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PYROLYSIS YIELDS FROM REFINERY RESIDUE USING A BATCH PROCESS

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A Dissertation submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, in fulfilment of the requirements of the degree of Master of Science in Engineering

Johannesburg 2012

DECLARATION

I declare that this dissertation is my own unaided work. It is being submitted for the Degree of Master of Science in Engineering in the University of the Witwatersrand, Johannesburg. To the best of my knowledge the work being presented contains no material previously published by any other person in fulfilment of any other degree/qualification in any University, except where due acknowledgment has been made.

Shaan Prithiraj

13th day of June 2012

ABSTRACT

Batch pyrolysis has proved to be a valuable process of assessing the potential of recovering and characterizing valuable products from various materials. Furthermore, the off-gases produced are easily handled by conventional gas clean-up processes in order to achieve environmental emission compliance. This research explores the pyrolysis of hydrocarbon rich refinery residues, left over from crude oil and other crude fraction conversion processes, in a 1200 liter electrically-heated batch retort. It also provides the novel offering of a cost effective and environmentally compliant method of assessing the recovery potential of valuable products. The process design has been formulated by careful consideration of key aspects of previous work cited in literature. The pyrolysis of the residue has shown significant oil *(70%)*, char *(14%)* and non-condensable gas *(6% by difference)* yields. The oil yield obtained shows a remarkably high calorific value *(~40MJ/kg)*, comparable to that of standard liquid fuels. The char obtained, with high carbon content *(~80%)*, could be a candidate for a solid fuel source. The non-condensable gas stream possesses significant calorific value *(240KJ/mol, estimated)* implying the potential generation of an additional heating source. The non-condensable gas stream was subjected to an oxidative process prior to gas clean-up, and continuous on-line monitoring of the vented gas demonstrated compliance with South African emission guidelines. The gas treatment is economically optimal as only a smaller portion of the original residue is subjected to emission-controlling steps. The current work is aimed at a semi-commercial batch pyrolysis plant which generates substantial quantities of material for the purposes of proving compliance with emission standard regulations.

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LIST OF SYMBOLS

Breadth	B
Density	ρ
Height	H
Length	L
Mass	M
Volume	V

1 INTRODUCTION

1.1 Background

The inherent disadvantage to the petrochemical industry has been the pursuit of greater production yields due to the increase in fuel and chemical demands *(International Energy Outlook, 2009).* This inevitably leads to an increased generation of non-distillable crude residue/hydrocarbon rich waste sludge *(Ngan et al. 2003).* Various high quality fuel and chemical products derived from crude were subjected to several processing and refining stages prior to being regarded as commercially viable or premium grade products. These various processing stages are well documented in the literature and include: catalytic cracking (*Funai et al. 2010), (Jiang et al. 2008), (Zhu et al. 2006),* catalyzed and uncatalyzed reforming (*Chan & Wang 2000), (Naidja et al. 2003), (Pacheco et al. 2003), (Qi et al. 2007),* hydrogenation *(Krichko and Maloletnev 1992), (Li et al. 2009), (Pawelec et al. 2006),* de-sulphurization *(Ali et al. 1992), (George and Schneider 1992), (Hoguet et al. 2009), (Song 2003),* distillation *(Wilson et al. 1982),* etc.

The dynamics and characteristics of distillation processes are based primarily on the feasibility of their operating potential, and do not possess the capability of elevated operating temperature, typically greater than 415°C *(Ngan et al. 2003).* This has lead to the generation of large quantities of non-distillable residues, containing entrained "hydrocarbon values", that have not been liberated in the thermal conversion process from liquid crude to gaseous phase distillable and condensable products. The work conducted by (*Ngan et al. 2003)* aimed at extending the capability of an ethylene furnace for flash pyrolysis of heavy crude fractions containing pitch. Here, pyrolysis was performed in order to recover a higher hydrocarbon fraction in vapor form for cracking purposes. Subsequently, the validation of pyrolysis as an effective means of recovering a higher hydrocarbon fraction was confirmed. But more importantly, this objective is not readily achievable in atmospheric or vacuum distillation columns.

This further proved the need for the present work, as material exhibiting characteristics similar to that of hydrocarbon-rich residues, which may be generated in future by any fuel manufacturing industry, would thus require an efficient and investigative method to evaluate the yield potential of the waste hydrocarbon feedstock. The feasibility of utilizing a pilot scale continuous pyrolysis unit becomes an issue of concern, especially in the global economic crisis which the world is currently faced with *(McCarthy 2009)*. Therefore, the present work is envisioned as a cost effective batch pyrolysis investigation to assess the potential product yields at minimal cost. This information is crucial prior to commitment of immense capital expenditure required for the design, fabrication, commissioning, installation & continuous operation of a full scale commercial facility.

The intensification of higher fuel volumes required to power our growing world and economies *(International Energy Outlook 2009)*, will invariably lead to an amplified generation rate of hydrocarbon residues. Currently, *Leeman (1985)* states that many hydrocarbon rich materials originating from refinery and petrochemical operations are categorized by the US EPA, as hazardous waste streams that are ultimately destined for permanent disposal. There are five hazardous waste streams identified by the EPA *(Leeman 1985)*, i.e. dissolved air flotation (DAF) float (K048), slop oil emulsion solids (K049), heat exchanger bundle cleaning solids (K050), API separator sludge (K051) and leaded gasoline tank bottoms (K052). This hazardous waste classification is limited to these five streams but also includes numerous other sources of hydrocarbon rich sludges from refinery site works, i.e. sludge from separator bottoms, heat exchanger sludge, slop oil emulsion solids and crude oil tank bottoms *(crude oil, distillates, decant oil, bunker)*.

The rapid generation rate and subsequent high volumes of hydrocarbon rich residues from refinery site operations such as the refinery residue used in the current study, poses a huge environmental concern. *Hogan (1996)* maintains that the option of permanent disposal via incineration of such material can be considered a waste of a

valuable resource. This can only be considered true unless energy recovery systems are introduced which are capable of accepting combustion products from these waste streams.

Waste utilization has been centered on combustion of all waste materials aiming at maximizing volume reduction, but the combustion route has proved problematic due to elevated generation of dioxin and CO_2 emissions *(Wenning 1993)*. The need for indirect material recycling was also identified, and explained as the conversion of wastes into raw materials for other important processes *(Wenning 1993)*. The conversion processes identified by *Wenning (1993)* were: hydrogenation, gasification and pyrolysis. Pyrolysis achieves thermal decomposition of organic or hydrocarbon substances in the absence of oxygen, where long-chain hydrocarbon structures are subsequently converted into higher hydrogen fractions, gas, oil & char *(Wenning 1993)*. Pyrolysis is chosen as the process utilization of choice compared to that of hydrogenation and gasification, due to the fact that the aim of the study is to assess the raw product yields of a specific feed material, i.e. refinery residue. This direction will ensure that a greater understanding of the quality of raw products are attained, prior to assessing further the potential upgrading and/or use of the raw products to obtain specifically desired polished products. Hydrogenation and gasification will serve as further conversion steps, once a qualitative understanding of the raw pyrolysis products are attained. *Ahmaruzzaman & Sharma (2008)* also state that when petroleum residue is subjected to cracking, the major product yield attainable is hydrocarbon oil and a minor product yield of coke and gas.

Moreover, *Hogan (1996)* endorses pyrolysis of waste materials opposed to the inherent disadvantages of incineration which require high temperature to affect incineration of nearly all the compounds contained in the feed stream. Therefore, none of the potential valuables are recovered which ultimately results in loss of valuable products. Concern is also expressed that incineration leads to an increased volume of combustion products *(especially CO_2)* which is subsequently generated

and released into the environment *(Hogan 1996)*. *Heuer (1991)* mentions an alternative of treating hazardous sludges via the use of specifically developed bacterial strains to promote the decomposition reaction of hydrocarbon sludge. However, this has two major disadvantages, i.e. (i) the metals contained in the resultant oil which remains in the soil and posses potential ground water and run-off contamination to the surrounding environment, and (ii) leading to loss of a potentially valuable resource. Fuel refineries previously recycled their waste oil sludges into delayed coke ovens, but this proved damaging to the coke quality resulting in a lower priced fuel coke product *(Heuer 1991)*. *Heuer (1991)* ultimately subjected the waste oil sludge to a series of volatizing *(pyrolysis)* and condensing steps in order to recover an oil product fit for further refining.

Therefore, the present approach of utilizing pyrolysis to derive marketable products is validated by virtue of capitalizing on an untapped resource which was previously considered as waste, by US EPA *(Leeman 1985)*. This waste would otherwise be destined for incineration as a final treatment option. The extraction of valuable products, especially commodity chemicals, from the hydrocarbon residue also reduces the volume of feedstock to be subjected to combustion, therefore resulting in a net reduction of CO_2 generation. From a global perspective, South Africa is currently the 11^{th} highest emitter of greenhouse gases *(Environment South Africa 2009)*. Therefore, processes such as pyrolysis as presented in this research will assist in mitigating incineration requirements of the entire volume of hydrocarbon waste sludge as a treatment option. Also presented in this research is compliance with emission regulation guidelines during the test work.

This dissertation looks at previous work conducted by various authors and key factors that were utilized in effectively applying pyrolysis to assess product yields. The batch equipment design was developed from research into previous work. A detailed discussion explains the deviations required in equipment design due to the specific nature of the present work. The final equipment design is discussed, prior to

presentation of the pyrolysis results and analyses of yield. Finally, the emissions results are quantified and presented, proving the effective use of batch pyrolysis as both a cost effective and environmentally sound solution to deriving valuable products from hydrocarbon rich refinery residue.

1.2 Aims and Objectives

This research is fundamentally an industrial project which is aimed specifically at fuel and chemical processing industries that utilize crude oil and hydrocarbon feed stocks. These processes which are designed to produce fuels and chemicals for specialized applications, also yield substantial volumes of hydrocarbon rich residues due to the inability to apply cleaner production principles as a result of the complexity of these chemical processes which restricts its application.

Therefore, the main aims of the study are as follows:

i. To provide cost effective batch pyrolysis equipment in order to assess the potential recovery/extraction of valuables, from a hydrocarbon rich waste stream.
ii. To quantify the product yields that can potentially be recovered from hydrocarbon rich residue.

The main objectives of the study are as follows:

i. To satisfy aim (ii) above, in an environmentally safe manner.
ii. To compare the quality/properties of the products yielded with generally acceptable parameters for commercial grade products and recommend potential utilization.

2 LITERATURE SURVEY

2.1 Literature for Experimental Equipment Design

Considerable work by others has been conducted thus far on pyrolysis of various waste materials which are synonymous with the extraction of valuable products such as hydrocarbon fuel oil, high carbon value solids and a valuable non-condensing gas stream. Pyrolytic extraction has been performed and documented in literature on various materials as seen in **Table 2.1**.

Table 2.1 Pyrolysis work documented in literature on various waste materials

Author	Type of waste materials
Bradley (2003)	waste tyres
Breu (1993)	organic wastes
Cornelissen et al. (2009)	biomass
Dobele et al. (2009)	wood
Fonts et al. (2009)	sewage sludge
Heuer (1991)	waste oil sludges
Hogan (1996)	solid waste
Hoffman & Fitz (1968)	municipal waste
Magedanz et al. (1983)	oil-containing minerals
Robertson (2002)	liquid & solid waste
Sanchez et al. (2008)	agricultural residues
Weggel (1972)	shale rock
Weinecke & Unterweger (2006)	waste tyres
Wenning (1993)	non-distillable residues; mixed plastics

Pyrolysis can be described as a mechanism that ensures the thermal decomposition of carbon based materials in the absence of oxygen. Pyrolysis is the first stage of combustion, therefore heat initially applied to the material will ensure that the decomposition reaction begins followed by the mass transfer of pyrolysis products formed. Combustion usually occurs when the pyrolysis products meets oxygen thereby leading to oxidation. In the case of pyrolysis, there exists an absence of oxygen therefore the pyrolysis products given off will be in the form of carbonaceous char, condensable and non-condensable gases. The carbonaceous char serves as the solid product, the condensable gases will report to liquid products, and the non-condensable gases are the gaseous products, of pyrolysis. Factors considered during pyrolysis such as temperature, residence time, heating rate, heat and mass transfer, results in the evolution of various forms of product species which are derived from the feed material.

Pyrolysis effected in a batch or continuous process also results in variations of effecting the abovementioned parameters. Batch pyrolysis was chosen as the method of effecting the required parameters due to the inherent nature of having more control over parameters such as the heating rate, mass transfer and temperature control using electrical elements, as well as the residence time, i.e. keeping the material in the batch chamber for a specified period of time.

The batch pyrolysis experimental equipment utilized in this study can be divided into two parts, the front-end *(pyrolysis and product recovery)* and the back-end *(gas clean-up complying with environmental regulations)*. The front-end design was developed from key operational criteria *(elements, functions and critical parameters)* as identified from various author's works. These authors affected pyrolysis on various types of materials, most of which were conducted under different circumstances. See **Tables 2.2 – 2.6** for a summary of the key criteria, corresponding author/s, and similarities or deviations from the literature that were considered and/or used in the front-end design of the present work. The back-end of the experimental

equipment follows generally accepted wet scrubbing processes for gas-cleanup operations.

Heuer (1991) validates the recovery of a commercially valuable oil product from refinery produced waste oil sludges. Their process consisted of initially centrifuging the waste oil sludge to effect as much mechanical separation as possible of the free oil and water from the solids. Thereafter, the resultant waste oil mixture was subjected to a heat induced series of volatizing and condensing steps in order to recover commercially valuable oil products. Subsequently, this led to the production of non-hazardous water and solid products. The high temperature oil and water vapor were recycled to provide the heating source to the process. It was not an objective of the present work to consider heat integration/utilization within the process. The primary objective of the present study was to determine the product yields attainable which included the gas stream and most importantly, to conduct the operation in an environmentally compliant manner. The gas stream also required identification in terms of its component concentrations prior to assessing its use as potential heating media.

An environmental concern arises when considering the direct utilization of the non-condensable gas stream via combustion, due to the presence of chlorine, if any. Since an environmentally sound solution is required with greater emphasis on the processing of hazardous materials, the presence of chlorine and aromatic compounds are recognized as a trigger for dibenzo-para-dioxin *(PCDD)* and dibenzofuran *(PCDF)* formation *(Tuppurainen et al. 1998)*. The 17 most toxic isomers of PCDD/Fs can be found in the 2,3,7,8,-substitued group *(Environment Australia 1999)*. Future heat utilization can be assessed following the identification of any triggers being present in the non-condensable gas stream. The present work determines the non-condensing gas yield as well as the constituents of the stream prior to an oxidative process. Thereafter, complete combustion ensures that the

hazardous components are destroyed, and gas clean-up assists in achieving environmental compliance with emission guidelines.

Heuer (1991) carried out separation of condensed oil and water in a settler, which was readily achievable due to the disparity in density of the two liquids. The gravity separation methodology was utilized in the present work. The present work condensed oil and moisture in two different stages, opposed to *Heuer (1991)* effecting the condensation of both water and oil in a single step. *Heuer (1991)* proposes multi-stage volatilization and condensing which could potentially yield a more efficient recovery of the oil and water.

Also, *Bradley (2003)* demonstrated the use of a number of indirectly cooled vertical condensers to fractionally condense and liquefy gaseous products originating from waste tyre carcasses or polyisoprene rubber pyrolysis. This ultimately results in a broader pyrolytic oil range attainable. *Dobele et al. (2009)* also states that the determination of pyrolysis oil composition or properties is efficiently achieved via fractionation. Wood was pyrolysed utilizing a two-chamber reactor in order to yield a pyrolysis oil product *(Dobele et al. 2009)*. The two-chamber pyrolytic system achieved moisture removal at 200°C in order to determine the soluble and insoluble compounds in the pyrolysis oils. The drying section of this work *(Dobele et al. 2009)* influenced the initial running temperature, i.e. 100°C, for the current investigation. The moisture content required removal and measurement prior to determination of the pyrolysis oil yields. It was expected that an insignificant amount of hydrocarbon constituents will be liberated at 100°C, resulting in negligible hydrocarbon losses. Initially removing moisture will ensure that an accurate oil yield determination can be obtained, as the oil yield determined would not be misrepresented by volatilized and condensed water.

The principle of fractional condensation was then considered in the present work in order to investigate the various oil fractions recoverable. The present study was undertaken at various temperatures, i.e. 100°C to determine moisture content, and 200°C, 400°C & 600°C, in order to liberate and condense the hydrocarbon oil components as per the boiling fractions corresponding with each temperature increment.

Weinecke & Unterweger (2006) established a specific process to achieve oil recovery originating from pyrolysis of shredded vehicle tyres and concludes that gas-liquid contact ensures a greater and more efficient recovery. Therefore, two packed tower oil spray condensers operating at specified temperatures to yield a heavy and light oil product respectively, was utilized by *Weinecke & Unterweger (2006).* The present work also utilized direct gas-liquid contact but not via a cooling liquid spray but rather via bubbling the pyrolysis gases through the cooling liquid. The decision of bubbling gases into the condensing media as a conversion of *Weinecke & Unterweger (2006)* oil spray also took cognizance of the droplet size attainable via spray nozzles. An oil spray nozzle generates a fine mist which increases the surface area for gas-liquid contact thereby attaining a greater condensation efficiency and subsequent recovery. In order to simulate this in the bubbling action, a top sieve/mesh plate was introduced above the pyrolysis gas discharge point. This ensured that the pyrolysis gas that was introduced into the condensing liquid as oversized bubbles could then be dispersed into tiny bubbles, simulating the increased surface area for gas-liquid contact.

Hogan (1996) carried out pyrolysis as a treatment option for solid waste with the primary objective of converting solid waste material into solid, liquid and gas phase products of economic value. *Hogan (1996)* effected pyrolysis within a rotating kiln, where the solid material was loaded into the rotating drum which was sealed from the surrounding environment, and the exterior of which was heated via a heater and gas burner arrangement. The present work utilized a stationary retort chamber *(batch*

process) as a cost effective means of effecting pyrolysis, as opposed to rotary retorts which are more expensive and undesirable for the yield determination stage. The batch retorting chamber in the present work was also externally heated. However, gas burners were not utilized, as electrical elements were preferred for the type of operation.

Volatile material *(mainly liquids)* contained in the feed were vaporized in the apparatus utilized by *Hogan (1996)*. Thereafter, the remaining solids were exposed to an oxidative environment for oxidation to take place of the minute particles and undesirable constituents. *Hogan (1996)* expresses the concern of contaminating the recovered oil with particulates, therefore promoting the removal of these particulates from the vapor stream via the utilization of a counter-current hot oil spray.

The present work affected the removal of the particulates in the gas stream via tray sieves. A two-stage tray sieve was utilized, i.e. above & below the pyrolysis vapour entry point into the condenser. The tray sieves served as the filter media thereby inhibited particulates *(>150 micron)* from reporting to the heavy and light oil phases. The top tray sieve thus doubled in functionality as it allowed for dispersion of large vapor bubbles for increased condensation efficiency, whilst simultaneously effecting particulate removal. Blinding of the sieves was not an issue of concern, as the experimental procedure called for cleaning of the sieves prior to each run.
Hogan (1996) believed that in order to attain a solid product which was safe to handle, the addition of an oxidizing section was required to oxidize the minute particles/solids and any reactive constituents contained in the solids, i.e. hydrocarbon or combustible compounds. However, *Hogan (1996)* also mentions the direct relationship of operating temperature of the retort and retention time, which affects the amount of energy absorbed in the waste material. Therefore, maximizing these parameters would ensure that the hydrocarbon constituents would be volatilized and any combustible material will be decomposed by pyrolysis.

The present work took cognizance of *Hogan (1996)* concern by ensuring that the solids were subjected to the required temperature for an adequate period of time, and thereafter cooled to room temperature prior to removal. This ensured a resultant solid product which could be handled safely. It was also not in the interest of the present work to expose the solids to an oxidative environment as it would promote oxidation of the heated solids, resulting in loss of one of the recoverable products, i.e. carbonaceous char. However, the principle of oxidation was utilized and applied to the non-condensable gas stream, rather than the solids stream. Following yield determination and sampling of the non-condensable gas, it was subjected to an oxidative process. The resultant combustion products were measured by online emission analyzers in order to assess whether these gaseous emissions are environmentally compliant as an acceptable gas release to the atmosphere.

Also, it can be noted that in order for there to be a negligible quantity of unwanted volatile chemicals left over in the solids, the feed material should be exposed to the thermal heating environment for an adequate period of time so as to liberate all the volatile constituents, i.e. adequate residence time. This was ensured by concluding each run only when the bubbling action had ceased, implying that the volatile content had been completely liberated from the hydrocarbon residue.

Hogan (1996) utilized exhaust gases from the retort burner to provide an inert atmosphere in the vaporization zone and also to prevent any condensable gases from flowing back into the retort. Additionally, *Hogan (1996)* incorporated the use of the heat contained in this gas stream to assist in the vaporization of the liquids in the retort. It was not an objective of the present work to incorporate heat integration as the scope of the study was to determine the product yields potentially extracted from hydrocarbon residues, including that of the non-condensable vapor stream *(containing significant calorific value).* The quantification and evaluation of the vapor stream would prove its viability as a potential heat generating stream.

The hydrocarbon constituents liberated during pyrolysis in the present work provided sufficient gases in the retort chamber thus contributing to non-oxidising conditions. Additionally, air ingress was kept at a minimum via sufficient sealing mechanisms on the retort chamber. This ensured that pyrolysis gases could not undergo oxidation prior to the condensation and recovery stages. The backflow of condensable gases, as stated by *Hogan (1996)* was addressed by ensuring that the outlet pipe carrying the pyrolysis vapors was in direct contact with the condensing liquid. This ensured that direct contact with the condensing liquid promoted an instantaneous phase conversion of pyrolysis gas to pyrolysis liquids.

Another deterring factor regarding heat integration in the present work was that the chamber was electrically heated therefore heat integration would only be possible via recycling of this gas stream directly into the retort chamber. Efficient utilization of this gas stream would be achieved via combustion of the gas stream which in turn would yield the desired energy required. *Ban (1967)* stated that the use of gases, especially containing combustion products, will decrease the heating value of the retort gases. By virtue of the fact that the gases could only be utilized inside the retort chamber and not outside due to the electrical elements, it was decided that heat integration should not be an objective of the present investigation.
The non-condensable gas stream is a potential product yield which requires identification prior to oxidation. A further requirement is the identification of the resultant combustion product concentrations in the gaseous emissions following oxidation. If a high CV is determined, theoretically, it could show the possibility of utilizing the oxidized gases/combustion product stream as a potential heating source.

Robertson (2002) provides an improved method and apparatus for the pyrolysis of various liquid and solid waste materials for the removal of volatile contaminants and the combustion of volatilized gases from the pyrolyzing retort. *Robertson (2002)* states that their pyrolysis and combustion method in utilizing their retorting apparatus is capable of treating/handling materials such as petrols, oils, grease, phenols, coal

tar, cyanide, poly-chlorinated biphenols *(PCBs),* organo-chlorine pesticides, etc. *Robertson (2002)* apparatus utilizes a rotary retort which is sealed to the atmosphere, and externally heated via the heated combustion products generated in the afterburner. The afterburner affects combustion of the entire volume of volatilized pyrolysis gases liberated from the liquid and solid waste streams being treated.

The present work followed the similar principle of external heating, but using electrically heated elements rather than utilizing external gas heating. The combustion of the off-gases was also conducted in the present work, but the combustion of which was subjected to the non-condensable gas stream only and not the total volatilized pyrolysis gas stream. The initial pyrolysis vapors in the present work were condensed to determine the pyrolysis oil yield achievable, thereafter the non-condensable gas stream required complete oxidation in order to meet environmentally acceptable emission limit guidelines.

A heating jacket was used by *Cornelissen et al. (2009)* to affect external heating of the pyrolysis reactor, whereas the present work affected external heating via electrical elements. *Cornelissen et al. (2009)* utilized a screw and injection system to feed biomass and biopolymers to affect pyrolysis of the mixture to yield improved pyrolysis oil characteristics. The present work also takes cognizance of the sealed screw as being the inhibitor for air ingress, and attained this via the use of a batch processing sealed retort chamber.

Wenning (1993) states, specifically, the use of an indirectly heated rotary kiln conducting pyrolysis of non-distillable residues from crude oil and coal tar processes in the VEBA OEL AG refineries in Gelsenkirchen, Germany. The pyrolysis gases were generated in the absence of oxygen and upgraded via hydrogenation to yield a saleable oil product. A further investigation also led into the pyrolysis of mixed plastics to yield a saleable oil product. *Wenning (1993)* explains the use of metering pumps to feed the residues, which are pumped into the system, and also notes the

pyrolysis taking place at a slight over-pressure of 10mbar in the absence of oxygen. The over-pressure is to facilitate the movement of the gases through the retort. In the present work conducted, the initial pressure of the retort chamber is atmospheric pressure but as the liberation of volatilized gases begins to progress, an increase in pressure is produced. This ultimately provides the driving force for the bubbling action of the pyrolysis gases into the condensing liquid.

Wenning (1993) regulated the pyrolysis temperature by adjusting the wall temperature and the maximum of which was set at a normal drum wall temperature of 600°C. The effective pyrolysis temperature inside the retorting chamber for the present work was similarly controlled via the adjustment of the wall temperature which was measured by a thermocouple. The heat transfer between the electrically heated elements and the retort chamber must be efficient such that there exists a negligible difference between the outer wall temperature and inner temperature of the pyrolyzing material. This is readily achievable by accurate selection of the materials of construction for the retort chamber.

Wenning (1993) recycled part of the non-condensable pyrolysis gases through the coke discharge outlet in order to prevent partial condensation of some of the higher boiling pyrolysis oil fractions at the coke discharge end of the kiln. The present work proved the inherent advantage of no rotary action, therefore retaining the subsequent solids or coke product in the batch retort chamber. The final char product would thus be virtually free of volatile and liquid constituents. *Wenning (1993)* utilized a two step condensation process via a direct recycled pyrolysis oil spray which simultaneously achieved scrubbing of particulates from the pyrolysis gas stream. *Wenning (1993)* used a first stage temperature set point of 300°C and as a second stage temperature set point of 35°C for the recovery of two specific oil fractions, i.e. light and heavy oil only.

The present work similarly utilized direct condensation, but the condensation was achieved by bubbling the pyrolysis gas directly into the condensing liquid, rather than utilizing an oil spray. The volatilization of each oil fraction was attained at various temperatures, i.e. 200°C, 400°C & 600°C. The condensing liquid was maintained at a temperature below 35°C by controlling the outside temperature of the condenser unit. A circulating liquid from a cooling tower was recycled to the outside of the condenser in order to remove heat of condensation radiating from the process. *Wenning (1993)* shows the removal of the non-condensable gases via pressure of an existing gas network. The present work similarly achieves the removal of non-condensable gases via the utilization of an induced draft fan, i.e. negative pressure.

Magedanz et al. (1983) conducted pyrolysis of oil containing minerals such as oil sand, diatomaceous earth and oil shale. Here, oil recovery was achieved via the use of a travelling grate. Hot gases were passed through a bed in the retorting zone to provide the required temperature, i.e. 400°C – 600°C. A pyrolysis vapor stream was produced which was later condensed into a pyrolysis oil product, and also in the process produced a solid char product. *Magedanz et al. (1983)* subjected the solid char product to a combustion process which also assisted in heating the bed to affect external heating. The present work also utilizes external heating, but via electrical elements rather than heating bed technology. A similar oil condensation and separation stage was included in the present work in order to determine the liquid product yield potential of the hydrocarbon rich residue. The solid char product generated was not burnt as conducted by *Magedanz et al. (1983)* but was quantified as per the scope of this study. It was envisioned that only through the analyses of the char product would it be possible to verify its potential as a co-processing solid fuel source.

Magedanz et al. (1983) passed the non-condensable gas stream through the bed to provide the retorting temperature required. However the present work utilized an externally heated retort chamber via electrical elements. Therefore, the option of passing the heated gas stream around the chamber did not exist. Even though the non-condensing gas stream could potentially be recycled into the retort chamber, it was not considered due to the scope of this study to prove compliance with emission regulation guidelines by subjecting the non-condensable gas stream to oxidation. Therefore, following complete oxidation of the non-condensable gases, it was required that the resultant gaseous emissions be measured prior to atmospheric discharge. A consequence of passing the oxidized stream into the retort chamber is the potential of carrying excess oxygen, which would transform the reducing conditions inside the chamber into one of an oxidizing atmosphere. Oxidation would take place rather than pyrolysis, resulting in the loss of valuable products.

Magedanz et al. (1983) also explains various preferred embodiments for heat integration within the system, but one must bear in mind that they had consistent feed material which in essence showed predictable constituents and exhibited known concentrations with very little variation. The hydrocarbon-rich residue utilized in the present work is essentially a mixed "hazardous waste stream". The constituents are unpredictable thereby causing uncertainty as to the heat/energy generation potential. Notwithstanding the fact that expensive controls are required in the form of a feedback control system for the detection of heat available, and heat demand requirements for the subsequent stages in the recovery process.

Magedanz et al. (1983) effects virtually complete retorting in the retorting zone, and similarly in the present work this is achieved via the use of a sealed chamber. The removal of the non-condensable gases and other gaseous products are affected by *Magedanz et al. (1983)* via the utilization of wind suction boxes, which is similarly achieved in the present work by an induced draft fan, i.e. negative pressure. *Magedanz et al. (1983)* makes specific reference to the control of air in the

combustion zone so as to maintain the bed at the highest possible temperature. The present work similarly takes cognizance of the control of combustion system parameters such as: providing the adequate amount of turbulence, residence time, and temperature in the oxidizer. This ensures complete combustion of the non-condensable gas stream in order to achieve a gas stream which is environmentally compliant with strict emission regulation guidelines.

Weggel (1972) prior to *Magedanz et al. (1983)* also utilized a travelling grate to recover oil from shale rock. The pyrolysis is combined with that of a combustion zone which was specific to the combustion of the residual carbon product generated in the process. *Weggel (1972)* utilized four specific zones: 1) pre-heating and oil condensing zone, 2) retorting zone, 3) combustion zone, and 4) cooling zone. The present work utilized all these principles excluding the pre-heating stage, but the principles of which were affected via various processing units/equipment. The condensing zone was substituted by directly bubbling the pyrolysis vapors into the condensing liquid. The retorting zone was simulated by the batch retorting chamber. The combustion zone in the present work was conducted in an oxidizer which served as a means for the oxidation of the non-condensable gas stream, but not for the residual carbon as conducted by *Weggel (1972).*

The cooling zone from *Weggel (1972)* work was simulated by removing the batch retort chamber from the vertical kiln and placing it in a cooling bath, thereby substituting the external heat source with a cooling liquid. *Weggel (1972)* utilized the principle of external heating but not in a conventional method as all other authors have done, but rather via the use of a plurality of heat transfer media such as alumina balls. The heat transfer was performed by passing an initial gas stream over the alumina balls, thus heating the alumina. Thereafter, a second low temperature gas stream is passed over the heated alumina balls, thus heating the second gas stream. Following heating of the second gas stream it is subsequently passed through the retorting zone to provide the temperature required for pyrolysis vapors to be liberated

from the feed material. The present work provides a cost effective means of effecting pyrolysis. Therefore, a simplistic and inexpensive means of providing an external heat source was attained via utilization of electrically-driven heating elements.

Breu (1993) utilized a pyrolytic converter in order to achieve pyrolysis oil and char recovery from various types of organic wastes, i.e. plastic wastes, waste tyres, rubber, leather, sewage sludge, oil shale, broken asphalt, etc. But *Breu (1993)* pyrolytic converter required highly elevated temperatures between 648°C – 815°C. Pyrolysis temperatures used in the present work was only considered up to a maximum of 600°C. It was envisioned that upon later investigation into the char product with particular reference to the volatile content, the presence of which will validate if elevated temperatures are required.

Breu (1993) also speaks of injection of the feedstock presenting material handling problems, since it is aimed at not introducing air into the pyrolyzer. The ingress of air was considered a dangerous condition due to the expansion and mix of organic pyrolysis vapours present in the retort chamber, as well as the elevated temperature inside the retort. All of which only requires oxygen to complete the loop to affect a spontaneous explosion, which could potentially result in fugitive emission releases. Therefore, inhibiting oxygen ingress is of utmost importance from a safety perspective. This was addressed in the present work via the utilization of a batch retorting chamber which is charged at the beginning of the process and thereafter adequately sealed thus inhibiting oxygen ingress and subsequent loss of valuable pyrolysis vapors.

Breu (1993) utilized a gas burner as the external heating source, whereas the present work affected pyrolysis and non-condensable gas oxidation via an electrically driven heat source. *Breu (1993)* achieved particulate removal by gravity which was also conducted similarly in the present work via the two-stage tray sieves as explained earlier. *Breu (1993)* utilized a series of three condensing tanks which the pyrolysis

vapors were passed through and condensed using a water cooling spray. The present work similarly utilized direct condensation but a series of condensing tanks were not required.

The condensing action in the present work was affected down to 32°C during each subsequent run. The temperature set point was preset on the retort chamber, for e.g. the run conducted at 400°C followed the run conducted at 300°C, therefore the oil product separated out during the 400°C run can be attributed to hydrocarbon boiling fractions between this specific temperature range. *Breu (1993)* achieved tar like heavy oil recovery which was removed at the bottom of the tank. In the present work any tar or heavy oil which exhibited a higher density than the condensing liquid, displaced the condensing liquid thereby settling to the bottom. Whereas the recovered oil product exhibiting a lower density to that of the condensing liquid, i.e. the lighter oil fraction/s, reported to the top of the condensing liquid.

Fonts et al. (2009) conducted pyrolysis in a fluidized bed reactor on anaerobically digested sewage sludge originating from wastewater treatment works. The present work utilizes a vertical retort, however the similarity between the systems is the pyrolysis heat provided via electrical energy. This is opposite to what most of the other authors in the field have used thus far. The characteristic of fluidized bed technology requires heat injected directly into the fluidized bed. In the present work external heating is affected upon the walls of the retort chamber in order to provide the pyrolysis heating requirement for liberation of the organic fractions contained in the feed material.

Hoffman & Fitz (1968) and *Sanchez et al. (2008)* also utilized external electrical heating for pyrolysis of municipal waste and agricultural residues respectively, in order to recover valuable products such as oil, char and gas. *Fonts et al. (2009)* system also comprised a cyclone and hot filter following the reactor to affect fine particulate removal from the gas stream. *Fonts et al. (2009)* explains that metals in

the char entrained particles would favour ageing of the liquid therefore stressing the importance of particulate removal. The present work combined the particulate removal and gas condensing stages into one unit, i.e. condenser with tray sieves. The pyrolysis gases bubbled into the system was dispersed via the tray sieve mesh for efficient condensation and was appropriately installed above the pyrolysis gas entry point. The sieve mesh simultaneously ensured that particulates were retained between the two sieve meshes, i.e. above and below the pyrolysis gas piping entry.

2.2 Summary of Key Operational Criteria *(elements, functions and critical parameters)*

Other authors cited in this research have successfully conducted pyrolysis on various materials identified as oil, char and gas producers but most of their experimentation was based on small laboratory scale. It has also been identified that they do not delve into the resultant emissions from their processes, and subsequent emission compliance. This could be due to the fact that a considerable volume and gas flow is required for online emission sampling and analysis, which is not readily achievable in laboratory scale experiments. The current study was aimed at bridging this gap by ensuring that an adequate gas volume and flow will make possible online emission monitoring, thereby being able to prove emission compliance whilst simultaneously extracting valuable products from refinery residue *(hazardous waste)*. The experimental batch equipment of the present study is operated on a pilot-scale *(semi-commercial operation)* which conforms to industry standards of construction and can be scaled up for full commercial operation without losing the integrity of the operational parameters required to satisfy emission compliance.

The front-end experimental equipment design in this study was informed from key elements as identified by various authors as discussed above, and the summary of considerations are shown in **Tables 2.2 – 2.6**, and depicted in **Figure 3.1**. Further note that the equipment references found in **Tables 2.2 – 2.6** can be found in the equipment list in **Table 3.1**.

Table 2.2 Summary of external heating operation, corresponding authors and applicability to present work

Key operational criteria	Author	Diminutive description	Present work
External heating	*Heuer (1991)*	High temperature oil and water vapor recycled from the process was used as a heating source.	Electrical energy provided by heating elements *(R101-E)* was used as the heat source which was on the outside wall of the retort, thereby allowing heat transfer to be affected externally through the retort chamber wall *(R101-C)*.
	Hogan (1996)	A heater comprising a burner was used where gases were burnt generating a hot exhaust as the heating source.	
	Robertson (2002)	Heat was recycled from the afterburner gas stream following combustion of the off-gases released from the feed material.	
	Wenning (1993)	A gas burner was utilized to generate a hot exhaust gas as the external heating source.	
	Magedanz et al. (1983)	Hot gases generated in the process are passed through the traveling grate bed in the retorting zone in order to heat the bed up to the required retorting temperature.	

Table 2.2 cont… Summary of external heating operation, corresponding authors and applicability to present work

Key operational criteria	Author	Diminutive description	Present work
External heating	*Weggel (1972)*	An initial gas stream containing combustion gases is passed into contact with a plurality of heat transfer media such as alumina balls. Upon contact of a second gas stream with the heated alumina balls, indirect heating takes place between the initial and second gas stream without co-mingling of the two gas streams. The heated second gas stream is passed through the shale in the retorting zone, in order to achieve the required retorting temperature for oil removal.	As specified in Table 2.2 above.
	Breu (1993)	A burner and associated combustion chamber utilizing gas was used as the heating media for the process.	
	Fonts et al. (2009)	The fluidized bed reactor was heated via an electrically driven furnace with specific heating zones for the relevant application, i.e. bed, free-board and cyclone.	
	Cornelissen et al. (2009)	The pyrolysis reactor was externally heated via a heating jacket.	
	Hoffman & Fitz (1968)	Utilization of an externally heated batch retort using electrical energy.	

Table 2.3 Summary of sealed retort operation, corresponding authors and applicability to present work

Key operational criteria	Author	Diminutive description	Present work
Sealed retort	*Hogan (1996)*	The rotary drum was sealed to ensure pyrolysis gases did not escape to the atmosphere.	A stationary sealed retorting chamber *(R101-S & R101-C)* was used to inhibit release of volatilized pyrolysis gases, prior to condensation. Also, the sealed chamber inhibited air ingress *(oxygen deficient)*, which prevented the pyrolysis gases from being destroyed by oxidation, prior to the gas being condensed to form the pyrolysis oil.
	Robertson (2002)	The rotary drum was sealed to ensure no loss of pyrolysis gases could occur and the seal also inhibits ingress of oxygen.	
	Wenning (1993)	Affected pyrolysis of non-distillable residues in the absence of oxygen by ensuring the retort was sealed from the surrounding atmosphere.	
	Magedanz et al. (1983)	Affects a virtually complete retorting in the retorting zone due to traveling grate system.	
	Weggel (1972)	Specific retorting zone to achieve oil educting conditions.	
	Breu (1993)	Particular attention drawn to the dangerous conditions achievable via feedstock mishandling prior to feeding into a pyrolytic converter, ultimately aiming at inhibiting ingress of oxygen.	
	Cornelissen et al. (2009)	Utilization of a screw feeding system to affect pyrolysis of a mixture with minimal ingress of air and to yield improved pyrolysis oil.	

Table 2.4 Summary of volatilization and condensing operation, corresponding authors and applicability to present work

Key operational criteria	Author	Diminutive description	Present work
Multi-stage volatilization, condensation & liquid product separation	*Heuer (1991)*	Multi-stage volatilization and condensing steps proposed which potentially yields a more efficient recovery of oil and water.	Initial heating of 100°C used to volatilize moisture only, thereby determining moisture content. Thereafter, oil removal was conducted at various operating temperatures provided by the heating elements *(R101-E)*, i.e. 200°C, 400°C & 600°C in order to simulate multi-stage volatilization & condensation. Therefore, volatilized oil & water are condensed at different stages, and separated via gravity in the condenser *(C101)*.
	Weinecke & Unterweger (2006)	Utilization of two packed tower oil spray condensers which were operated at specific temperatures in order to yield a heavy and light oil product respectively.	
	Breu (1993)	Utilized a series of three condensing tanks with the subsequent pyrolysis vapors and a water cooling spray.	
	Heuer (1991)	Volatilized oil & water contained in the feed material are condensed together, and separated via gravity in a settler.	
	Bradley (2003)	Utilization of a number of indirectly cooled vertical condensers to fractionally condense and liquefy pyrolysis products resulting in a broader pyrolytic oil range yield.	

Table 2.4 cont… Summary of volatilization and condensing operation, corresponding authors and applicability to present work

Key operational criteria	Author	Diminutive description	Present work
Multi-stage volatilization, condensation & liquid product separation	*Wenning (1993)*	Two stage condensation processes utilized at 300°C & 35°C respectively.	As specified in Table 2.4 above.
	Dobele et al. (2009)	Stated that determination of pyrolysis oils composition and/or properties is efficiently achieved via fractionation. Specifically utilized a drying section for removal of moisture at 200°C.	
Condensing liquid temperature control	*Wenning (1993)*	Oil spray temperature for two condensation stages was controlled to 300°C & 35°C by removing the required amount of heat from the oil spray stream via a cooler.	The condensing liquid was maintained below 35°C *(T2)* by controlling outside temperature of condenser *(C101)* with circulating cooling liquid *(C101-W)* from the cooling tower, which was recycled to remove heat of condensation from the process.

Table 2.5 Summary of particulates & solids removal operation, corresponding authors and applicability to present work

Key operational criteria	Author	Diminutive description	Present work
Particulate removal	*Hogan (1996)*	The vapor stream containing particulates was subjected to a counter-current hot oil spray for particulate removal.	A two-stage tray sieve mesh was utilized, i.e. above & below the pyrolysis gas entry point into the condenser *(C101)*. The top stage sieve mesh *(C101-SMt)* inhibited light particulates from reporting to the light oil phase *(top of condensing liquid)*, and the bottom sieve mesh *(C101-SMb)* inhibited heavy particulates from reporting to the heavy oil phase *(bottom of condensing liquid)*.
	Wenning (1993)	Particulates were scrubbed utilizing an oil spray which was simultaneously used as a condensing spray.	
	Breu (1993)	Particulates were removed by gravitational settling.	
	Fonts et al. (2009)	The fluidized bed system utilized a cyclone and a hot filter which was installed directly after the reactor to ensure fine particulate removal from the gas stream.	

Table 2.5 cont… Summary of particulates & solids removal operation, corresponding authors and applicability to present work

Key operational criteria	Author	Diminutive description	Present work
Solids cooling	*Hogan (1996)*	The processed solids flow through a cooling section of the rotating drum which have no external heating present thus radiating the heat out of the drum.	Final cooling of the solids following complete processing was affected via the removal of the sealed retort chamber *(R101-C)* and by lowering half of the chamber into a cooled water bath.
Solids combustion	*Hogan (1996)*	The heated solids passed through an oxidising section containing oxygen thereby promoting the combustion of the solids and undesirable compounds in order to yield heated combustion products for utilization in the form of process heat integration.	It was not desired to contact the heated solids with an oxygen source as it would promote oxidation of the heated solids, which would result in the loss of one of the valuable product yields. However, the solid char product was quantified as per the scope of this study, and it was also envisioned that through the analyses of the char product would it be possible to verify if it could potentially be utilized as a co-processing carbon fuel source.
	Magedanz et al. (1983)	The solid char product was passed through a combustion zone in order to generate an adequate amount of heat to transfer into the traveling grate bed in the retorting zone.	

Table 2.6 Summary of various gas operations, corresponding authors and applicability to present work

Key operational criteria	Author	Diminutive description	Present work
Inert atmosphere	*Hogan (1996)*	Exhaust gases from the retort burner was used to provide an inert atmosphere in the vaporization zone.	The hydrocarbon gaseous constituents liberated during pyrolysis provided sufficient gases in the retort chamber *(R101-C)*, which contributed to the non-oxidising atmosphere.
Off-gas combustion	*Robertson (2002)*	The total pyrolysis gas yield was subjected to combustion thereby oxidizing all the gaseous constituents in an afterburner.	The pyrolysis gas was initially condensed *(C101)* in order to produce a non-condensable gas stream which was quantified, sampled *(S1)* and thereafter subjected to combustion in an oxidizer *(C201)*.
Non-condensable gas removal	*Wenning (1993)*	Removal of the non-condensable gases from the system was affected via the pressure of an existing gas network.	The present work achieves the removal of the non-condensable gas stream via the utilization of an induced draft fan (ID-f) situated at the back end of the process, i.e. negative pressure system.
	Magedanz et al. (1983)	The removal of the non-condensable gases and other gaseous products are affected via the utilization of wind suction boxes.	

Table 2.6 cont… Summary of various gas operations, corresponding authors and applicability to present work

Key operational criteria	Author	Diminutive description	Present work
Non-condensable gas recycling	*Wenning (1993)*	Part of the non-condensable pyrolysis gases is recycled through the coke discharge outlet in order to prevent partial condensation of some of the higher boiling pyrolysis oil fractions at the discharge end of the rotating tube, for the removal of the coke product.	No recycle of non-condensable gases used due to absence of rotary action. The batch chamber *(R101-C)* utilized ensured that the subsequent solids or coke product was retained in the retort chamber, which by the conclusion of the final run would be virtually free of liquid volatile constituents.
	Magedanz et al. (1983)	The non-condensable gases were passed through the bed to attain the retorting temperature required.	The option of passing the heated gas stream around the retort chamber *(R101-C)*, did not exist due to the chamber being externally heated via electrical elements *(R101-E)*. Non-condensing gas stream was quantified prior to passing through a thermal oxidizer *(C201)* for gas treatment.

3 EXPERIMENTAL METHOD AND APPARATUS

3.1 Process Description and Experimental Procedure

The pyrolysis experiments were carried out in the experimental design equipment shown in **Appendix A**, **Figure A1** and **Figure A2**, corresponding to the reference list in **Table 3.1**. *(**Figure A2** is an alternative representation of **Figure A1** which includes detailed labeling consistent with the reference list on Table 3.1).* It must be noted that the experimental procedure must be read with the equations designed specifically for the quantification of the feed material, moisture content, liquid and solid product yields. The equations of which can be found in **Appendix B**, which also includes the discussion of the experimental procedure and concomitant calculations required for the investigation. In order to maintain brevity of this section without duplication, the applicable equation reference number will be used thereby also cross-referencing the applicable experimental procedure and discussion.

The materials of construction of the vertical retort *(R101)* and the batch retorting chamber *(R101-C)* were fabricated from special alloy steel. Even though the total capacity of the retort chamber was 1200 liters, for the purpose of the experiment, a material volume of approximately 1000 liters was used during each investigation. The dimensions of the retort chamber proved to be important as it formed an integral part of the experimental procedure regarding cross-referencing the product yield calculations, (**eq.1, eq.2, eq.3, eq.4, Appendix B**). Prior to loading of the retort chamber the residue feedstock was subjected to continuous stirring over a 24 hour period which ensured a homogeneous mixture was used during the experimentation. Once the homogenous sample was loaded into the retorting chamber, the height of the feed material was measured and used in combination with the proportions of the retort chamber in order to accurately establish the initial volume of feedstock used in the experimental investigation, (**eq.1, Appendix B**).

Thereafter, the specialized lid mechanism with a high temperature resistant gasket *(R101-S)* was installed and adequately sealed which maintained a closed system which was kept under vacuum by initiating the induced draft fan *(ID-f)*. This ensured that:

i) As much air could be removed from the closed system as possible,
ii) gaseous pyrolysis vapors formed during the heating process, did not escape to atmosphere, and
iii) air ingress was inhibited into the retort chamber, thereby maintaining the highest degree of pyrolytic conditions as possible.

Approximately 600 liters of the condensing liquid was loaded into the condenser *(C101)* up to the set point stipulated on the graduated sight glass *(C101-S)*. Each experimental run was initiated by bringing the retort up to the pyrolysis temperature requirement of each specific run, i.e. 100°C, 200°C, 400°C & 600°C. The heating rate of the material was approximately 20°C/min and measured continuously for each of the experimental runs, in order to maintain consistency. The retort chamber was indirectly heated using electrically driven elements *(R101-E)* which was controlled by a thermocouple *(T1)*. The bubbling action began in each subsequent run once the temperature stood at the desired set point for a required time period. The volatilized pyrolysis gases bubbled through the condenser liquid to yield pyrolysis oil fractions. The level of the feed material decreased in the retort chamber following the completion of each run at the various temperature setpoints as mentioned above. The subsequent decrease in the feed material liquid level is therefore measured and calculated, (**eq.2, eq.3, eq.4, Appendix B**).

However, during the final experimental run at 600°C, only solid carbonaceous char remains in the retort chamber, which is stripped of volatile organic material. The char product contained in the retort chamber requires cooling prior to opening the retort lid, as lack of cooling could cause the carbonaceous char to ignite upon exposure to air. Therefore, the cooling of the char following complete processing was effected by removing the sealed

retort chamber and submerging half the chamber into a cooling bath. Thereafter, the cooled char product is thus collected, weighed and sampled. The char sample is then crushed and added to a container of known volume, thereafter it is weighed for calculation of its density, and finally subtracted from the initial volume of feed material prior to the run at 600°C, (**eq.5, Appendix B**).

The effective temperature inside the condenser was measured using a thermocouple *(T2)*, which adequately maintained the condensing liquid temperature at below 35°C by controlling the outside temperature of the condenser unit with a circulating cooling liquid *(C101-W)*. This cooling liquid was recycled from a cooling tower to remove heat of condensation radiating from the process. A two-stage tray sieve mesh was utilized, i.e. above and below the pyrolysis gas entry point into the condenser *(C101)*. The top sieve mesh *(C101-SMt)* inhibited light particulates from reporting to the light oil phase *(top of condensing liquid)*, and the bottom sieve mesh *(C101-SMb)* inhibited heavy particulates from reporting to the heavy oil phase *(bottom of condensing liquid)*. The top sieve mesh *(C101-SMt)* also allowed for dispersion of large pyrolysis bubbles, thereby increasing the surface area for gas-liquid contact.

During each run the discontinuation of the bubbling action indicated that the de-volatilization reaction is complete for boiling fractions liberated at that specific temperature set point. The oil product yield was determined by the rise of the liquid height measured on the graduated site glass, and the resultant volume calculated accordingly, (**eq.6, eq.7, eq.8, eq.9, Appendix B**). In order to determine the percentage of the non-condensable gas product yield, a level measurement was taken to determine the volume of feed volatilized following each run. The subsequent difference between the volume volatilized and the volume of liquid condensed resulted in an accurate means of determining the non-condensable gas product yield, (**eq.10, eq.11, eq.12, eq13, Appendix B**).

The negative pressure on the system was affected by the induced draft fan *(ID-f)*, situated at the back end of the experimental plant. The induced draft facilitated the movement of the pyrolysis gases through the thermal oxidizer *(C201)* operated at 1200°C for gas oxidation, and venturi scrubber *(C301)* and packed column *(C401)* for conventional gas clean-up operations. The gaseous stream exiting the condenser unit is a non-condensable gas which was sampled *(S1)* prior to entering the thermal oxidizer for complete oxidation.

The oxidative conditions provided in the oxidizer allows for: adequate residence time, required turbulence and high temperatures which are measured by thermocouples *(T3, T4, T5)*. Maximizing these parameters ensures that non-condensing hydrocarbon pollutants are oxidized to yield combustion products such as CO, CO_2, H_2O, SO_2 & HCl prior to gas scrubbing and eventual discharge to atmosphere. In order to assess if the pyrolysis-recovery process conformed to emission regulation guidelines, continuous online emission monitoring equipment *(CEMS-S2)* was utilized and the exiting gas stream measured for CO, CO_2, SO_2 & HCl. The emission monitoring equipment was standardized using certified calibration gas.

It should be noted that for the purposes of gas analysis and monitoring a large initial feed was required so that a reasonable flow rate was achieved. Furthermore, the downstream processing would be most efficient for large gas flow rates as achieved in the experiments. Many of the previous authors cited in the literature have conducted their pyrolysis experiments in laboratories, using very small quantities of feed material. The current work is aimed at being a fit-for-purpose *(semi-commercial scale)* batch pyrolysis plant which generates a substantial quantity of yield, allowing for steady-state to be reached, as well as providing an adequate gas flow rate for the purposes of proving compliance with emission standard regulations.

Following each subsequent run the recovered oil product is drained from the condenser *(C101)* to a settling tank *(C101-ST).* Prior to the condenser being loaded with fresh condenser liquid, the two-stage tray sieve meshes *(C101-SMt & C101-SMb)* were removed and cleaned.

Table 3.1 Reference list for Figure A1

#	Description	Ref.	#	Description	Ref.
1	Retort seal	R101-S	16	Thermal oxidizer	C201
2	Electrical element	R101-E	17	Thermocouple	T5
3	Thermocouple	T1	18	Thermocouple	T4
4	Vertical retort	R101	19	Thermocouple	T3
5	Retort chamber	R101-C	20	Water spray	-
6	Condenser	C101	21	Water recycling pump	-
7	Sight glass	C101-S	22	Water to cooling tower	-
8	Water level	-	23	Venturi scrubber	C301
9	Tray sieve mesh	C101-SMt	24	Packed column	C401
10	Thermocouple	T2	25	Water spray	-
11	Condensed oil to tank	C101-ST	26	Water recycling pump	-
12	Tray sieve mesh	C101-SMb	27	Water from cooling tower	-
13	Cooling water level	-	28	Water to cooling tower	-
14	Cooling tower water	C101-W	29	Induced draft fan	ID-f
15	Sample point	S1	30	Emission monitoring	CEMS-S2

4 DISCUSSIONS AND RESULTS

4.1 Characterization of feed material

The experiments were performed on hydrocarbon-rich residue which can be categorized as hazardous due to the presence of compounds such as benzene, xylene, dibenzo-para-dioxin *(PCDD)*, dibenzofuran *(PCDF)* as well as poly-aromatic hydrocarbons *(PAH)*, all of which lends themselves to the hazardous nature of the feed material. Hazardous waste classification includes numerous sources of hydrocarbon rich sludge from refinery site works, i.e. sludge from separator bottoms, heat exchanger sludge, slop oil emulsion solids and crude oil tank bottoms *(crude oil, distillates, decant oil, bunker) (Leeman 1985)*. The hazardous classification of the hydrocarbon rich sludge reduces its utilization, as is, into other refinery processes, as the risk of jeopardizing the integrity of other refinery produced products will be substantially increased.

The characterization of feed material used in this study was determined by proximate and ultimate analyses, **Figure 4.1**, showing a carbon rich *(68.4%)* feedstock, high oxygen content *(14.5%)* and also exhibiting a significant quantity of sulphur *(2.1%)*. The ash content *(3.2%)* is relatively low, opposed to the high volatile content *(86.4%)*, and also containing 10.5% moisture. The calorific value of the feedstock is 17.8 MJ/kg. The physical characteristics of the feed material constituted a thick, highly viscous, non-flowing and brown-black material at room temperature, and also emitted a pungent odour which is an irritant to the respiratory system.

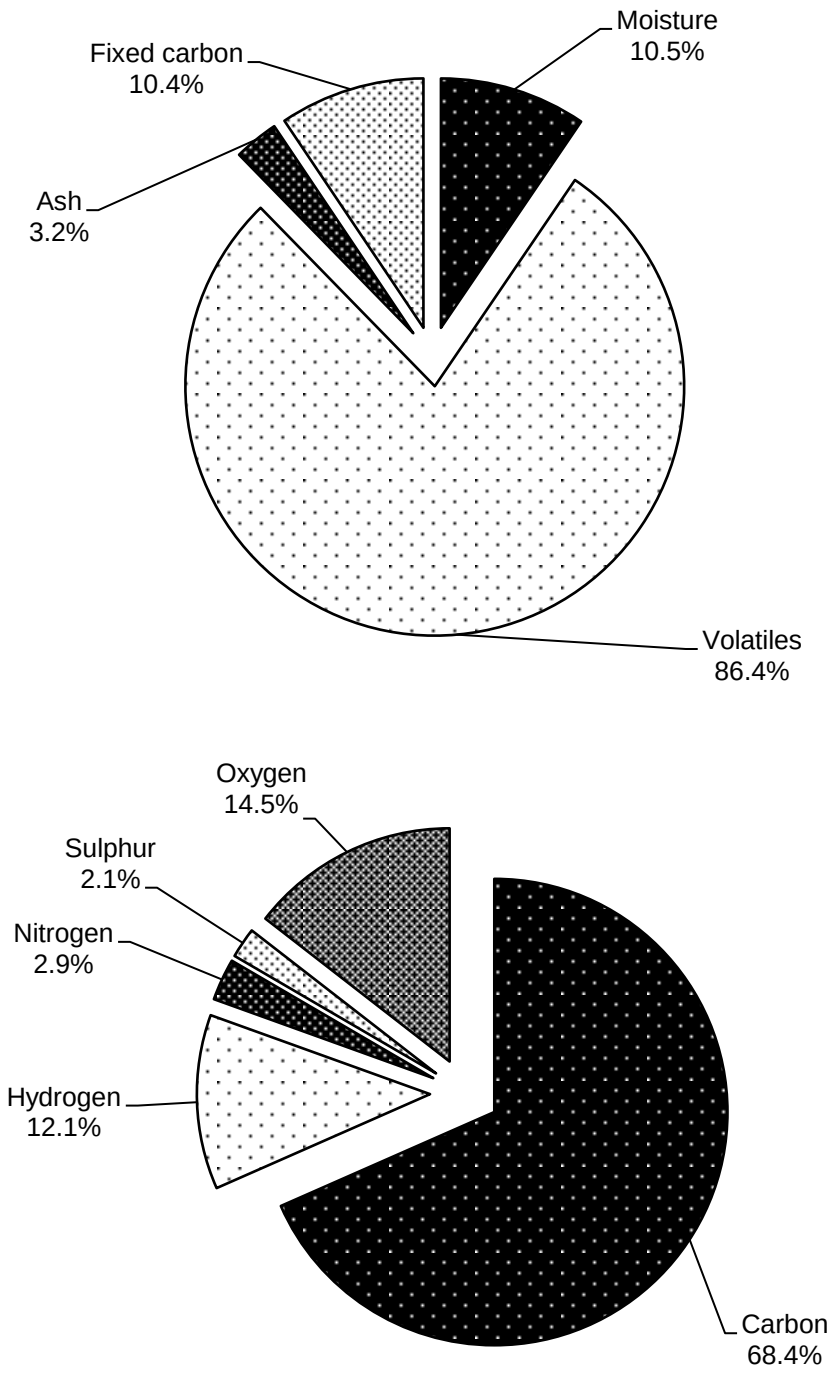

Figure 4.1 Proximate and ultimate analyses of feed material

4.2 Pyrolysis product yields

Table 4.1 shows the product yields attained at intermediate temperatures of 100°C - 600°C, of the oils, non-condensable gases and char *(only at 600°C).* It is interesting to note that equal amounts of non-condensable gases are produced between 200°C - 400°C. These could be attributed to the formation of radicals and subsequent formations of light alkanes and hydrogen. However, a larger yield of oils results at 400°C. At 600°C, it is observed that the rate of non-condensable gases decreases to 1%, where mostly carbonaceous oxides are being released. The relative oil yield is still higher than at 200°C with char being formed at the end of the completed run.

It must be noted that even though the experimental runs were conducted utilizing the different temperatures, it was mainly aimed at quantifying the cut fractions of pyrolysis oil attainable at those specific temperature set points, and simultaneously producing adequate amounts of non-condensable gases for quantification and gas analyses. It was not possible to quantify the char product formed during the 200°C and 400°C runs as the char formed will still remain in the retort chamber together with unprocessed feedstock, **Table 4.1**. Therefore, following the initial quantification of the pyrolysis oils attained at the inter-stage temperatures, a holistic approach was taken to quantify the char yield following the run at 600°C, as all the carbonaceous char formed from all the runs will remain in the retort chamber.

Table 4.1 Product yields at inter-stage experimental temperatures *(100°C, 200°C, 400°C & 600°C)*

Temperature	Product Yield
100°C	10% moisture
200°C	2.5% Pyrolysis oil, 2.5% non-condensable gas, % carbon char produced (unknown)
400°C	40% Pyrolysis oil, 2.5% non-condensable gas, % carbon char produced (unknown)
600°C	27.5% Pyrolysis oil, 1% non-condensable gas, 14% carbon char

The cumulative product yields determined following the pyrolysis of the hydrocarbon residue were 70% pyrolysis oil, 14% solid carbonaceous char, 10% moisture content and 6% non-condensable gas, **Figure 4.2**. *Wenning (1993)* conducted pyrolysis on four types of residues, i.e. crude oil residue, heavy hydrogenation residue, coal hydrogenation residue and coal tar, utilizing a continuous rotating retort operated at 650°C, also utilizing external heating but contrary to this study, Wenning utilized gas burners. Wenning's process incorporated the use of a two-stage condensing system at temperatures of 350°C and 35°C respectively, in order to ascertain the light and heavy pyrolysis oil yields. According to *Wenning (1993)*, the product composition from pyrolysis of crude oil residue gave 68% pyrolysis oil, 20% coke, and 12% gas, **Figure 4.3**, which is surprisingly similar to the pyrolysis yields attained in this research work. Residues with low aromatic content only achieves low conversion to coke *(Wenning 1993)*, which could have been the case in the feed material used in the present study.

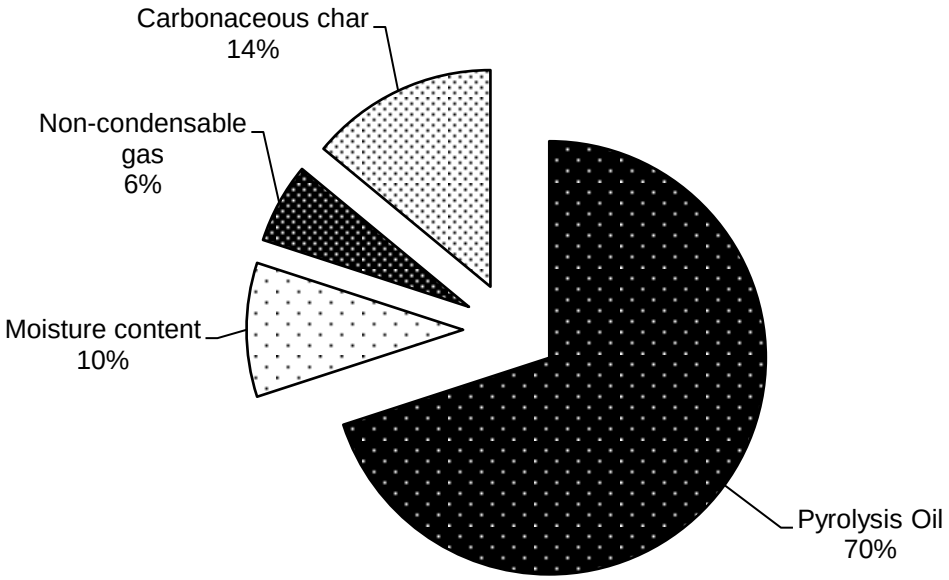

Figure 4.2 Main product yields from batch pyrolysis *(up to 600°C)*

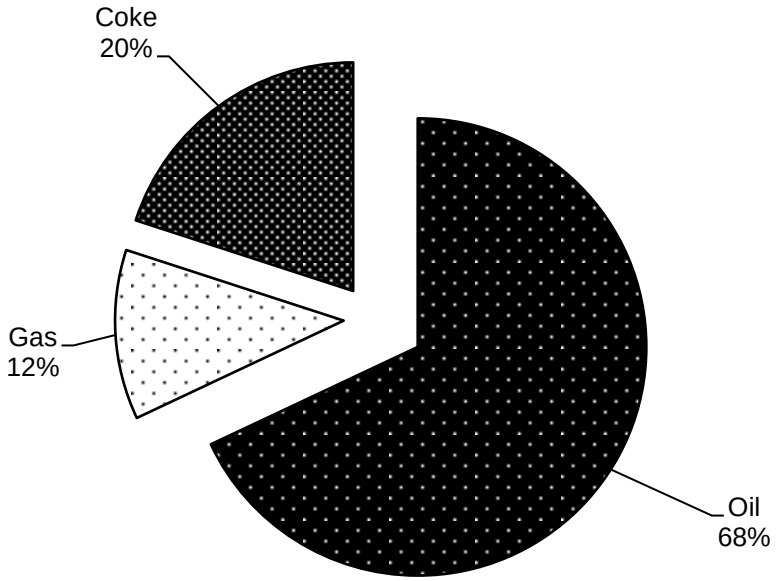

Figure 4.3 Product yields from pyrolysis of crude oil residue. *Journal of Analytical and Applied Pyrolysis, vol. 25, 301 - 310 (derived from Wenning 1993)*

Figure 4.2 is a representation of the rounded average of the results attained from the ten day experimental testing period. The matrix of tests was conducted in order to verify the reproducibility of results over various runs. The data captured from the various tests can be seen in **Appendix C: Experimental Data - Yields**. Also in **Appendix C** are calculated values using the raw data, which are clearly defined and distinguished by the key stipulated in this appendix. Sample calculations and rationale are shown in **Appendix B: Sample Calculations and Method Discussion**. As can seen from **Table 4.2,** the reproducibility of results show very consistent trends in the yields attained, which was primarily due to the mixing action of the entire refinery residue sample (approximately 10 tons) in order to sustain a homogenous mixture of the feed material.

Table 4.2 Product yields over the 10 day experimental test period

	Feed Volatilized (%)	**Pyrolysis Oil (%)**	**Moisture content (%)**	**Non-condensable gas (%)**	**Carbonaceous char (%)**
Day 1	85.8	70.1	10.3	5.4	14.2
Day 2	86.2	70.2	9.6	6.4	13.8
Day 3	85.7	69.5	10.0	6.2	14.3
Day 4	86.4	70.7	9.9	5.7	13.6
Day 5	85.6	70.0	10.0	5.6	14.4
Day 6	86.2	70.1	10.3	5.8	13.8
Day 7	85.5	69.6	9.8	6.1	14.5
Day 8	86.1	70.0	10.0	6.1	13.9
Day 9	85.5	70.4	9.7	5.4	14.5
Day 10	85.6	70.2	9.6	5.8	14.4
Average (rounded)	**86.0**	**70.0**	**10.0**	**6.0**	**14.0**

4.3 Characterization of liquid products

As explained earlier, the feed material was initially heated to 100°C in order to volatilize moisture only, thereby determining the total moisture content prior to determination of pyrolysis oils. Oil removal was conducted at various operating temperatures, i.e. 200°C, 400°C & 600°C in order to simulate multi-stage volatilization & condensation. Therefore, volatilized water and oil are condensed at different stages respectively, and separated via gravity in the condenser according to their disparity in density.

4.3.1 Moisture content determination

The initial 100°C run proved its validity, as the bubbling action yielded a 10% reduction of the initial volume of feed material. **Table 4.3** clearly shows that there are no common elemental or hydrocarbon pollutants present in the condenser liquid. Also, the acidity or alkalinity of the liquid is an adequate indicator as to the components contained in the condensing liquid. Following the run, the pH of the condenser liquid changed from 7.09 to 7.17, which proved the presence of other volatilized organics, but in negligible quantities, **Table 4.3**. But most important, the moisture content can be considered as accurately determined, as the analysis of the condensing liquid showed non-detectable hydrocarbon constituents.

Table 4.3 Elemental and hydrocarbon analyses of condensing liquid following pyrolysis at 100°C

Elemental pollutants	**ppm**
Arsenic	Non-detectable < 0.02
Bromine	Non-detectable < 0.02
Cadmium	Non-detectable < 0.02
Cobalt	Non-detectable < 0.02
Chlorine	Non-detectable < 0.02
Chromium	Non-detectable < 0.02
Lead	Non-detectable < 0.02
Lithium	Non-detectable < 0.02
Manganese	Non-detectable < 0.02
Mercury	Non-detectable < 0.02
Molybdenum	Non-detectable < 0.02
Nickel	Non-detectable < 0.02
Vanadium	Non-detectable < 0.02
Zinc	Non-detectable < 0.02
Hydrocarbon pollutants	**percentage (%)**
Benzene	Non-detectable < 0.01
Toluene	Non-detectable < 0.01
Ethylene	Non-detectable < 0.01
Xylene	Non-detectable < 0.01
Phenols	Non-detectable < 0.01
Cresols	Non-detectable < 0.01
Other Hydrocarbons	Non-detectable < 0.01
pH	7.17

4.3.2 Characterization of pyrolysis oil

Sanchez et al. (2008) states that oil derived from pyrolysis is one of the more desired products, mainly due to it being a carbon-rich oxygen fuel having a small proportion of nitrogen and sulphur. From the proximate analysis conducted on the pyrolysis oil, this can be seen as confirmation to *Sanchez et al. (2008)* description of pyrolysis oil. **Table 4.4** shows the various properties of the pyrolysis oils at 200°C, 400°C & 600°C. The final boiling points are consistent with the change in the programmed heating rate corresponding to the different temperatures. The densities indicate that lighter oils are produced at lower temperature where most of the rapid devolatilization occurred. Higher temperatures allow secondary reactions to form longer and denser oils as depicted by the increase in the density at 600°C.

The ash content is of particular interest as it indicates that the ash composition of the heavier oil is the lowest. It is not clear whether this is due to the lack of vigorous devolatilization at higher temperatures or that char particles are entrained at lower temperatures leading to higher ash contents, *(200°C & 400°C)*. From physical inspection, it can be seen that the oil yield obtained at 600°C was of a darker grey color opposed to the previous two oil yields which where opaque *(200°C & 400°C)*. This is indicative of the heavy tar compounds contained in the oil product at 600°C. Therefore, it rules out the possibility that higher ash content could be a result of entrainment of particulates, as the expectation of this would be greater at 600°C resulting from condensation of tar-like compounds which lends itself to higher entrainment of heavy compounds, due to the increased viscosity and pour point of the condensed droplets. Therefore, the decreasing ash content could be a result of a less vigorous devolatilization. This is due to the reduced heat transfer penetration through the coated carbonized solids to the outer walls of the retort chamber.

The viscosities of the oil products show an increasing trend from 3.07 – 5.52 centistokes *(cSt)*, which is comparable to the diesel oil viscosity ranges stipulated by ASTM standards *(ASTM D445)* for kinematic viscosity @ 40°C. *Karayildirim et al. (2006)* reported an oil viscosity of 5.38 cSt from pyrolysis of petrochemical sludge, which falls within the viscosity range of pyrolysis oil attained in this study. *Karayildirim et al. (2006)* also maintains that further consideration must be taken prior to utilizing such viscous oils as fuels or chemical feed stocks. Further adjustment of the viscosity would need to be explored to reduce the viscosity to within the stipulated range *(i.e. 2.0 – 4.5)*, if the fuel is to be utilized as a burner fuel. This consideration needs to take cognizance of increased viscosity as it affects fuel atomization, because higher viscosity fuels results in larger droplets which subsequently reduces combustion efficiency.

The oil obtained at 200°C showed the highest heating value of 42.3 MJ/kg, compared to the 41.9 MJ/kg at 400°C & 40.5 MJ/kg at 600°C, **Table 4.4**. But the percentage recovery of oils yielded at 200°C was only 2.5% opposed to the oil yield of 40% and 27.5% at temperatures 400°C & 600°C respectively, **Table 4.1**. Therefore, the oil obtained above 400°C is of greater interest in the present study. As can be seen from **Figure 4.4** the carbon content of the recovered oils has increased significantly by 14.3% and 15.7% at temperatures 400°C & 600°C respectively, as compared to that of the feed material. This is indicative of the increased heating values obtained in the pyrolysis oil compared to the relatively low heating value of the feed material. The increase in carbon content of these oils *(400°C & 600°C)* now show 82.7% and 84.1% respectively, which is comparable to *Karayildirim et al. (2006)* pyrolysis oil from petrochemical sludge which showed a carbon content of 84.5%. Moreover, *Karayildirim et al. (2006)* compared commercial diesel fuel showing an 86.5% carbon content. As identified by *Ngan et al. (2003)* the capability of elevated operating temperatures above 415°C is not readily available in distillation columns, and a pyrolysis process could easily meet this requirement. Therefore, the densities of the pyrolysis oils could be predicted as being indicative of heavy crude components.

This was verified by the 400°C & 600°C pyrolysis oils, which exhibited densities of 971 kg/m^3 and 996 kg/m^3 respectively.

Sanchez et al. (2008) also refers to low ash and low sulphur content identified by *Ozcimen & Karaosmanoglu (2004)* which validates the potential use of pyrolysis oil as a heating fuel. However, cognizance needs to be taken regarding the presence of sulphur as the combustion of which would result in the generation of SO_2 which requires gas-scrubbing processes. The present work utilized an oxidizer and gas-scrubbing equipment in order to attain a clean off-gas stream which was reported within South African National emission limit guidelines.

The extraction of pyrolysis oil from hydrocarbon residue has resulted in the conversion of hazardous waste, which is recognized/considered as material recycling *(Wenning 1993)*. In environmental terms, the extraction of oil from the residue has not only resulted in obtaining a valuable product, but has also contributed positively to the reduction of volume of hazardous waste which would previously have been incinerated as a method of disposal.

Table 4.4 Properties and Proximate analysis of pyrolysis oils *(200°C, 400°C & 600°C)*

	200°C	**400°C**	**600°C**
Heating value (MJ/kg)	42.3	41.9	40.5
Density (kg/m3)	682	971	996
Final Boiling Pt. (°C)	202	390	503
Ash Content (%)	0.128	0.106	0.004
Viscosity @ 40 °C (cSt)	(3.07 – 5.52)		

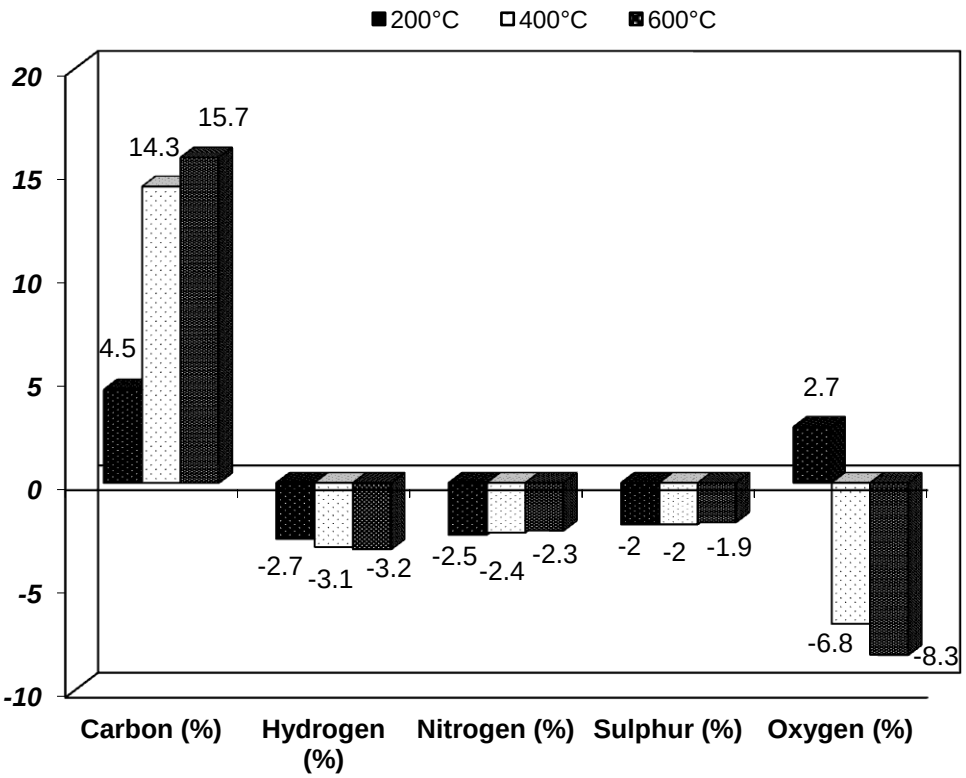

Figure 4.4 Differences in chemical analyses of original feed material and oil yields

4.4 Characterization of solid char product

A solid char product was obtained following complete volatilization of the organic fractions contained in the feed material after the subsequent 600°C run. The physical nature of the char product was a brittle material which took the shape of the retort chamber. This occurred due to the carbonization reaction which took place and the deposits of which settled to the bottom of the chamber thus molding and forming inside the retort chamber. The char product can easily be milled to a specific size characterization in order to serve as a pulverized solid fuel co-feed to a boiler for example. The density of the char was reported at 1390 kg/m^3.

Proximate and ultimate analysis was conducted on the char product. As predicted from pyrolysis, a carbon-rich char product is obtained which demonstrates an increased fixed carbon content of 77.6% to that of the original feed material exhibiting only 10.4%, **Figure 4.5**, also largely dependent on the ash content as identified by *Fonts et al. (2009).* The carbon content is a positive 82.1%, and the subsequent low sulphur content of 1.1% proves that the char product can be utilized as a potential solid fuel source, **Figure 4.10**. Even though sulphur content is relatively low the presence of which cannot be ignored, as explained earlier. A decrease in the hydrogen content from 12.1% to 3% can be seen, **Figure 4.5**, which could be due mainly to the hydrogen reporting to the volatilized stream, possibly promoting a minimal amount of hydrogenation of the gaseous stream, thereby forming more valuable compounds which condensed to the high heating value liquid product *Li et al. (2009).* But literature suggests that a major portion of which will exit the condensation process constituting part of the non-condensable gas stream *(Fonts et al. 2009), (Hoffman & Fitz 1968), (Sanchez et al. 2008),* the validation of which can be seen in **Figure 4.6**, as H_2 constitutes 18.8% of the non-condensable gas stream.

Due to the elevated temperatures affected inside the retort chamber, it could be predicted that the moisture and volatiles contained in the char product would be in trace amounts, i.e. moisture and volatile content are 0.9% and 1.4% respectively. The heating value of the char product *(32.2 MJ/kg)* is substantially higher than the feed material *(17.8MJ/kg)*. According to *Sanchez et al. (2008)* this could be attributed to a low ash content of between 22 – 29% and low oxygen content. The analytical results show an oxygen content of 11.7% and also an ash content of 20.9% which is less than the low ash range explained by *Sanchez et al. (2008)*, thereby validating the high heating value.

The subsequent heating value of the solid char product showed similarities to heating fuels which are generally accepted in literature *(Inguanzo et al. 2002)*. Also see **Figure 4.10** for potential utilization of the solid char product. The extraction of pyrolysis char from hydrocarbon residue can also be recognized/considered as material recycling, as described by *Wenning (1993)*. In environmental terms, the extraction of char from the hazardous feed has resulted in gaining a valuable product. This also contributes positively to the reduction of volume of the hazardous waste which would previously have been incinerated, and the resultant ash sent to a classified landfill as a method of disposal.

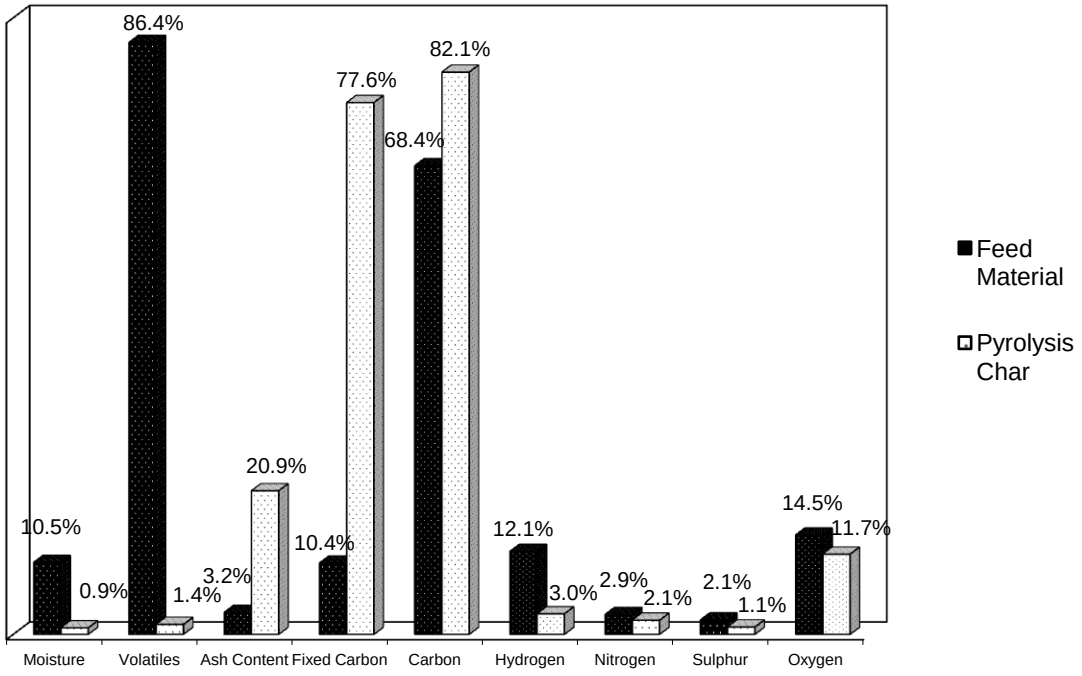

Figure 4.5 Comparison of proximate & ultimate analyses of original feed material and carbon char product

4.5 Characterization of gases

4.5.1 Characterization of non-condensable gas product

Ahmed et al. (2009) and *Wenning (1993)* maintains that high temperature pyrolysis results in the decomposition of long chain hydrocarbons into shorter hydrocarbon chains. Evidence of this can be seen in the present work, as the lighter fractions contained in the off-gas, **Figure 4.7,** can potentially be utilized as a heating stream as it contains light hydrocarbons such as methane, ethane, etc. which exhibit much higher heating values as compared to that of heavier hydrocarbon fractions. The determination of the non-condensable gas yield has shown an overall 6% throughout the experimentation. Moreover, the identification of the components of this gas stream would accurately determine if the use of this gas stream as a potential heating source is a viable option. The gas stream was analyzed by GC-MS[1] and GC-FID[2]. The major constituents of the non-condensable gas stream amounting to over 71.2%, **Figure 4.7**, was that of CO_2, CO and H_2, making up 31.6%, 20.7% and 18.9% respectively, **Figure 4.6**.

The lighter fractions of CH_4, C_2H_6 and C_2H_2 contributes positively to an overall higher heating value, but their total concentration only amounts to 25.5%, which is relatively low, **Figure 4.7**. The presence of CS_2 again shows that gas-scrubbing processes would be required if this gas stream is subjected to combustion to yield heat. The potential use of the non-condensable gas stream as a heat source following combustion via stoichiometric oxygen addition was theoretically calculated, and the estimated gross calorific value is approximately 240KJ/mol. This is comparable to pure hydrogen of 285KJ/mol. The estimated value is lower due to the presence of

[1] Gas Chromatography – Mass Spectroscopy
[2] Gas Chromatography – Flame Ionization Detector

CO_2 *(31.6%)* but the presence of the light alkanes/alkenes *(~890KJ/mol)* brings the overall to a reasonable 240KJ/mol.

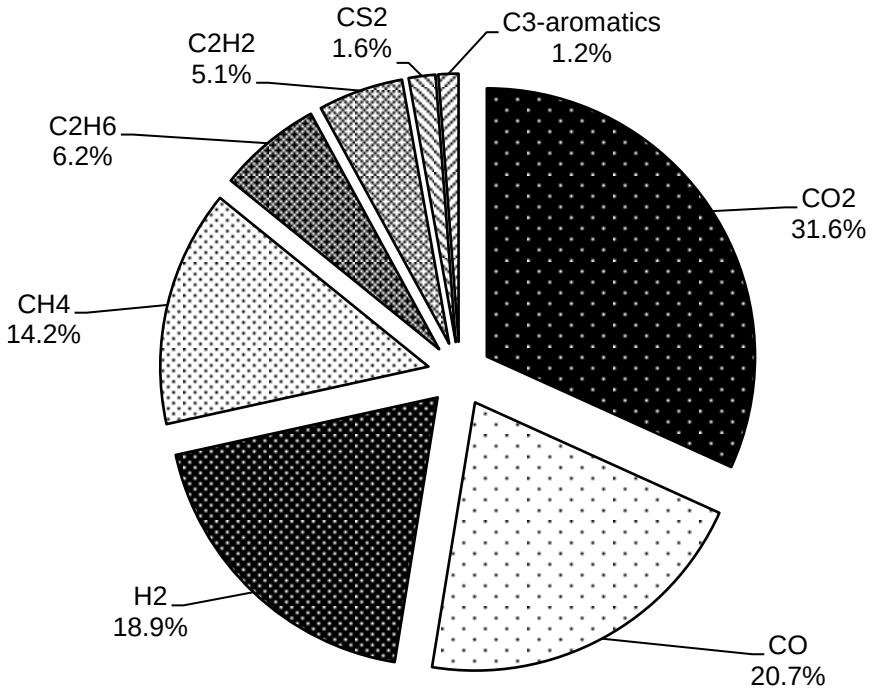

Figure 4.6 Composition of the non-condensable gas stream

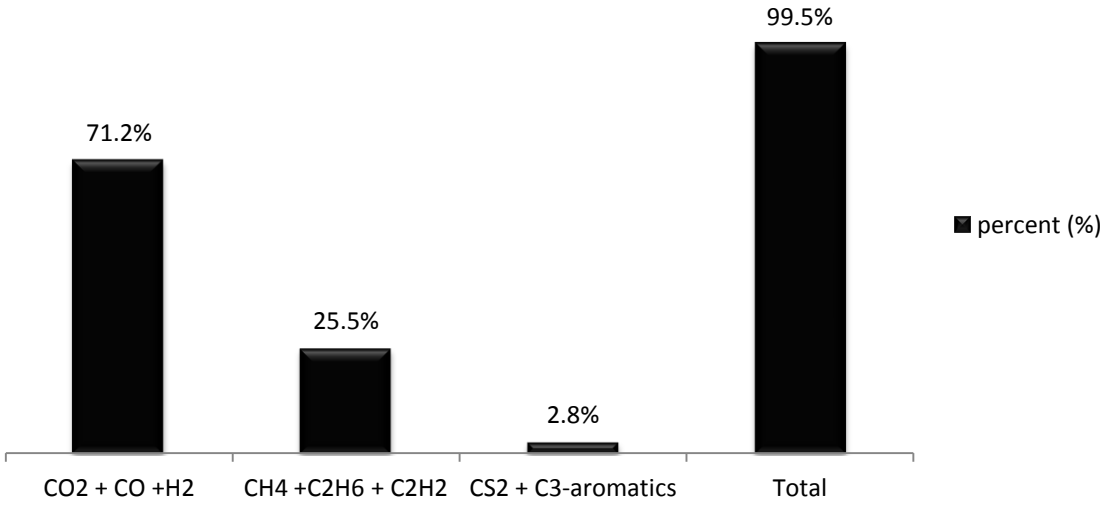

Figure 4.7 Composition of non-condensable gas product stream from pyrolysis of hydrocarbon residue

4.5.2 Characterization of combustion products

The non-condensable gas stream contains hydrocarbons *(25.5%)* which require complete oxidation, prior to gas scrubbing processes and the subsequent release of the compliant gases to the atmosphere. Therefore, the non-condensable gas stream pollutants were passed through a thermal oxidation process. The thermal oxidizer is provided with sufficient turbulence *(centripetal gas flow)* and adequate residence time *(> 2 seconds)* which ensures that the entering gas stream is completely oxidized, yielding combustion products such as CO_2, H_2O, SO_2 and HCl. The subsequent gas stream containing combustion products is passed through a gas-cleanup system comprising of a quench and venturi caustic scrubber, as well as a raschig ring packed column, prior to the gas stream being discharged to atmosphere. The gas-cleanup system contains cooling sprays which ensure that the gas stream exiting the oxidizer is adequately cooled, and acid gases are condensed to a liquid phase acid solution. This reduces the amount of chlorine *(available in gas form)* leaving the process via the stack.

The subsequent liquid acid which is formed is neutralized with a caustic solution, thereby promoting the production of a neutralized liquid containing resultant salts and precipitates. The packed column provides adequate residence time for gases to be in contact with the cooling liquid for adequate removal of particulates, halides and heavy metals, if any. Finally, the neutralized liquid containing dissolved salts, particulates, and any other heavy metals are filtered to affect adequate removal of these materials, prior to recycling as a cooling liquid. A fresh cooling liquid feed is charged into the liquid recycling system, once saturation tests prove too high thereby reducing the scrubbing efficiency. Also, a significant amount of the cooling liquid which contacts the hot gases instantaneously converts to steam, which is expelled through the stack, and constitutes a major portion of the stack gas leaving the process. The gas-cleanup system serves as a final polishing step which ensures that

combustion product pollutants are reduced to a minimum prior to atmospheric discharge.

In order to assess if the pyrolysis of hydrocarbon residue conformed to emission regulation guidelines, continuous online emission monitoring equipment was utilized and the exiting gas stream measured for CO_2, CO, SO_2 and HCl, at the stack. The hourly average for emission measurements taken during the testing period can be seen in **Appendix D: Experimental Data – Emissions**. can be It can be seen from **Figure 4.8** that throughout the experimental runs, the contaminant levels were well below South African National emission limit guidelines *(Environment South Africa 2009)*. Emission results reported was also compared to International European *(DIRECTIVE 2000/76/EC)*, and United States Environmental Protection Agency *(Environmental Protection Agency 2005)* emission limit guidelines, **Table 4.5**.

Table 4.5 National *(SA)* & International *(EU & US EPA)* emission guidelines

Determinant	US EPA Guidelines	EU Guidelines	SA Guidelines
CO_2 (%)	-	-	< 21
CO (mg/m^3)	100	50	50
SO_2 (mg/m^3)	-	50	50
HCl (mg/m^3)	-	10	10

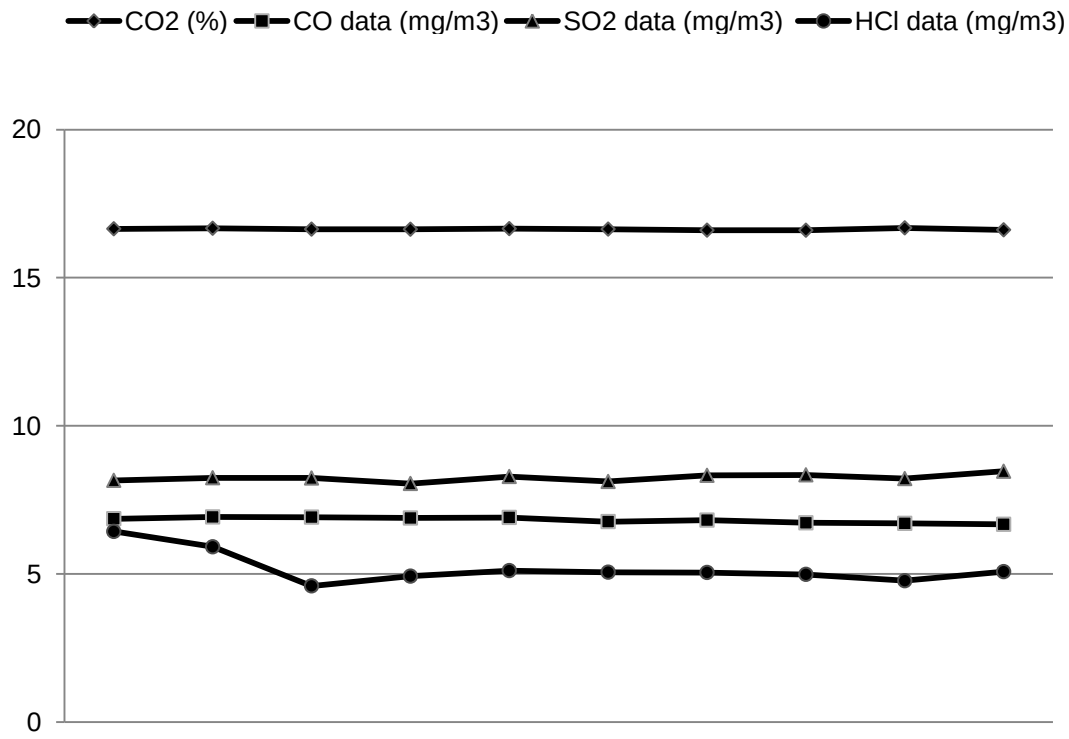

Figure 4.8 Online emission monitoring of carbon dioxide *(CO_2)*, carbon monoxide *(CO)*, sulphur dioxide *(SO_2)* and hydrogen chloride *(HCl)*

4.6 Mass balance

In order to conduct a mass balance to determine the composition distribution, the summary of values as seen in **Table 4.6** required to be normalized based on the percentage of each subsequent pyrolysis yield, thereby making them comparable to each other. A basis of 100kg was used as a representative quantity of feed material. Following normalization, a composition distribution was generated showing the initial weight of each component and the distribution of that component throughout the recovered products, **Figure 4.9**. The initial experimental run at 100°C had as its primary objective to determine the moisture content of the sample. According to the proximate analysis of the feed 10.5kg of moisture was present, the majority of which was liberated during the first run at 100°C, and a small amount of 0.126kg remained in the char product, **Figure 4.9.** The mass balance yielded 3.56% which was unaccounted for, but can be considered as an acceptably low deviation.

According to the feed analyses *(proximate)* 86.4kg of volatile material was present, and **Figure 4.9** shows that a total of 86.2kg was accounted for, with a negligible 0.24% deviation. The ash distribution across the products amounted to a total of 2.97kg of the total ash content from the feed analyses of 3.2kg, **Figure 4.9**, which ultimately showed an acceptable deviation of 7.1%. The analyses of the feed material suggests that the fixed carbon amounts to only 10.4kg but according to the analyses of the char, fixed carbon amounted to 10.8kg which is a slight over-representation of 4.27%, **Figure 4.9**. The mass balance has proven the integrity of the results obtained from the utilization of the experimental pyrolysis equipment, with acceptable deviations.

Table 4.6 Summary and comparison of composition analyses of feed, liquid products and char product

Determinant	Feed	Liquid	Oil			Char
		100°C	200°C	400°C	600°C	
Moisture (%)	10.5	10 (calculated experimentally)	-	-	-	0.9
Volatiles (%)	86.4	-	-	-	-	1.4
Ash (%)	3.2	-	0.128	0.106	0.004	20.9
Fixed carbon (%)	10.4	-	-	-	-	77.6
Carbon (%)	68.4	-	72.9	82.7	84.1	82.1
Hydrogen (%)	12.1	-	9.4	9	8.9	3
Nitrogen (%)	2.9	-	0.4	0.5	0.6	2.1
Sulphur (%)	2.1	-	0.1	0.1	0.2	1.1
Oxygen (%) (by difference)	14.5	-	17.2	7.7	6.2	11.7
Heating value (MJ/kg)	17.8	-	42.3	41.9	40.5	32.2

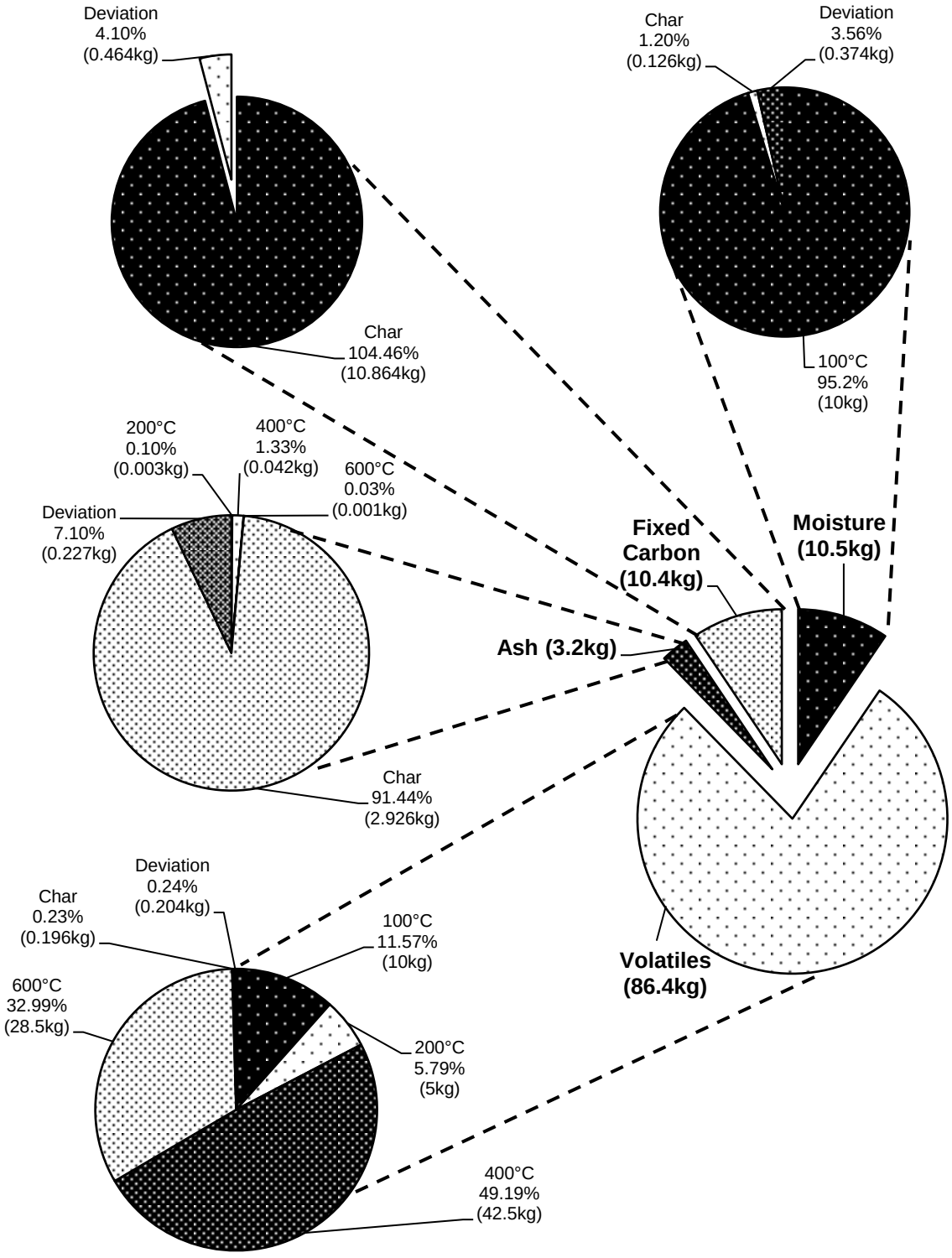

Figure 4.9. Mass balance for moisture, volatiles, ash and fixed carbon distributions

4.7 Current utilization versus projected utilization

The aim of the study was to provide a cost effective and environmentally compliant method to quantify the pyrolysis yield potential from hydrocarbon waste residue. Once quantified, a general assessment of the potential use of pyrolytic products was carried out, in order to understand the advantages of the recovery process *(projected utilization)* compared to incineration as a final disposal option *(current utilization)*. Hydrocarbon waste residues are merely subjected to incineration which leads to by-products such as ash and combustion gas, therefore the generation of heat energy from the combustion gas is the only recovery potential it possesses, **Figure 4.10**. According to the current utilization the ash product is destined for disposal to a classified landfill site suitable to accept the ash.

The off-gas is released into the atmosphere once the heat energy is stripped, and the gases scrubbed prior to release. Incineration of the entire volume of waste residue is seen as being a means of maximizing volume reduction but the resultant high levels of CO_2 produced becomes the issue of concern *(Wenning 1993)*. Even though many of the processes identified in the projected utilization ultimately subjects the final products to some form of combustion, it implies that the CO_2 generation will not be reduced. But the by-products could potentially be sold as feedstock to be used for the manufacture of chemical products, thus reducing CO_2 generation. Furthermore, the quantifiable value of the present work lies in an offset of the carbon footprint of the products, as these products would have originated from refinery processes utilizing fresh crude feedstock and other natural resources. The present work thus offers the advantage of supplementing the production of the abovementioned valuable by-products through material recycling, rather than fresh crude feedstock.

The projected utilization of the hydrocarbon waste residue following pyrolysis produces pyrolytic products such as oil, char and gas which then lead to the possibility of material recycling which converts the waste to usable raw materials, as seen in **Figure 4.10**, or sold as feedstock for chemical product manufacture. Pyrolysis yields attained in this study shows potential for further polishing processes due to its carbon-rich value and elemental characteristics. Generally accepted literature suggests that the utilization of pyrolytic products could potentially yield valuable byproducts and alternative power resources via its utilization in burners/boilers for heat generation *(Calabria et al. 2007), (Cui & Stubington 2001), (Sheng 2007),* and in engines/turbines for electricity generation *(Chiaramonti et al. 2007), (Gokalp & Lebas 2004), (Murugan et al. 2009),* **Figure 4.10**.

The possibility exists for the pyrolytic products to be utilized as a feedstock to gasifiers *(Ahmaruzzaman 2008), (Erincin et al. 2005), (Misirlioglu et al. 2007), (Sues et al. 2009), (Zabaniotou & Stavropoulos 2003), (Zhu et al. 2008),* catalytic crackers *(Teinturier et al. 2003), (Zhu et al. 2006),* and reformers for hydrogen production *(Davidian et al. 2007), (Garcia et al. 2000), (Iojoiu et al. 2007), (Kan et al. 2009),* **Figure 4.10**. Valuable feedstock can be attained for upgrading and synthesis processes *(Baldauf et al. 1994),* for the production of transportation fuels, **Figure 4.10**. A potential use of higher boiling crude fractions such as the pyrolysis oil attained in this study is the production of light olefins *(Gwyn 2001), (Basily et al. 2006).*

The projected utilization as identified in **Figure 4.10** depicts the advantages of pyrolysis in contrast to incineration, with regard to material recycling.

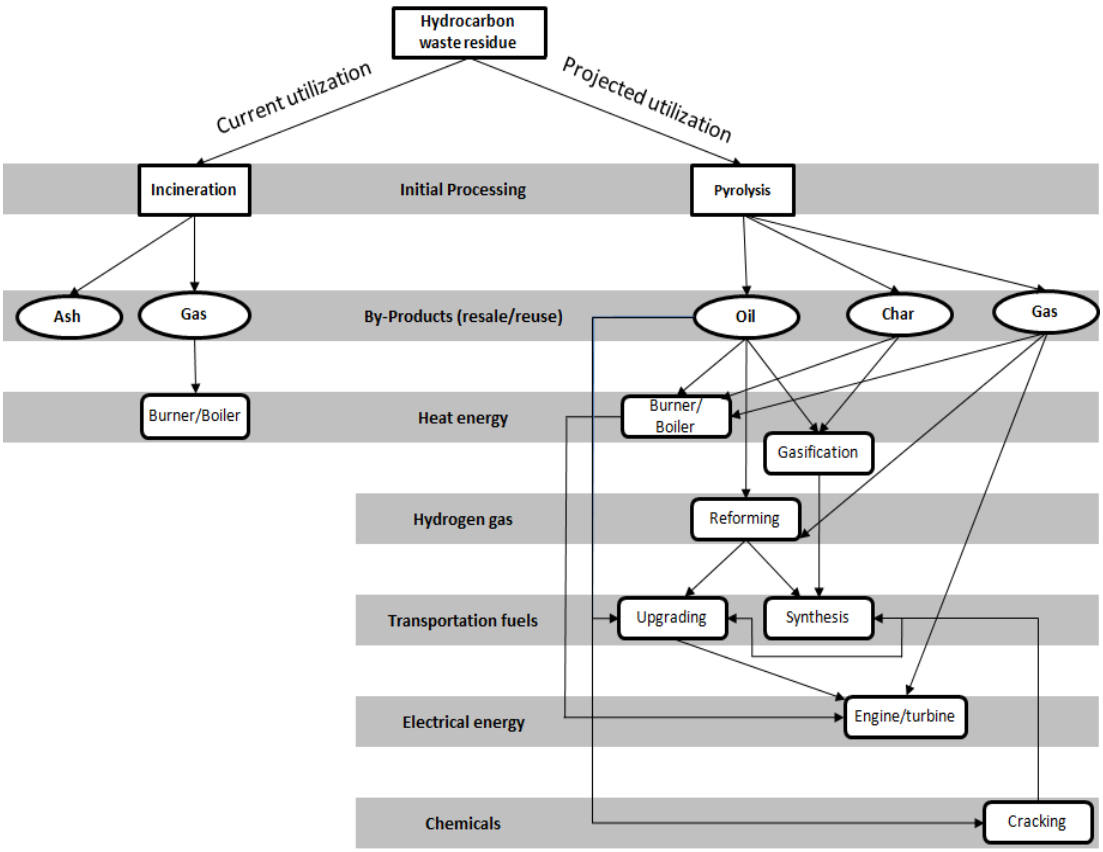

Figure 4.10 Current utilization of hydrocarbon waste residue versus projected utilization for end-product recovery

5 CONCLUSIONS AND RECOMMENDATIONS

The apparatus as designed and constructed in the present work utilizing key criteria *(elements, functions and critical parameters)* has proven its validity of effecting batch pyrolysis in order to determine the product yields attainable. The matter of high volume generation of non-distillable residue from crude processes is an issue of concern to any fuel and chemical manufacturer or will be for a future manufacturer desiring to enter the fuel/chemical producing market. An investigation as conducted in the present work would greatly assist such a newcomer to the industry in determining the potential product yields attainable prior to immense CAPEX[3] outlay for a continuous pilot scale pyrolysis unit. The study has proven the validity of utilizing batch pyrolysis to adequately assess product yields such as pyrolysis oils, char and gas from hydrocarbon residue, as well as keeping within environmental emission compliance.

An overall mass balance on the batch pyrolysis equipment yielded good agreement with the proximate results performed by a TGA[4]. The added advantage of the large initial feed charge provided individual determination of oils and components in the non-condensable gas. Furthermore, there is a striking similarity of product distribution with *Wenning (1993)* that used a continuous rotary kiln with crude oil residue as feed. This suggests the robustness of the existing batch method for quick evaluations of yields as well as to identify the required steps to handle gas emissions. Pyrolysis has also exhibited its potential to reduce expensive waste treatment via incineration and simultaneously yield valuable by-products for the purpose of material recycling and feedstock for chemical product manufacturing. Pyrolysis affords the advantage of being able to efficiently upgrade the energy content of waste whilst removing the hazardous fractions or undesired constituents. This enables one to substitute process specific raw materials/feed stocks used for the manufacture of

[3] Capital Expenditure
[4] Thermal Gravimetric Analysis

premium grade fuels/chemical products. The current investigation yielded positive results with regard to the attainable yields and greater confidence in the application and associated parameters was gained.

Therefore, the conversion of the batch process into a continuous industrial process requiring higher CAPEX outlay is thus easily justifiable with minimized risk. The envisioned future of this project is to subject hydrocarbon residue as well as other waste such as plastics and rubbers, to continuous flash pyrolysis. Future work will take cognizance of parameters identified in this study and further streamlining in order to achieve product recovery on a continuous basis, whilst keeping within environmental emission compliance regulations.

The successful use of pyrolysis in this study and the issue of high volumes of hydrocarbon waste residue which is generated globally, warrants others to potentially further this work in the following manner:

- Assess specific product utilization by investigating product substitution/upgrading in fuel processing applications with that of the product yields attained, with reference to the product/s quality.
- Assess the stability of the various products in order to meet requirements for safe storage, utilization for specific chemical applications, and transportation requirements.
- If adequate funds are available, investigate continuous pyrolysis utilizing rotary retort, fluidized bed, or spouted bed technology in order to produce adequate amounts of gas which can be treated, and assess its compliance with environmental emission standards and applicable legislation.

It must be noted specifically that this work started with waste, and yielded higher potential products which would have been lost through treatment/disposal processes. Therein lies the motivation for further work to be conducted in this field of study, as per the above recommendations. It is imperative that resources of this nature be harnessed, for the betterment of sustaining an environmentally conscious fuel and chemical industry.

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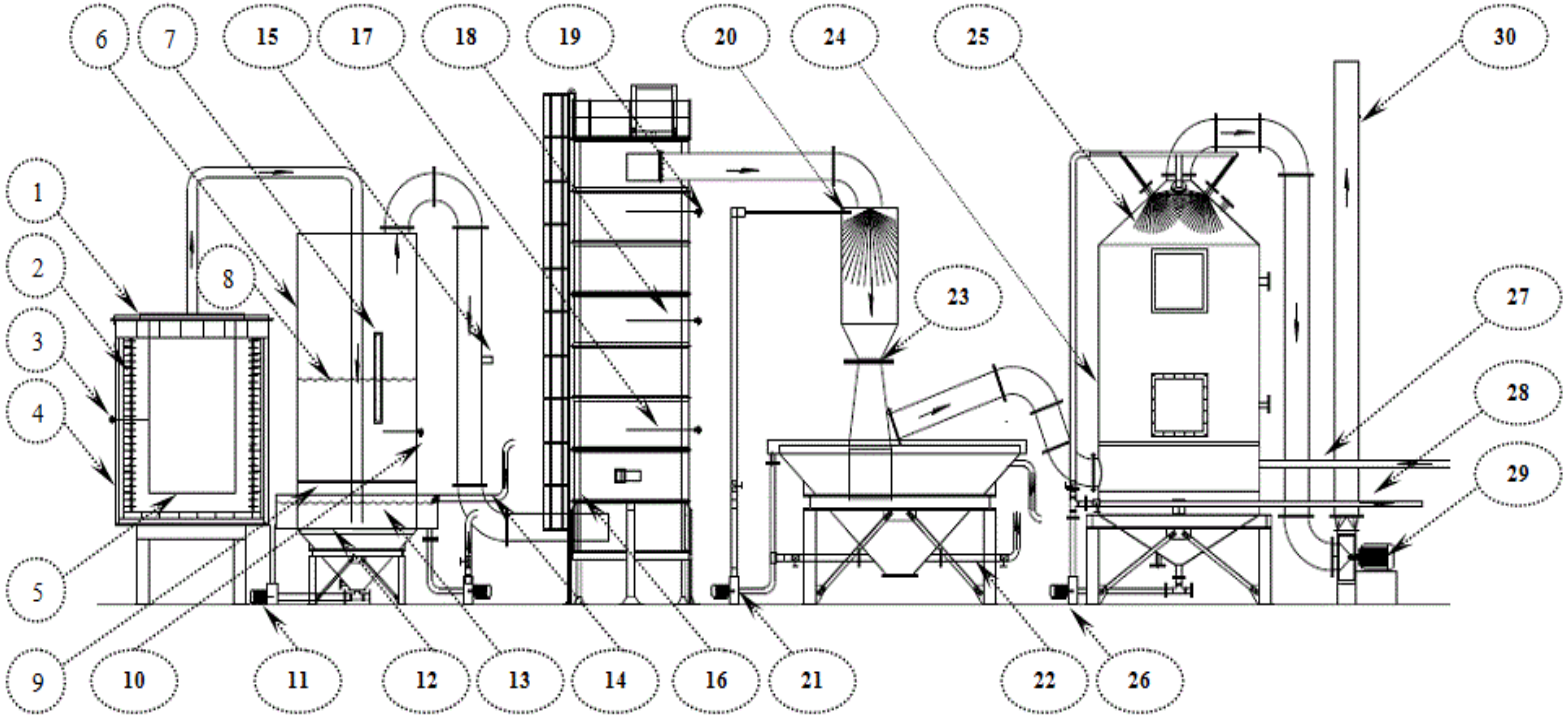
APPENDIX A



#	Description	Ref.	#	Description	Ref.	#	Description	Ref.	#	Description	Ref.	#	Description	Ref.
1	Retort seal	R101-S	7	Sight glass	C101-S	13	Cooling water level	-	19	Thermocouple	T3	25	Water spray	-
2	Electrical element	R101-E	8	Water level	-	14	Water from cooling tower	C101-W	20	Water spray	-	26	Water recycling pump	-
3	Thermocouple	T1	9	Tray sieve mesh	C101-SMt	15	Sample point	S1	21	Water recycling pump	-	27	Water from cooling tower	-
4	Vertical retort	R101	10	Thermocouple	T2	16	Thermal oxidiser	C201	22	Water to cooling tower	-	28	Water to cooling tower	-
5	Retort chamber	R101-C	11	Condensed oil to tank	C101-ST	17	Thermocouple	T5	23	Venturi scrubber	C301	29	Induced draft fan	ID-f
6	Condenser	C101	12	Tray sieve mesh	C101-SMb	18	Thermocouple	T4	24	Packed column	C401	30	Continuous online monitoring	CEMS-S2

Figure A1 Experimental apparatus designed from key operational criteria *(elements, functions and critical parameters)*

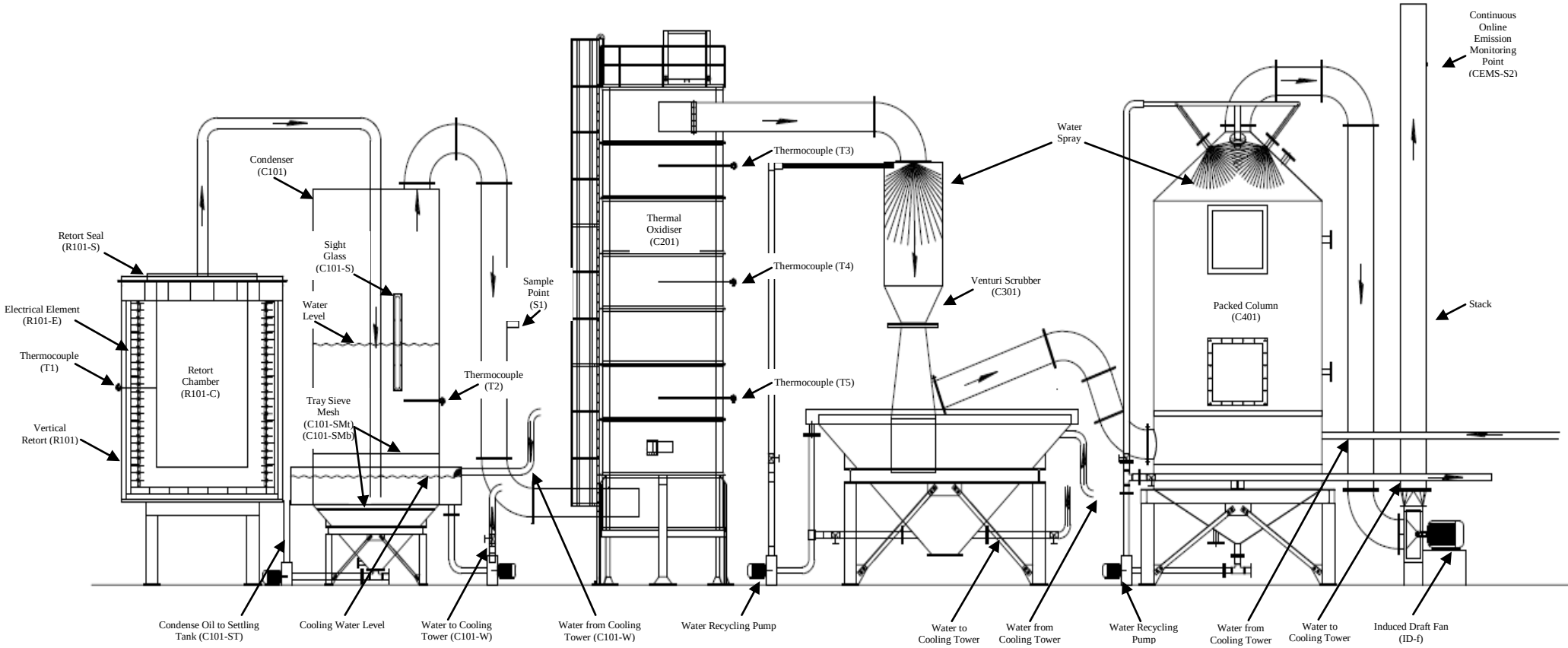


Figure A2 Detailed Representation of Figure A1

APPENDIX B

SAMPLE CALCULATIONS AND METHOD DISCUSSION

The basis for the product yield calculations were defined as a function of the feed material (i.e. refinery residue). Therefore the volume of the refinery residue required quantification prior to each day of pyrolysis testing, the calculations of which utilized dimensions of the retort chamber. This method of quantification was used in order to calculate the concomitant volumes of feedstock, moisture content, oil yields and char yields, as well as differentiate between the condensable and non-condensable gas yields.

Volume of Feed (V_{feed}) = Length of retort chamber (L_{rc}) × Breadth of retort chamber (B_{rc}) × Height of liquid level in retort chamber ($H_{rc,\ liq}$)

$$V_{feed} = L_{rc} \times B_{rc} \times H_{rc,\ liq} \quad \text{(eq.1)}$$

Thereafter, the experimental runs were initiated with the commencement of Run 1 at 100°C, and further runs utilizing intermediate temperatures of 200°C, 400°C and 600°C respectively. The level of feed material will decrease in the retort chamber following the completion of each run. The subsequent decrease in the Height of Liquid level ($\Delta H_{rc,\ liq}$) in the retort chamber, is then used to calculate the volume of refinery sludge which volatized and exited the retort chamber in gaseous form.

Therefore,

Volume of feed material volatized ($V_{volitized}$) = Length of retort chamber (L_{rc}) × Breadth of retort chamber (B_{rc}) × Height of liquid level in retort chamber($\Delta H_{rc, liq}$)

$$V_{volitized,\ 100\ °C} = L_{rc} \times B_{rc} \times \Delta H_{rc,\ liq,\ 100°C} \ldots\ldots\ldots (eq.2)$$

Similarly,

$$V_{volitized,\ 200\ °C} = L_{rc} \times B_{rc} \times \Delta H_{rc,\ liq,\ 200°C} \ldots\ldots\ldots (eq.3)$$

$$V_{volitized,\ 400\ °C} = L_{rc} \times B_{rc} \times \Delta H_{rc,\ liq,\ 400°C} \ldots\ldots\ldots (eq.4)$$

However, the calculation of the volume volatized at 600°C ($V_{volitized,\ 600\ °C}$) could not be calculated by the level measurement, as no liquid is present at the end of the run, i.e. only carbonaceous char remains in the retort chamber. The char product was collected and weighed (M_{char}). A small sample of known volume was crushed and weighed independently in order to calculate its density (ρ_{char}). The effective volume of the char is then calculated using M_{char} and ρ_{char}, and thereafter subtracted from the initial volume at the beginning of the run at 600 °C ($V_{start,\ 600°C}$).

Therefore,

$$V_{volitized,\ 600\ °C} = V_{start,\ 600°C} - (M_{char} \div \rho_{char}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (eq.5)$$

The Volume calculated ($V_{volatized}$) indicates only the volume of mainly volatile organic compounds (VOCs) converted into a gaseous fraction which exited the retort chamber. However, one must take cognisance of pyrolysis gas products which constitutes both condensable and non-condensable gas fractions. Therefore, the gaseous products require characterization, i.e. condensable or non-condensable gases. In order to calculate these volumes of condensable ($V_{condensable}$) and non-condensable gases ($V_{non\text{-}condensable}$) contained in the volatized pyrolysis gases ($V_{volatized}$), the basis

and principle of a change in the Height of condenser liquid ($\Delta H_{condenser\ liq.}$) was used. Therefore the volume of gas which condensed will result in a proportionate rise in the condenser water level ($\Delta H_{condenser\ liq.}$).

Therefore,

Volume of condensable gases ($V_{condensable}$) = Length of condenser pot (L_{cp}) × Breadth of condenser pot (B_{cp}) × Height of condenser liquid level ($\Delta H_{condenser\ liq.}$)

$$V_{condensable,\ 100°C} = L_{cp} \times B_{cp} \times \Delta H_{condenser\ liq.,\ 100°C} \text{....(eq.6)}$$

Similarly,

$$V_{condensable,\ 200\ °C} = L_{cp} \times B_{cp} \times \Delta H_{condenser\ liq.,\ 200°C} \text{....(eq.7)}$$

$$V_{condensable,\ 400\ °C} = L_{cp} \times B_{cp} \times \Delta H_{condenser\ liq.,\ 400°C} \text{....(eq.8)}$$

$$V_{condensable,\ 600\ °C} = L_{cp} \times B_{cp} \times \Delta H_{condenser\ liq.,\ 600°C} \text{...(eq.9)}$$

Thereafter, the Volume of the non-condensable gas fraction was calculated as the difference between the Volume of feed volatized, and the Volume of gas condensed, for each subsequent run.

Therefore,

$$V_{non\text{-}condensable,\ 100°C} = V_{volatized,\ 100°C} - V_{condensable,\ 100°C} \text{.....(eq.10)}$$

Similarly,

$$V_{non\text{-}condensable,\ 200°C} = V_{volatized,\ 200°C} - V_{condensable,\ 200°C} \text{.....(eq.11)}$$

$$V_{non\text{-}condensable,\ 400°C} = V_{volatized,\ 400°C} - V_{condensable,\ 400°C} \text{.....(eq.12)}$$

$$V_{non\text{-}condensable,\ 600°C} = V_{volatized,\ 600°C} - V_{condensable,\ 600°C} \text{.....(eq.13)}$$

Sample calculation using equations 1 to 13 as defined above.

Example: Day 1 - Run 1 @ 100°C, Run 2 @ 200°C, Run 3 @ 400°C, & Run 4 @ 600°C.

Using equation 1:

$V_{feed} = L_{rc} \times B_{rc} \times H_{rc,\ liq}$

$= 1m \times 1m \times 1{,}02m$

$= 1.020\ m^3$

$\cong$ 1020 Liters

Using equation 2:

$V_{volitized,\ 100\ °C} = L_{rc} \times B_{rc} \times \Delta H_{rc,\ liq,\ 100°C}$

$= 1m \times 1m \times 0.105m$

$= 0.105m^3$

$\cong$ 105 Liters

Using equation 3:

$V_{volitized,\ 200\ °C} = L_{rc} \times B_{rc} \times \Delta H_{rc,\ liq,\ 200°C}$

$= 1m \times 1m \times 0.05m$

$= 0.05m^3$

$\cong$ 50 Liters

Using equation 4:

$V_{volitized,\ 400\ °C} = L_{rc} \times B_{rc} \times \Delta H_{rc,\ liq,\ 400°C}$

$= 1m \times 1m \times 0.435m$

$= 0.435m^3$

$\cong$ 435 Liters

Using equation 5:

$V_{volitized,\ 600\ °C} = V_{start,\ 600°C} - (M_{char} \div \rho_{char})$

$= 0.43m^3 - (203\ kg / 1399\ kg.m^{-3})$

$= 0.2849\ m^3$

$\cong$ 284.9 Liters

Using equation 6:

$V_{condensable,\ 100°C} = L_{cp} \times B_{cp} \times \Delta H_{condenser\ liq.,\ 100°C}$

$= 1m \times 1m \times 0.105m$

$= 0.105m^3$

$\cong$ 105 Liters

Using equation 7:

$V_{condensable,\ 200\ °C} = L_{cp} \times B_{cp} \times \Delta H_{condenser\ liq.,\ 200°C}$

$= 1m \times 1m \times 0.025m$

$= 0.025m^3$

$\cong$ 25 Liters

Using equation 8:

$V_{condensable,\ 400\ °C} = L_{cp} \times B_{cp} \times \Delta H_{condenser\ liq.,\ 400°C}$

$= 1m \times 1m \times 0.41m$

$= 0.41m^3$

$\cong$ 410 Liters

Using equation 9:

$V_{condensable,\ 600\ °C} = L_{cp} \times B_{cp} \times \Delta H_{condenser\ liq.,\ 600°C}$

$= 1m \times 1m \times 0.28m$

$= 0.28m^3$

$\cong$ 280 Liters

Using equation 10:

$V_{non\text{-}condensable,\ 100°C} = V_{volatized,\ 100°C} - V_{condensable,\ 100°C}$

$= 105\ L - 105\ L$

$= 0$ Liters

Using equation 11:

$V_{non\text{-}condensable,\ 200°C} = V_{volatized,\ 200°C} - V_{condensable,\ 200°C}$

$= 50\ L - 25\ L$

$= 25$ Liters

Using equation 12:

$V_{non\text{-}condensable,\ 400°C} = V_{volatized,\ 400°C} - V_{condensable,\ 400°C}$

$= 435\ L - 410\ L$

$= 25$ Liters

Using equation 13:

$V_{non\text{-}condensable,\ 600°C} = V_{volatized,\ 600°C} - V_{condensable,\ 600°C}$

$= 284.9\ L - 280\ L$

$= 4.9$ Liters

These calculations were completed for each test run over the ten day testing period. Once the results were calculated, their subsequent percentages were also calculated in relation to the initial feed material, and cumulative yields calculated thereafter via summation.

APPENDIX C

EXPERIMENTAL DATA - YIELDS

The tables presented in **Appendix C** consist of experimental data collected during each day of testing under the various temperature condition set points as required by the pyrolysis experiments, as well as the concomitant calculated results utilizing equations as set out in **Appendix B**. The identification and differentiation of these values must be read in the following manner:

- **Raw data** collected during the experiments are denoted by **Bold font**, and
- *Calculated values* are denoted by *Italic font*.

Experimental Data for pyrolysis experiments conducted on Day 1.

Table C1 Experimental results for retort chamber - Day 1

Retort Chamber										
Run no:.	Temp. (°C)	Length (m)	Breadth (m)	**Start level (cm)**	*Starting Volume (L)*	**End level (cm)**	*Ending Volume (L)*	*Height Difference (cm)*	*Liters volitized (L)*	*% of feed volitized*
1	100	1	1	**102**	*1020*	**91.5**	*915*	*10.5*	*105*	*10.3%*
2	200	1	1	**91.5**	*915*	**86.5**	*865*	*5*	*50*	*4.9%*
3	400	1	1	**86.5**	*865*	**43**	*430*	*43.5*	*435*	*42.6%*
4	600	1	1	**43**	*430*	-	-	-	*284.9*	*27.9%*

Table C2 Experimental results for the condenser - Day 1

Condenser								
Run no:.	Temp. (°C)	Length (m)	Breadth (m)	**Liquid level increase (cm)**	*Condensate (L)*	*% of feed Condensed*	*Cumulative % oil condensed*	*Cumulative % water condensed*
1	100	1	1	**10.5**	*105*	*10.3%*	-	*10.29%*
2	200	1	1	**2.5**	*25*	*2.5%*	*2.45%*	-
3	400	1	1	**41**	*410*	*40.2%*	*42.65%*	-
4	600	1	1	**28**	*280*	*27.5%*	*70.10%*	-

Table C3 Experimental results calculated for the non-condensable gas fraction - Day 1

Run no:.	Temp. (°C)	*Liters non-Condensable (L)*	*% of feed that is non-Condensable*
1	100	*0*	*0%*
2	200	*25*	*2.45%*
3	400	*25*	*2.45%*
4	600	*4.9*	*0.48%*

Table C4 Experimental results for char product - Day 1

Char weight after Run 4 [kg]	**203**
Weight of container + crushed char product [g]	**280.9**
Weight of empty container [g]	141
Weight of crushed char product (100ml) [g]	*139.9*
Density of char product [kg/m^3]	*1399*
Volume of char product [L]	*145.1*

Experimental Data collected during pyrolysis experiments conducted on Day 2

Table C5 Experimental results for retort chamber - Day 2

Retort Chamber										
Run no:.	Temp. (°C)	Length (m)	Breadth (m)	**Start level (cm)**	*Starting Volume (L)*	**End level (cm)**	*Ending Volume (L)*	*Height Difference (cm)*	*Liters volitized (L)*	*% of feed volitized*
1	100	1	1	**109**	*1090*	**98**	*980*	*11*	*110*	*10.1%*
2	200	1	1	**98**	*980*	**92.5**	*925*	*5.5*	*55*	*5.0%*
3	400	1	1	**92.5**	*925*	**46.5**	*465*	*46*	*460*	*42.2%*
4	600	1	1	**46.5**	*465*	**-**	-	-	*314.74*	*28.9%*

Table C6 Experimental results for the condenser - Day 2

Condenser								
Run no:.	Temp. (°C)	Length (m)	Breadth (m)	**Liquid level increase (cm)**	*Condensate (L)*	*% of feed Condensed*	*Cumulative % oil condensed*	*Cumulative % water condensed*
1	100	1	1	**10.5**	*105*	*9.63%*	-	*9.63%*
2	200	1	1	**3**	*30*	*2.75%*	*2.75%*	-
3	400	1	1	**43.5**	*435*	*39.91%*	*42.66%*	-
4	600	1	1	**30**	*300*	*27.52%*	*70.18%*	-

Table C7 Experimental results calculated for the non-condensable gas fraction - Day 2

Run no:.	Temp. (°C)	*Liters non-Condensable (L)*	*% of feed that is non-Condensable*
1	100	*5*	*0.46%*
2	200	*25*	*2.29%*
3	400	*25*	*2.29%*
4	600	*14.74*	*1.35%*

Table C8 Experimental results for char product - Day 2

Char weight after Run 4 [kg]	**206**
Weight of container + crushed char product [g]	**278.1**
Weight of empty container [g]	141
Weight of crushed char product (100ml) [g]	*137.1*
Density of char product [kg/m^3]	*1371*
Volume of char product [L]	*150.3*

Experimental Data collected during pyrolysis experiments conducted on Day 3.

Table C9 Experimental results for the retort chamber - Day 3

Retort Chamber										
Run no:.	Temp. (°C)	Length (m)	Breadth (m)	**Start level (cm)**	*Starting Volume (L)*	**End level (cm)**	*Ending Volume (L)*	*Height Difference (cm)*	*Liters volitized (L)*	*% of feed volitized*
1	100	1	1	**110**	*1100*	**99**	*990*	*11.00*	*110*	*10.0%*
2	200	1	1	**99**	*990*	**93.5**	*935*	*5.50*	*55*	*5.0%*
3	400	1	1	**93.5**	*935*	**47**	*470*	*46.5*	*465*	*42.3%*
4	600	1	1	**47**	*470*	**-**	-	-	*313.08*	*28.5%*

Table C10 Experimental results for the condenser - Day 3

Condenser								
Run no:.	Temp. (°C)	Length (m)	Breadth (m)	**Liquid level increase (cm)**	*Condensate (L)*	*% of feed Condensed*	*Cumulative % oil condensed*	*Cumulative % water condensed*
1	100	1	1	**11**	*110*	*10%*	-	*10%*
2	200	1	1	**2.5**	*25*	*2.27%*	*2.27%*	-
3	400	1	1	**44**	*440*	*40%*	*42.27%*	-
4	600	1	1	**30**	*300*	*27.27%*	*69.55%*	-

Table C11 Experimental results calculated for the non-condensable gas fraction - Day 3

Run no:.	Temp. (°C)	*Liters non-Condensable (L)*	*% of feed that is non-Condensable*
1	100	*0*	*0%*
2	200	*30*	*2.73%*
3	400	*25*	*2.27%*
4	600	*13.08*	*1.19%*

Table C12 Experimental results for char product - Day 3

Char weight after Run 4 [kg]	**220**
Weight of container + crushed char product [g]	**281.2**
Weight of empty container [g]	141
Weight of crushed char product (100ml) [g]	*140.2*
Density of char product [kg/m^3]	*1402*
Volume of char product [L]	*156.9*

Experimental Data collected during pyrolysis experiments conducted on Day 4.

Table C13 Experimental results for the retort chamber - Day 4

Retort Chamber										
Run no:.	Temp. (°C)	Length (m)	Breadth (m)	**Start level (cm)**	*Starting Volume (L)*	**End level (cm)**	*Ending Volume (L)*	*Height Difference (cm)*	*Liters volitized (L)*	*% of feed volitized*
1	100	1	1	**116**	*1160*	**104.5**	*1045*	*11.5*	*115*	*9.9%*
2	200	1	1	**104.5**	*1045*	**98.5**	*985*	*6*	*60*	*5.2%*
3	400	1	1	**98.5**	*985*	**49.5**	*495*	*49*	*490*	*42.2%*
4	600	1	1	**49.5**	*495*	**-**	-	-	*336.68*	*29.0%*

Table C14 Experimental results for the condenser - Day 4

Condenser								
Run no:.	Temp. (°C)	Length (m)	Breadth (m)	**Liquid level increase (cm)**	*Condensate (L)*	*% of feed Condensed*	*Cumulative % oil condensed*	*Cumulative % water condensed*
1	100	1	1	**11.5**	*115*	*9.91%*	-	*9.91%*
2	200	1	1	**3**	*30*	*2.59%*	*2.59%*	-
3	400	1	1	**46.5**	*465*	*40.09%*	*42.67%*	-
4	600	1	1	**32.5**	*325*	*28.02%*	*70.69%*	-

Table C15 Experimental results calculated for the non-condensable gas fraction - Day 4

Run no:.	Temp. (°C)	*Liters non-Condensable (L)*	*% of feed that is non-Condensable*
1	100	*0*	*0%*
2	200	*30.00*	*2.59%*
3	400	*25.00*	*2.16%*
4	600	*11.68*	*1.01%*

Table C16 Experimental results for char product - Day 4

Char weight after Run 4 [kg]	**215**
Weight of container + crushed char product [g]	**276.8**
Weight of empty container [g]	141
Weight of crushed char product (100ml) [g]	*135.8*
Density of char product [kg/m^3]	*1358*
Volume of char product [L]	*158.3*

Experimental Data collected during pyrolysis experiments conducted on Day 5.

Table C17 Experimental results for the retort chamber - Day 5

Retort Chamber										
Run no:.	Temp. (°C)	Length (m)	Breadth (m)	**Start level (cm)**	*Starting Volume (L)*	**End level (cm)**	*Ending Volume (L)*	*Height Difference (cm)*	*Liters volitized (L)*	*% of feed volitized*
1	100	1	1	**105**	*1050*	**94.5**	*945*	*10.5*	*105*	*10%*
2	200	1	1	**94.5**	*945*	**89**	*890*	*5.5*	*55*	*5.2%*
3	400	1	1	**89**	*890*	**44.5**	*445*	*44.5*	*445*	*42.4%*
4	600	1	1	**44.5**	*445*	**-**	-	-	*294.1*	*28%*

Table C18 Experimental results for the condenser - Day 5

Condenser								
Run no:.	Temp. (°C)	Length (m)	Breadth (m)	**Liquid level increase (cm)**	*Condensate (L)*	*% of feed Condensed*	*Cumulative % oil condensed*	*Cumulative % water condensed*
1	100	1	1	**10.5**	*105*	*10%*	-	*10%*
2	200	1	1	**2.5**	*25*	*2.38%*	*2.38%*	-
3	400	1	1	**42**	*420*	*40%*	*42.38%*	-
4	600	1	1	**29**	*290*	*27.62%*	*70%*	-

Table C19 Experimental results calculated for the non-condensable gas fraction - Day 5

Run no:.	Temp. (°C)	*Liters non-Condensable (L)*	*% of feed that is non-Condensable*
1	100	*0*	*0%*
2	200	*30*	*2.86%*
3	400	*25*	*2.38%*
4	600	*4.1*	*0.39%*

Table C20 Experimental results for char product - Day 5

Char weight after Run 4 [kg]	**209**
Weight of container + crushed char product [g]	**279.5**
Weight of empty container [g]	141
Weight of crushed char product (100ml) [g]	*138.5*
Density of char product [kg/m^3]	*1385*
Volume of char product [L]	*150.9*

Experimental Data collected during pyrolysis experiments conducted on Day 6.

Table C21 Experimental results for the retort chamber - Day 6

Retort Chamber										
Run no:.	Temp. (°C)	Length (m)	Breadth (m)	**Start level (cm)**	*Starting Volume (L)*	**End level (cm)**	*Ending Volume (L)*	*Height Difference (cm)*	*Liters volitized (L)*	*% of feed volitized*
1	100	1	1	**112**	*1120*	**100.5**	*1005*	*11.5*	*115*	*10.3%*
2	200	1	1	**100.5**	*1005*	**94.5**	*945*	*6*	*60*	*5.4%*
3	400	1	1	**94.5**	*945*	**47**	*470*	*47.5*	*475*	*42.4%*
4	600	1	1	**47**	*470*	**-**	-	-	*315.26*	*28.1%*

Table C22 Experimental results for the condenser - Day 6

Condenser								
Run no:.	Temp. (°C)	Length (m)	Breadth (m)	**Liquid level increase (cm)**	*Condensate (L)*	*% of feed Condensed*	*Cumulative % oil condensed*	*Cumulative % water condensed*
1	100	1	1	**11.5**	*115*	*10.27%*	-	*10.27%*
2	200	1	1	**3**	*30*	*2.68%*	*2.68%*	-
3	400	1	1	**44.5**	*445*	*39.73%*	*42.41%*	-
4	600	1	1	**31**	*310*	*27.68%*	*70.09%*	-

Table C23 Experimental results calculated for the non-condensable gas fraction - Day 6

Run no:.	Temp. (°C)	*Liters non-Condensable (L)*	*% of feed that is non-Condensable*
1	100	*0*	*0%*
2	200	*30*	*2.68%*
3	400	*30*	*2.68%*
4	600	*5.26*	*0.47%*

Table C24 Experimental results for char product - Day 6

Char weight after Run 4 [kg]	**214**
Weight of container + crushed char product [g]	**279.3**
Weight of empty container [g]	141
Weight of crushed char product (100ml) [g]	*138.3*
Density of char product [kg/m^3]	*1383*
Volume of char product [L]	*154.7*

Experimental Data collected during pyrolysis experiments conducted on Day 7.

Table C25 Experimental results for the retort chamber - Day 7

Retort Chamber										
Run no:.	Temp. (°C)	Length (m)	Breadth (m)	**Start level (cm)**	*Starting Volume (L)*	**End level (cm)**	*Ending Volume (L)*	*Height Difference (cm)*	*Liters volitized (L)*	*% of feed volitized*
1	100	1	1	**107**	*1070*	**96**	*960*	*11*	*110*	*10.3%*
2	200	1	1	**96**	*960*	**90.5**	*905*	*5.5*	*55*	*5.1%*
3	400	1	1	**90.5**	*905*	**45**	*450*	*45.5*	*455*	*42.5%*
4	600	1	1	**45**	*450*	**-**	-	-	*295.12*	*27.6%*

Table C26 Experimental results for the condenser - Day 7

Condenser								
Run no:.	Temp. (°C)	Length (m)	Breadth (m)	**Liquid level increase (cm)**	*Condensate (L)*	*% of feed Condensed*	*Cumulative % oil condensed*	*Cumulative % water condensed*
1	100	1	1	**10.5**	*105*	*9.81%*	-	*9.81%*
2	200	1	1	**2.5**	*25*	*2.34%*	*2.34%*	-
3	400	1	1	**42.5**	*425*	*39.72%*	*42.06%*	-
4	600	1	1	**29.5**	*295*	*27.57%*	*69.63%*	-

Table C27 Experimental results calculated for the non-condensable gas fraction - Day 7

Run no:.	Temp. (°C)	*Liters non-Condensable (L)*	*% of feed that is non-Condensable*
1	100	*5*	*0.47%*
2	200	*30*	*2.80%*
3	400	*30*	*2.80%*
4	600	*0.12*	*0.01%*

Table C28 Experimental results for char product - Day 7

Char weight after Run 4 [kg]	**219**
Weight of container + crushed char product [g]	**282.4**
Weight of empty container [g]	141
Weight of crushed char product (100ml) [g]	*141.4*
Density of char product [kg/m^3]	*1414*
Volume of char product [L]	*154.9*

Experimental Data collected during pyrolysis experiments conducted on Day 8.

Table C29 Experimental results for the retort chamber - Day 8

Retort Chamber										
Run no:.	Temp. (°C)	Length (m)	Breadth (m)	**Start level (cm)**	*Starting Volume (L)*	**End level (cm)**	*Ending Volume (L)*	*Height Difference (cm)*	*Liters volitized (L)*	*% of feed volitized*
1	100	1	1	**115**	*1150*	**103.5**	*1035*	*11.5*	*115*	*10.0%*
2	200	1	1	**103.5**	*1035*	**97.5**	*975*	*6*	*60*	*5.2%*
3	400	1	1	**97.5**	*975*	**48.5**	*485*	*49*	*490*	*42.6%*
4	600	1	1	**48.5**	*485*	-	-	-	*324.77*	*28.2%*

Table C30 Experimental results for the condenser - Day 8

Condenser								
Run no:.	Temp. (°C)	Length (m)	Breadth (m)	**Liquid level increase (cm)**	*Condensate (L)*	*% of feed Condensed*	*Cumulative % oil condensed*	*Cumulative % water condensed*
1	100	1	1	**11.5**	*115*	*10%*	-	*10%*
2	200	1	1	**2.5**	*25*	*2.17%*	*2.17%*	-
3	400	1	1	**46.5**	*465*	*40.43%*	*42.61%*	-
4	600	1	1	**31.5**	*315*	*27.39%*	*70.00%*	-

Table C31 Experimental results calculated for the non-condensable gas fraction - Day 8

Run no:.	Temp. (°C)	*Liters non-Condensable (L)*	*% of feed that is non-Condensable*
1	100	*0*	*0%*
2	200	*35*	*3.04%*
3	400	*25*	*2.17%*
4	600	*9.77*	*0.85%*

Table C32 Experimental results for char product - Day 8

Char weight after Run 4 [kg]	**224**
Weight of container + crushed char product [g]	**280.8**
Weight of empty container [g]	141
Weight of crushed char product (100ml) [g]	*139.8*
Density of char product [kg/m^3]	*1398*
Volume of char product [L]	*160.2*

Experimental Data collected during pyrolysis experiments conducted on Day 9.

Table C33 Experimental results for the retort chamber - Day 9

Retort Chamber										
Run no:.	Temp. (°C)	Length (m)	Breadth (m)	**Start level (cm)**	*Starting Volume (L)*	**End level (cm)**	*Ending Volume (L)*	*Height Difference (cm)*	*Liters volitized (L)*	*% of feed volitized*
1	100	1	1	**108**	*1080*	**97**	*970*	*11.00*	*110.00*	*10.2%*
2	200	1	1	**97**	*970*	**91.5**	*915*	*5.50*	*55.00*	*5.1%*
3	400	1	1	**91.5**	*915*	**45.5**	*455*	*46*	*460.00*	*42.6%*
4	600	1	1	**45.5**	*455*	**-**	-	-	*298.60*	*27.6%*

Table C34 Experimental results for the condenser - Day 9

Condenser								
Run no:.	Temp. (°C)	Length (m)	Breadth (m)	**Liquid level increase (cm)**	*Condensate (L)*	*% of feed Condensed*	*Cumulative % oil condensed*	*Cumulative % water condensed*
1	100	1	1	**10.5**	*105*	*9.72%*	-	*9.72%*
2	200	1	1	**3**	*30*	*2.78%*	*2.78%*	-
3	400	1	1	**43.5**	*435*	*40.28%*	*43.06%*	-
4	600	1	1	**29.5**	*295*	*27.31%*	*70.37%*	-

Table C35 Experimental results calculated for the non-condensable gas fraction - Day 9

Run no:.	Temp. (°C)	*Liters non-Condensable (L)*	*% of feed that is non-Condensable*
1	100	*5*	*0.46%*
2	200	*25*	*2.31%*
3	400	*25*	*2.31%*
4	600	*3.6*	*0.33%*

Table C36 Experimental results for char product - Day 9

Char weight after Run 4 [kg]	**221**
Weight of container + crushed char product [g]	**282.3**
Weight of empty container [g]	141
Weight of crushed char product (100ml) [g]	*141.3*
Density of char product [kg/m^3]	*1413*
Volume of char product [L]	*156.4*

Experimental Data collected during pyrolysis experiments conducted on Day 10.

Table C37 Experimental results for the retort chamber - Day 10

Retort Chamber										
Run no:.	Temp. (°C)	Length (m)	Breadth (m)	**Start level (cm)**	*Starting Volume (L)*	**End level (cm)**	*Ending Volume (L)*	*Height Difference (cm)*	*Liters volitized (L)*	*% of feed volitized*
1	100	1	1	**104**	*1040*	**93.5**	*935*	*10.5*	*105*	*10.1%*
2	200	1	1	**93.5**	*935*	**88.5**	*885*	*5*	*50*	*4.8%*
3	400	1	1	**88.5**	*885*	**44.5**	*445*	*44*	*440*	*42.3%*
4	600	1	1	**44.5**	*445*	**-**	-	-	*294.93*	*28.4%*

Table C38 Experimental results for the condenser - Day 10

Condenser								
Run no:.	Temp. (°C)	Length (m)	Breadth (m)	**Liquid level increase (cm)**	*Condensate (L)*	*% of feed Condensed*	*Cumulative % oil condensed*	*Cumulative % water condensed*
1	100	1	1	**10**	*100*	*9.62%*	-	*9.62%*
2	200	1	1	**2.5**	*25*	*2.4%*	*2.4%*	-
3	400	1	1	**42**	*420*	*40.38%*	*42.79%*	-
4	600	1	1	**28.5**	*285*	*27.4%*	*70.19%*	-

Table C39 Experimental results calculated for the non-condensable gas fraction - Day 10

Run no:.	Temp. (°C)	*Liters non-Condensable (L)*	*% of feed that is non-Condensable*
1	100	*5*	*0.48%*
2	200	*25*	*2.4%*
3	400	*20*	*1.92%*
4	600	*9.93*	*0.95%*

Table C40 Experimental results for char product - Day 1

Char weight after Run 4 [kg]	**205**
Weight of container + crushed char product [g]	**277.6**
Weight of empty container [g]	141
Weight of crushed char product (100ml) [g]	*136.6*
Density of char product [kg/m^3]	*1366*
Volume of char product [L]	*150.1*

APPENDIX D

EXPERIMENTAL DATA - EMISSIONS

The tables presented in Appendix D consist of experimental emissions data collected during each day of the pyrolysis experiments. The continuous emission monitoring sample measurements were taken automatically at an interval of 2 minutes, thereby recording 30 readings on an hourly basis, per gas being measured.

One must also take cognizance of the fact that each day of experimentation consisted of 12 hours process time, therefore the emission measurements amounts to approximately 14400 values, which is voluminous in nature to include in Appendix D, as raw data.

Therefore, for the purpose of showing the data, the hourly average was calculated for the 12 processing hours for each subsequent experimental day and tabulated accordingly, with a final average shown which represents the overall emission value for that specific experimental day.

Table D1 Experimental Emissions Data for pyrolysis experiments - Day 1

Day 1	CO_2 (%)	CO data (mg/m^3)	SO_2 data (mg/m^3)	HCl data (mg/m^3)
Hourly average 1	16.76	6.90	7.82	6.33
Hourly average 2	16.66	6.88	7.91	6.67
Hourly average 3	16.66	6.87	7.94	6.87
Hourly average 4	16.65	6.85	8.04	6.89
Hourly average 5	16.64	6.84	8.19	6.87
Hourly average 6	16.65	6.85	8.09	6.76
Hourly average 7	16.67	6.86	8.26	6.75
Hourly average 8	16.67	6.86	8.44	6.56
Hourly average 9	16.66	6.76	8.38	6.28
Hourly average 10	16.64	6.74	7.97	6.11
Hourly average 11	16.64	6.87	7.97	6.07
Hourly average 12	16.62	6.89	8.14	6.02
Daily Average	***16.66***	***6.85***	***8.10***	***6.52***

Table D2 Experimental Emissions Data for pyrolysis experiments - Day 2

Day 2	CO_2 (%)	CO data (mg/m^3)	SO_2 data (mg/m^3)	HCl data (mg/m^3)
Hourly average 1	16.62	6.98	8.55	5.90
Hourly average 2	16.57	6.81	8.61	5.81
Hourly average 3	16.58	6.97	8.60	5.78
Hourly average 4	16.99	7.01	8.41	5.79
Hourly average 5	16.61	7.04	8.53	5.85
Hourly average 6	16.63	7.00	8.60	5.85
Hourly average 7	16.69	6.93	8.38	5.91
Hourly average 8	16.69	6.87	8.31	6.03
Hourly average 9	16.66	6.82	7.92	6.00
Hourly average 10	16.66	6.88	7.80	5.97
Hourly average 11	16.66	6.91	7.91	5.96
Hourly average 12	16.66	6.92	7.95	5.89
Daily Average	***16.67***	***6.93***	***8.30***	***5.89***

Table D3 Experimental Emissions Data for pyrolysis experiments - Day 3

Day 3	CO_2 (%)	CO data (mg/m^3)	SO_2 data (mg/m^3)	HCl data (mg/m^3)
Hourly average 1	16.67	6.89	8.01	6.01
Hourly average 2	16.67	6.86	8.11	5.89
Hourly average 3	16.68	6.89	8.36	5.60
Hourly average 4	16.69	6.78	8.49	5.46
Hourly average 5	16.68	6.79	8.47	4.90
Hourly average 6	16.67	6.81	8.04	3.79
Hourly average 7	16.65	6.88	7.82	4.23
Hourly average 8	16.63	6.89	8.03	4.28
Hourly average 9	16.61	6.94	8.30	4.17
Hourly average 10	16.59	6.96	8.27	4.13
Hourly average 11	16.58	7.00	8.38	3.97
Hourly average 12	16.58	7.04	8.43	4.03
Daily Average	***16.64***	***6.89***	***8.22***	***4.70***

Table D4 Experimental Emissions Data for pyrolysis experiments - Day 4

Day 4	CO_2 (%)	CO data (mg/m^3)	SO_2 data (mg/m^3)	HCl data (mg/m^3)
Hourly average 1	16.62	7.07	8.36	4.29
Hourly average 2	16.63	7.03	8.32	4.43
Hourly average 3	16.65	6.98	8.10	4.48
Hourly average 4	16.64	6.95	7.96	4.53
Hourly average 5	16.64	6.88	7.86	4.91
Hourly average 6	16.63	6.82	7.84	5.50
Hourly average 7	16.61	6.83	7.85	5.36
Hourly average 8	16.62	6.82	8.00	5.09
Hourly average 9	16.64	6.83	8.03	4.75
Hourly average 10	16.62	6.86	8.01	4.79
Hourly average 11	16.63	6.86	8.03	4.82
Hourly average 12	16.65	6.84	8.06	5.17
Daily Average	***16.63***	***6.90***	***8.03***	***4.84***

Table D5 Experimental Emissions Data for pyrolysis experiments - Day 5

Day 5	CO_2 (%)	CO data (mg/m^3)	SO_2 data (mg/m^3)	HCl data (mg/m^3)
Hourly average 1	16.65	6.78	8.19	5.33
Hourly average 2	16.63	6.82	7.93	5.33
Hourly average 3	16.62	6.83	8.05	5.28
Hourly average 4	16.62	6.84	8.17	5.15
Hourly average 5	16.63	6.87	8.31	5.15
Hourly average 6	16.60	6.92	8.38	5.07
Hourly average 7	16.58	6.94	8.49	4.99
Hourly average 8	16.58	6.96	8.49	4.97
Hourly average 9	16.78	6.95	8.49	4.87
Hourly average 10	16.77	6.96	8.38	4.96
Hourly average 11	16.78	6.98	8.42	5.18
Hourly average 12	16.74	6.96	8.35	5.13
Daily Average	***16.66***	***6.90***	***8.30***	***5.12***

Table D6 Experimental Emissions Data for pyrolysis experiments - Day 6

Day 6	CO_2 (%)	CO data (mg/m^3)	SO_2 data (mg/m^3)	HCl data (mg/m^3)
Hourly average 1	16.62	6.84	7.93	5.09
Hourly average 2	16.63	6.82	7.87	5.08
Hourly average 3	16.64	6.76	7.89	4.89
Hourly average 4	16.64	6.75	7.85	4.85
Hourly average 5	16.64	6.77	7.98	4.79
Hourly average 6	16.64	6.78	8.05	4.86
Hourly average 7	16.61	6.76	8.23	4.88
Hourly average 8	16.61	6.76	8.30	4.88
Hourly average 9	16.64	6.77	8.35	5.16
Hourly average 10	16.67	6.68	8.47	5.30
Hourly average 11	16.67	6.71	8.39	5.31
Hourly average 12	16.66	6.74	8.08	5.27
Daily Average	***16.64***	***6.76***	***8.12***	***5.03***

Table D7 Experimental Emissions Data for pyrolysis experiments - Day 7

Day 7	CO_2 (%)	CO data (mg/m^3)	SO_2 data (mg/m^3)	HCl data (mg/m^3)
Hourly average 1	16.61	6.85	8.42	5.14
Hourly average 2	16.57	6.88	8.50	5.13
Hourly average 3	16.54	6.92	8.62	5.13
Hourly average 4	16.52	6.93	8.56	5.05
Hourly average 5	16.63	6.90	8.55	5.09
Hourly average 6	16.57	6.91	8.46	5.23
Hourly average 7	16.59	6.87	8.34	5.18
Hourly average 8	16.66	6.89	8.42	5.14
Hourly average 9	16.67	6.85	8.36	5.09
Hourly average 10	16.70	6.72	8.20	5.17
Hourly average 11	16.60	6.74	8.02	5.02
Hourly average 12	16.60	6.67	8.17	4.94
Daily Average	***16.61***	***6.84***	***8.38***	***5.11***

Table D8 Experimental Emissions Data for pyrolysis experiments - Day 8

Day 8	CO_2 (%)	CO data (mg/m^3)	SO_2 data (mg/m^3)	HCl data (mg/m^3)
Hourly average 1	16.59	6.67	8.17	4.62
Hourly average 2	16.59	6.71	8.18	4.63
Hourly average 3	16.58	6.68	8.37	4.65
Hourly average 4	16.59	6.69	8.47	4.63
Hourly average 5	16.63	6.68	8.45	4.84
Hourly average 6	16.64	6.60	8.40	4.94
Hourly average 7	16.64	6.66	8.16	4.95
Hourly average 8	16.63	6.68	8.04	5.11
Hourly average 9	16.61	6.70	8.07	5.13
Hourly average 10	16.59	6.74	8.28	5.19
Hourly average 11	16.55	6.78	8.46	5.26
Hourly average 12	16.53	6.82	8.60	5.27
Daily Average	***16.60***	***6.70***	***8.30***	***4.93***

Table D9 Experimental Emissions Data for pyrolysis experiments - Day 9

Day 9	CO_2 (%)	CO data (mg/m^3)	SO_2 data (mg/m^3)	HCl data (mg/m^3)
Hourly average 1	16.62	6.91	8.54	5.25
Hourly average 2	16.75	6.93	8.44	5.20
Hourly average 3	16.71	6.89	8.51	5.18
Hourly average 4	16.71	6.86	8.47	5.16
Hourly average 5	16.68	6.81	8.20	5.05
Hourly average 6	17.04	6.75	8.04	4.97
Hourly average 7	16.84	6.71	7.91	4.69
Hourly average 8	16.62	6.62	7.94	4.56
Hourly average 9	16.60	6.58	8.13	4.33
Hourly average 10	16.75	6.93	8.44	5.20
Hourly average 11	16.59	6.56	8.16	4.36
Hourly average 12	16.62	6.54	8.27	4.57
Daily Average	***16.71***	***6.76***	***8.25***	***4.88***

Table D10 Experimental Emissions Data for pyrolysis experiments - Day 10

Day 10	CO_2 (%)	CO data (mg/m^3)	SO_2 data (mg/m^3)	HCl data (mg/m^3)
Hourly average 1	16.62	6.55	8.33	4.79
Hourly average 2	16.64	6.38	8.39	4.87
Hourly average 3	16.63	6.56	8.28	4.94
Hourly average 4	16.62	6.59	8.11	5.01
Hourly average 5	16.60	6.59	8.25	5.03
Hourly average 6	16.56	6.67	8.58	5.34
Hourly average 7	16.56	6.67	8.58	5.34
Hourly average 8	16.55	6.72	8.68	5.21
Hourly average 9	16.95	6.77	8.66	5.08
Hourly average 10	16.95	6.77	8.66	5.08
Hourly average 11	16.54	6.81	8.62	5.10
Hourly average 12	16.54	6.81	8.56	5.09
Daily Average	***16.65***	***6.66***	***8.47***	***5.08***