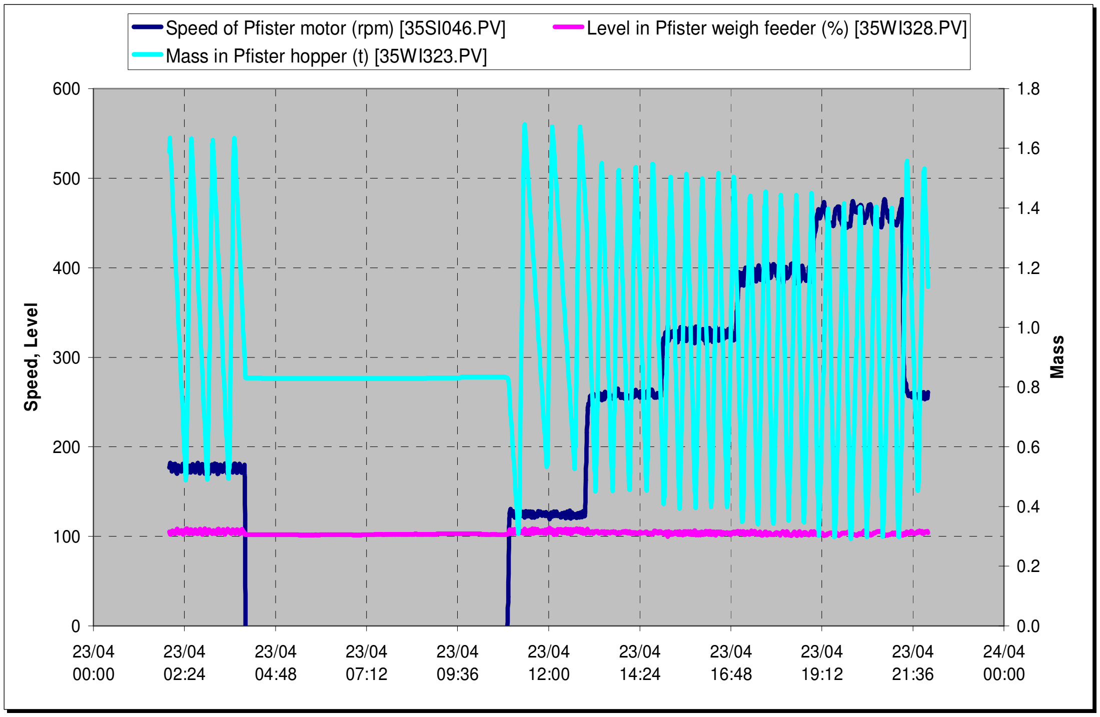


Figure 6.19: Level in Pfister hopper, weighfeeder and speed of Pfister motor

The figures 6.18 and 6.19 show the data relevant to Pfister feeder system. The pressure in between the Pfister outlet and kiln inlet has been increased proportionally to the animal meal feed rate.

The speed of the weighfeeder motor is measured in pulses from a tachometer and is in a range of 0-3200 rpm. The motor has been operated around 15% of full capacity even with maximum animal meal feed rate. The typical current of the weighfeeder motor is ranged from 0-18.8 A.

The mass in the hopper has been smoothly controlled between 300 kg and 1500 kg. No matter the discharge rate, the level inside weighfeeder was always kept 100% filled with material for simple operation.

Hence, it can be concluded that the Pfister feeder system has been operated smoothly during the whole test period.

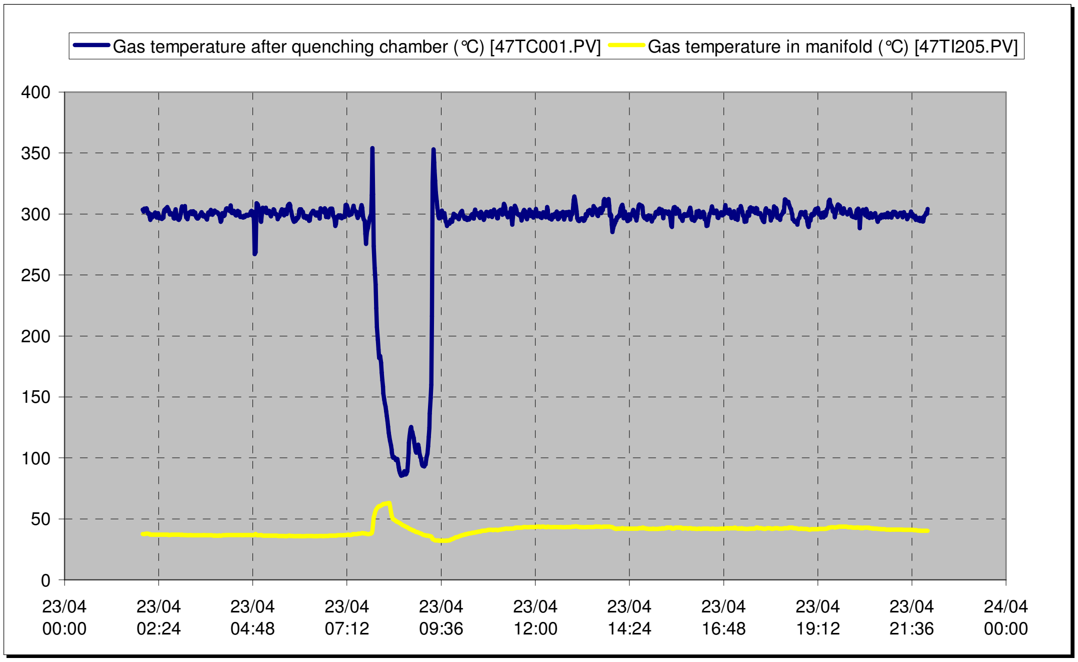


Figure 6.20: Gas temperatures in by pass system

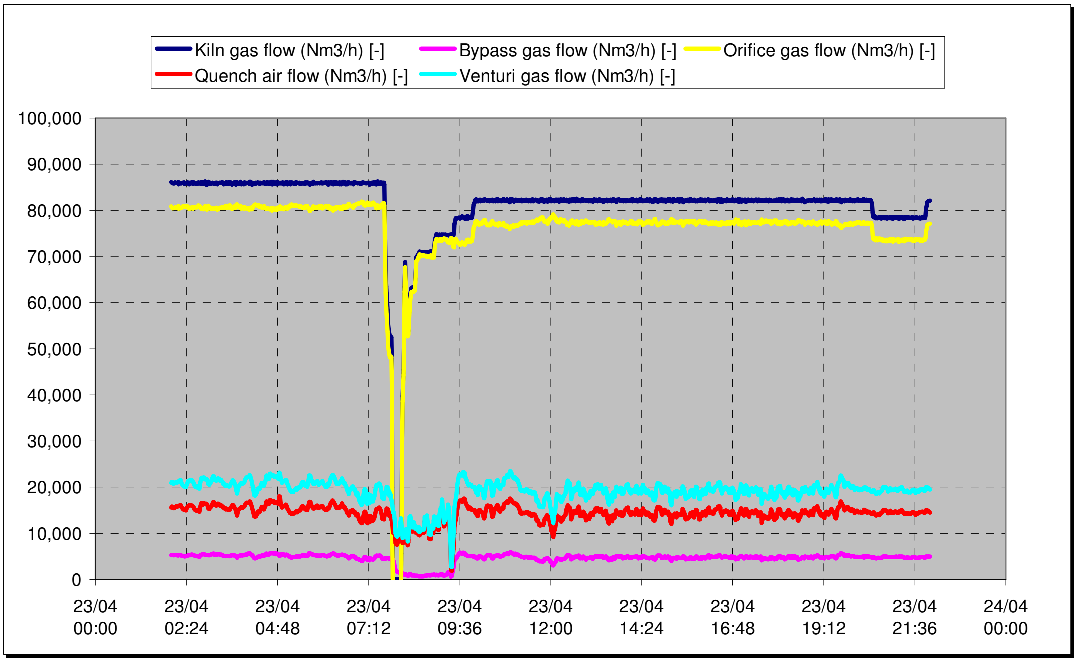


Figure 6.21: Gas flows under normal conditions

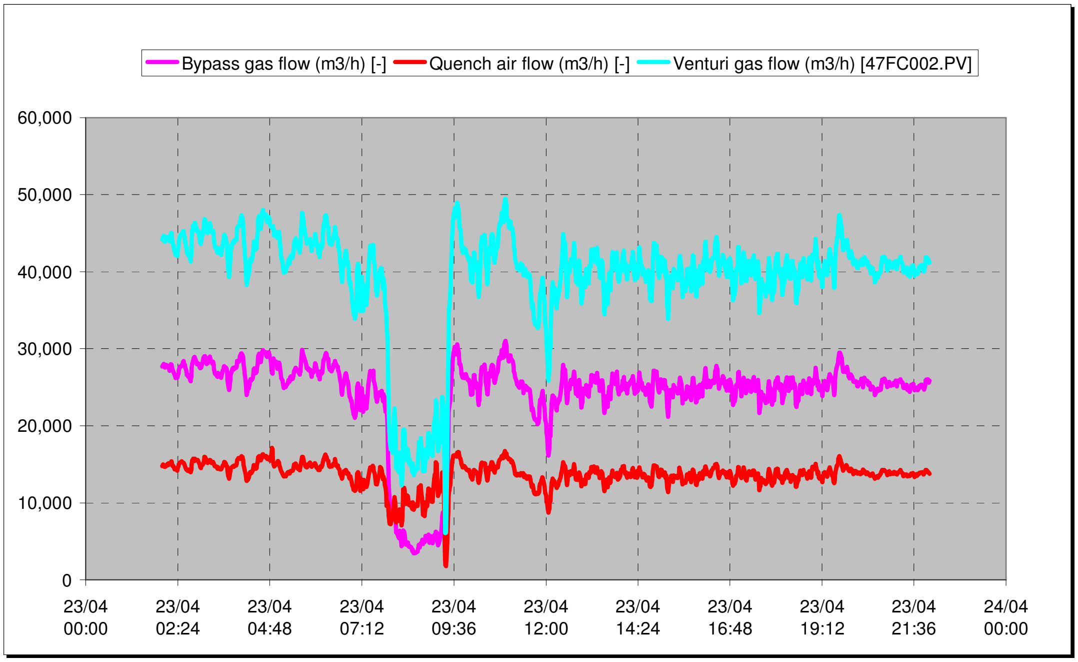


Figure 6.22: Gas flows under actual conditions

The figures 6.20, 6.21 and 6.22 show some data relevant to bypass system. All three graphs indicate a quite typical operation of the bypass system during the test. Generally, the by pass ratio is linearly proportional to venturi gas flow (maximum 50,000 m^3/hr). Therefore, using historical and above gas flow data, it can be concluded that the by pass ratio was around 5-6% which is desired by the system.

7 Conclusions and future work

7.1 Conclusions

- Basically, the alternative fuels are derived from waste materials and can be categorized into agricultural biomass, non-agricultural biomass, chemical and hazardous waste, petroleum-based fuels and miscellaneous alternative fuels based on their origin.
- Before any alternative fuel is considered for the use in cement kilns, its characteristics should be determined in order to overcome the handling, dosing, operational, environmental and process issues. However, some cement plants have achieved up to 70% of alternative fuel substitution in energy basis through proper optimization strategies (Murray & Price, 2008).
- The petroleum based products; most of plastics, tyres and waste oils have the highest energy content among all alternative fuels, around 30-40 MJ/kg. The carbon neutrality of biomass is one incentive for using biomass in spite of low energy content (8-20 MJ/kg). The emissions should be carefully controlled when using alternative fuels which might contain heavy metals, chlorine and other toxics. However, not only the fuel properties, the abundance and easy provision (continuous supply) of fuel are also very important factors when selecting alternative fuels by cement plants.
- Among the alternative fuels, the MSW derived fuels (e.g. RDF) are very heterogeneous by nature and therefore representative sampling and characterization is very difficult to perform, however it is needed especially when evaluating emissions.
- In the present study, the determination of biomass content of RDF was carried out using selective dissolution method according to the technical specification CEN/TS 15440:2006. The average biomass, non-biomass and ash content of RDF by weight were 43.75% (dry basis), 14.65% (dry basis) and 41.60% (dry basis), respectively. A very small standard deviation (1.92%) reveals the reliability of experimental results. The ash content of this RDF sample was twice high as typical.
- The results obtained for the moisture, ash and energy content of the original RDF sample were very much compatible with the analyses given by Renor (the company which carries out fuel analyses for Norcem- Brevik cement plant) which proves the reliability of procedures and instruments used at TUC laboratories for the experiments.

- Though the technical specification simply defines x_B and x_{NB} as “biomass” and “non-biomass” fractions of RDF, those should be defined as the weight percentage of “combustible part of biomass” and “combustible part of non-biomass” fractions respectively unless the ash of those fractions is dissolved in acid solution.
- Some unlikely values were found when determining the biomass content of RDF by calorific value (average 36.4% (dry) of biomass and 63.6% (dry) of non-biomass) using the same method. It can be concluded that the error might be either encountered with the determination of ash content of residue or the calorific value of residue. According to the experimental results, the average ash content of the residue is 73.78% (dry basis) and the average calorific value of the residue is 16.558 MJ/kg (dry basis) which is practically impossible. However, taking representative primary sample and laboratory sample of RDF is the major challenge here.
- It can be concluded that even though the selective dissolution method seems reliable for RDF characterization, the method and accuracy should be more validated. Also, more explanatory details are needed in some areas like when differentiating inert and other ash material which comes from biomass and non-biomass fractions. Even though, the determined biomass and non-biomass fractions of RDF by weight could be accepted, the determination by calorific value should be further investigated.
- The manual sorting test trial carried out for RDF showed that the most of biomass fraction is composed by paper and cardboard followed by wood. The soft and rigid plastics prevail in non-biomass fraction. Typically it is not much inert content (glass, ceramic, metal, etc) contained in RDF according to manual sorting results.
- Total time consumption for the selective dissolution experiment is around three days and more time should be allocated for primary sampling and laboratory sampling. The characterization of RDF by manual sorting method is also a time and labour intensive.
- Further the thermal behaviour of pure components composed of RDF (rigid plastic, polyethylene, polystyrene, wood, paper, cardboard, fabric) was analysed using thermogravimetric analysis. The high energy value of fossil materials like plastics could be described by high volatiles fraction (99 wt%), less moisture (0 wt%) and less ash content (1 wt%). The low energy value of biomass fractions like wood, paper, fabric, etc is due to high oxygen content, high ash content (3-15 wt%) and high water content (1-8 wt%) of the material. The proximate analyses of those materials reveal good agreement with results from previous studies.

- Even though, the TGA 7 available at TUC is better for analysis of pure or homogeneous materials, the results will not be that reliable for materials like RDF which is very heterogeneous, because the volume limitation of the sample pan of the instrument will restrict the use of sufficiently enough samples for representative analysis.
- The gas bag transfer technique methodology for coupling TGA and FTIR instruments was reviewed and documented with reference to a previous study (Arvoh & Ariyaratne, 2008).
- The full-scale combustion test conducted with animal meal feeding at the main burner through the new Pfister feeder system at Norcem-Brevik showed quite typical operation in kiln system and bypass system, more over a smooth operation in Pfister feeder system through out the whole experiment even with 7 t/hr of animal meal feed rate and 220 t/hr raw meal feed rate. The emissions were also considerably lower than the allowable emission limit during the test. The clinker quality was also in acceptable range, only the free lime content of the clinker (3%) was above the recommended limit (2.5%) when animal feed rate at 7 t/hr with moderate raw meal feeding rate. However, the clinker quality could be acceptable with animal meal feeding rate up to 6 t/hr. It was found that the increase of free lime content with animal meal feeding might be due to the following reasons.
  - The increase of alternative fuel consumption at main burner, which might reduce the flame temperature due to lower calorific value compared to coal and hence reduce proper burnability
  - The introduction of extra calcium at the kiln outlet via a high calcium phosphate content in animal meal will accumulate and add to the clinker without proper burning since that calcium does not have enough residence time for complete reaction at kiln outlet

  However, these bottlenecks should be further investigated.
- If the relatively short residence time of the animal meal in the kiln proves to be not a limiting factor for complete reactions to occur, the introduction of CaO via animal meal feeding could be an extra benefit in clinker production, since it must reduce the demand for high grade limestone in the production process

7.2 Recommendations for future work

- For more accurate results in RDF characterization experiments, a proper sampling technique should be used to take representative samples according to CEN/TS 15442:2006. At the same time the laboratory sample preparation should be carried out according to CEN/TS 15443:2006 for precise evaluation.
- The results from biomass content determination of RDF done by the selective dissolution method should be verified by some other means too. It is recommended to validate the accuracy of used instruments and methods by performing them in an external laboratory.
- It is recommended to carry out more laboratory experiments for selective dissolution method with less inert RDF sample (typical sample) and investigate the fate of inert and ash. However, the chemistry behind the selective dissolution test should be further investigated.
- The manual sorting method for RDF characterization should be carried out with representative sample of pure RDF. The sample taken for the trial test in this study was not real RDF but a mixture of RDF and SHW.
- In the full-scale experiments, it could be observed that the free lime content is increased with animal meal feeding and two possible reasons have been pointed out in chapter 6. These two possibilities should be further investigated to find out the real phenomena behind that effect. i.e. carry out a test under same conditions with another alternative fuel which does not include Ca compounds
- More full-scale experiments should be carried out in kiln 6; Norcem-Brevik, with new Pfister feeder system and other alternative fuels (e.g. shredded plastics, SHW, fuel mix, etc) at main burner. The limitations and required modifications should be identified for optimization of the new alternative feeding system. The issues which were not focused in the present animal meal capacity test should also be further investigated.
- It is recommended to analyse the combustion characteristics and flow regimes of the kiln system with alternative fuels using a CFD simulation software for improved understanding of the process.

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Appendices