Pyrolysis of Chlorinated Hydrocarbons using Induction Heating

By

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Declaration

All work that is submitted in this thesis is my own, except as otherwise specifically acknowledged in the text. This work has not been submitted in part, or in whole to any other University.

This project was undertaken in the School of Chemical Engineering at the University of Natal under the supervision of Prof D Arnold and co-supervised by R Rawatlal.

_____   _____

Kruben Pillay   Date

Declaration by supervisor

I Prof D Arnold acknowledge that I have read and understood all the work presented in this thesis by K Pillay. I therefore approve this thesis for submission.

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Prof D Arnold   Date

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Abstract

Chemical and allied industries produce significant quantities of chlorinated wastes each year. Thermal treatment of these chlorinated wastes has a long and controversial history. The most common and contentious method of waste destruction is incineration. Although waste incinerators are designed to provide greater control over the combustion process, toxic products are inevitably formed from incomplete combustion and released in stack gases and other residues. The most notable group belonging to the products of incomplete combustion (PICs) are dioxins and furans. The fact that oxygen is an integral part of the molecular structure of dioxins and furans suggests that the formation of these particular PICs may be reduced or avoided by minimizing or completely excluding oxygen from thermal waste treatment.

Pyrolysis using induction heating is a relatively new technology that has shown much promise from the initial work performed by Pillay (2001). This research was an extension of that study, and investigated equipment and process optimization as well as macroscopic modeling of different systems. The objective of this study was to establish the technology of pyrolysis using induction heating as a competitive alternative to existing waste destruction systems.

The novel approach of pyrolysing compounds using induction heating was demonstrated by destroying chlorinated aliphatic, aromatic and a mixture of these compounds. These experiments were conducted at atmospheric pressure in a tubular laminar flow reactor (5.2cm I.D) under a thermally transparent argon atmosphere. In this system heat was generated in an embedded graphite tube using induction heating. Thermal degradation occurred through the bombardment of the compounds by the photons emitted from the heated graphite tube. The compounds were pyrolysed at temperatures ranging from $330^{\circ}C$ to $1000^{\circ}C$ and at mean residence times from 0.47s to 2.47s. In addition to these process variables the effects of reactant concentration and additives were investigated.

The major species formed from this thermal treatment were solid carbon black and gaseous hydrogen chloride. Destruction efficiencies (DE) of the order of 99.9999% (six nines) and greater were obtained for the different feed mixtures at their respective operating conditions. A minimum DE of six nines adequately satisfies the regulation set by the Environmental Protection Agency (EPA) for successful waste destruction.

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Nomenclature

$\overline{X}$	– Mean conversion
CFC	– Chlorofluorocarbon
CFD	– Computational fluid dynamics
CHC	– Chlorinated hydrocarbon
DE	– Destruction Efficiency
DRE	– Destruction and removal efficiency
$E(\lambda)$	– RTD Function
EDS	– Energy dispersive spectroscopy
$F(\lambda)$	– Cumulative RTD function
GC	– Gas chromatograph
k	– Rate constant
LBDE	– Lowest bond dissociation energy
MS	– Mass selective
ODS	– Ozone depleting substance
PCB	– Polychlorinated biphenyl
PCDD	– Polychlorinated dibenzodioxin
PCDF	– Polychlorinated dibenzofuran
PDE	– Partial differential equation
PIC	– Product of incomplete combustion
POP	– Persistent organic pollutant
r_A	– Reaction rate
Re	– Reynolds number
RTD	– Residence time distribution
SEM	– Scanning electron microscope
UNEP	– United Nation Environment Programme
V	– Volume
X	– Conversion
λ	– Life expectancy of a molecule
t_m	– Mean residence time
θ	- Age of a molecule

Chapter 1: Introduction

1.1 Project introduction and scope

Chlorinated hydrocarbons have an extensive range of applications namely: solvents in syntheses, cleaning agents, starting materials in polymerisation, dielectric fluids and other product manufacturing applications. These chlorinated hydrocarbons are present in the atmosphere, municipal and hazardous material combustion, as well as in destruction processes related to the above mentioned industrial applications.

Although industry is reliant on these chemicals they are very toxic and have the potential to produce compounds that have a much higher toxicity e.g. dioxins and furans. Even the lower chlorinated mixtures can be toxic at concentrations of 0.5mg per m^3 of air (Mohr, 1997). When their toxicity was discovered in the late 1970's, the production of some of the more toxic compounds, namely polychlorinated biphenyls (PCBs), were banned in many countries. Chlorinated hydrocarbons fall under the category of persistent organic pollutants (POPs) since they show poor degradability when released into the environment as they resist metabolic processes that would normally break down toxic compounds into simpler chemical components.

Although production of PCBs was banned in the 1970's large amounts had already been manufactured and needed proper disposal. Society in general (industrial and private sectors) is still dependant on chlorinated hydrocarbons hence the production of the less toxic members still continues. This means that waste destruction technologies are still essential not only for the safe destruction of previously produced chlorinated wastes but for future wastes as well.

Traditionally landfilling was used to control the threat of these compounds. This method is extremely ineffective as it only postpones the problem. Furthermore, landfilling causes air pollution by generating greenhouse gases and unpleasant smells. It also causes water pollution by leakage of these toxic chemicals and soil pollution by generating a build-up of hazardous substances in the soil. Incineration was the first technology that was developed to address this waste disposal problem. The most common definition of an incineration process is a combustion process carried out on a controlled basis; which means that the oxygen to fuel ratio is adjusted to give the desired reaction conditions. Incineration processes are able to destroy large amounts of chlorinated wastes; however, they produce waste gases that are:

(1) less toxic than the feed material but in excessively large quantities e.g. CO, CO_2, acid gases
(2) trace amounts of extremely toxic compounds e.g. dioxins and furans

These two factors contribute largely to the reason why incinerators are criticised and face great public opposition.

In past years, members of the scientific community were of the opinion that the problems associated with incineration could be solved through extensive research {Taylor (1996); Tanabe (1988)}. Most modern day incinerators are able to comply with governing air pollution control regulations through complex and costly gas cleaning systems (Williams, 2000). However incinerators are still prone to failures since they can only work safely in a very small operating window in terms of dioxin production. Many environmentalists are of the opinion that even if incineration becomes the perfect waste destruction technology it is unlikely that it will be accepted due to its poor reputation. It is well acknowledged that in our present society decisions can no longer be based only on technical considerations since socio-political considerations can easily outweigh these. (Fife, 1973)

Currently South African ambient air quality laws are rather relaxed, which means that waste technologies like incineration are used without regard to the pollution it causes. However this is likely to change with the drafting of a new air quality bill which is set to bring South Africa on par with international standards. The air quality bill that is likely to go before parliament is a comprehensive document that takes into account a number of international protocols, to which South Africa is a signatory. These include the Montreal Protocol that regulates chlorofluorocarbons (CFCs) that have an impact on the ozone layer and the Kyoto Protocol, which attempts to reduce greenhouse gases (Reddy, 2003). With the promulgation of the air quality bill the South African government will make it clear to industry that it will have to conform to standards that meet international trends, or face stiff penalties.

Widespread environmental concern over the safe disposal of chlorinated wastes using incineration presented an opportunity which lead to the emergence of a number of different waste destruction technologies. Although some of these technologies are efficient they are by no means perfect, each with their distinct disadvantages. Thus there is still an opportunity for more effective waste destruction technologies.

One of the most promising and exciting waste destruction technologies to emerge is pyrolysis using induction heating. Like incineration, pyrolysis is a thermal degradation process. In contrast pyrolysis is a process in which complex materials are decomposed into smaller fragments by means of thermal degradation in an oxygen free atmosphere. Because air is not used in pyrolysis reactions the volume of exhaust gas is likely to be far less than the volume of gas produced from incineration. The most important difference is the fact that pyrolysis is an endothermic process whilst incineration is an exothermic process.

The pyrolysis process has been used for many years by industry; for example in the production of charcoal and methanol from wood, and coal gasification. Similarly induction heating has also been used in industry for a number of years, particularly for the application

of curing metals. These two technologies provide the core of a very efficient system capable of chlorinated waste destruction.

The first stage of the research focused on optimising the reactor setup which was key to the success of the project. In addition the secondary aim of this project was to provide a more fundamental understanding of the chemistry of reductive pyrolysis for different classes of chlorinated hydrocarbons. Providing an elementary understanding was not only limited to the chemistry but also extended to energy transfer processes that added another dimension to understanding the pyrolysis system. The final stage involved using a classical residence time distribution model to predict reaction kinetics.

The overall focus of the research was to demonstrate the competitiveness of the pyrolysis technology with other existing waste destruction technologies whilst providing a more fundamental understanding of the technology and contributing to knowledge concerning pyrolysis reactions. To this effect the chemicals that were used were carefully selected according to a number of criteria as detailed below.

1.2 Motivation for studying dichloromethane destruction

The primary reason why dichloromethane was selected as a model chlorinated hydrocarbon to perform initial experiments was due to the fact that the system was still largely in its development stage. This meant that changes were continually being made to firstly get the system fully operational and secondly optimized (Chapter 4). Thus during this equipment design and optimization phase of the project, compounds that had high toxicities could not be used since they would pose a serious safety hazard in the event of a problem. Dichloromethane differs from conventional solvents (e.g. ethyl ether) in the sense that at atmospheric pressure and room temperature it is not flammable, which contributes to safety issues (Coffee, 1972).

The fact that dichloromethane has a strong tendency to form the major products of solid carbon and gaseous hydrogen chloride at high destruction efficiencies, without the formation of higher toxic chlorinated compounds, was also a significant contributing factor. This has been shown by the experiments performed by Tirey (1990), Taylor (1991), Taylor (1999) and Pillay (2001).

Chlorinated methanes are also commonly found in hazardous and toxic wastes for example they are common water pollutants from the pulp and paper industry. Since they are the simplest chlorinated hydrocarbons, the study of their thermal decomposition can furnish fundamental information which can be extended to the degradation of more complex chlorinated hydrocarbons and eventually to that of more complex waste streams. The

simplest chlorinated methane is chloromethane (CH_3Cl); however, this compound is considerably more expensive than dichloromethane.

1.3 Motivation for studying chlorobenzene destruction

Chlorobenzene was the first aromatic compound to be pyrolysed using the designed pyrolysis system. The main reasons for this choice were:

➢ Simplest chlorinated aromatic, hence the most logical starting point for the transition from chlorinated aliphatics to aromatics.

➢ Surveyed literature stated that chlorobenzene had a low sooting propensity compared to its higher chlorinated counterparts. This was important due to the physical limitation of the system to handle large amounts of carbon black production.

➢ Principal organic hazardous constituents (POHCs) are compounds which are used to determine the destruction efficiencies in hazardous waste treatment processes. Chlorobenzene is ranked number 15 out of 320 on the POHCs list generated by Dellinger (1990); in addition it is also the preferred choice by many regulatory bodies e.g. Environmental Protection Agency.

➢ The final and most important reason why chlorobenzene was chosen as a model aromatic compound is because it is chemically related to polychlorinated biphenyls.

2. Literature Survey

The current work builds upon previous work (Pillay, 2001) by incorporating material acquired from numerous sources during the course of on-going work in year 2002 on the issue of waste destruction. Additional literature research was conducted specifically for this initiative.

2.1 The History of Waste Destruction of Polychlorinated Biphenyls (PCBs)

Introduction

Persistent organic pollutants (POPs) are highly stable organic compounds that have extensive uses in industry, or that are unintentionally produced as by-products of industrial processes and other human activity.

The criteria to classify a pollutant as a POP are under continuous evolution, due to the progress in understanding their environmental fate and the necessity to prevent and remedy their effects on human health and environment: lipophilicity, persistence and toxicity. Since POPs are semi-volatile they may be transported around the planet in the atmosphere and as they are fat soluble by definition (accumulate in the fatty tissues of living organisms) a bio-magnification process generally takes place. (Rahuman M, 1998)

PCBs are a class of POPs that consist of industrial products, mainly synthetic oils. In common with many of them (polychlorinated dibenzodioxin / polychlorinated dibenzofuran and pesticides) is the fact that they contain chlorine. The threat of POPs on the environment and the health of the population on a planetary scale is so serious that it requires urgent and effective measures. More than 100 national governments agreed to a Global Programme of Action, which aims to phase out POPs and in particular PCBs. It has been estimated that 31% of the total world production of PCBs (370, 000 tons) has already been released to the environment. More than 60% remains in use or in storage and only 4% has been destroyed (Tanabe S, 1988).

2.1.1 Source of PCBs

Industrial production of PCBs started in the 1930's. The high chemical stability and electrical resistance of PCBs, together with their low volatility and poor tendency to combust, made them ideal for wide-spread application in heavy-duty transformers and capacitors (Jones, 1989). Other industrial uses are the formulation of hydraulic and heat-exchange fluids, incorporation into protective coatings for wood, metal, and concrete, usage

in plastics, printing inks, plasticisers, adhesives, and lubricating additives. The technical mixtures have been marketed world-wide under trade names such as Aroclor, Phenoclor and Delor.

In Japan 1968 cooking oil was contaminated with a complex mixture of PCBs, dibenzofurans and quaterphenyls. Due to the contamination 1700 people were affected with a number of severe clinical manifestations. In addition, because these chemicals persist in human tissue, offspring were also affected (Chen, 1985). As a result of this incident the toxic nature of these chemicals became apparent which sparked a worldwide investigation into these class of compounds.

In the late 1970s most Western countries, banned the production of PCBs (Kimbrough, 1989). Many countries and intergovernmental organizations had banned or severely restricted the production, use, handling, transport and disposal of PCBs. However in Western Europe and the United States alone, over 800 million tons of PCBs had been produced, and a large part has become distributed in the environment whilst significant quantities are still being used in old transformers and capacitors.

2.1.2 Background to waste destruction

More than twenty years ago knowledge on PCBs affect on health was less extensive and detailed than at the present time thus available technologies were limited to mainly to landfill and incineration, while innovative chemical treatment technologies were less proven. Burning waste to destroy it has always appeared to be an attractive and simplistic solution to make waste "disappear" (Tanabe, 1988).

Thermal treatments to destroy these wastes have a long and controversial history. The most established and controversial technology is incineration. Incineration has increasingly come under critical scrutiny especially during the past decade due to the fact that it actually creates more pollution than it takes away. The technology of incineration of waste has undergone many advances in the past decades. From simple kilns, today's modern incinerators can be equipped with very sophisticated pollution control equipment, and be designed for specific waste streams such as municipal solid waste, hospital waste, industrial waste, or hazardous waste.

However, owing to the basic process of burning, it has inherent problems and these get magnified when the process is not carried out as per recommended standards. But even where standards are strictly maintained, production of toxic byproducts like dioxins and furans by incinerators are inevitable.

The fact that oxygen is an integral to the molecular structure of dioxins and furans suggests that the formation of these particular products of incomplete combustion may be reduced or eliminated by minimizing or completely excluding oxygen from thermal waste treatment. When oxygen levels in an incinerator are reduced to levels below the optimum for combustion, the incinerator is said to operate in a "starved air" or "pyrolytic" mode.
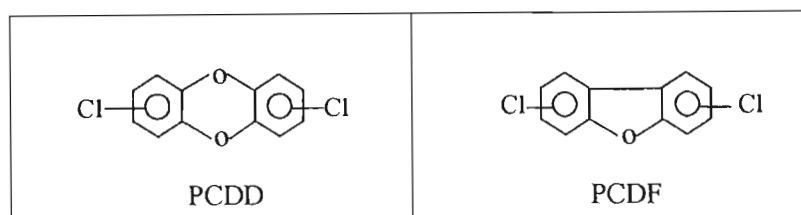
Figure 2-1: General molecular structure of polychlorinated dibenzo-p-dioxins (PCDDS) and dibenzofurans (PCDFs).

Thermal destruction of complex organic substances that occur in the absence of oxygen is defined as pyrolysis. Some polymers will depolymerize in the presence of excessive temperatures either to polymers of lower molecular weight, or back to the monomers from which they were derived.

Pyrolysis is typically carried out in a temperature range of 400-800°C. At these temperatures waste materials are transformed into gases, liquids and a solid residue. The relative proportions of gases, liquids and residue depend on the composition of the wastes, temperature and the time that the temperature is applied for. Short exposure to high temperatures is termed flash pyrolysis, which maximizes the amount of liquids generated. If lower temperatures are applied for longer periods of time, solids predominate.

While many proponents of modern waste treatment systems refer to pyrolysis as being a new technology, this is not the case. For centuries pyrolysis has been used in the manufacture of charcoal, and it is also used extensively in the petroleum and chemical industries. Many incinerator designs make use of pyrolysis by operating via a two stage process namely: a pyrolysis chamber followed by an afterburner or combustion chamber.

2.1.3 Properties and Toxicity of PCBs

PCBs are aromatic, synthetic chemicals which do not occur naturally in the environment. They consist of the biphenyl structure with two linked benzene rings in which some or all of the hydrogen atoms have been substituted by chlorine atoms.
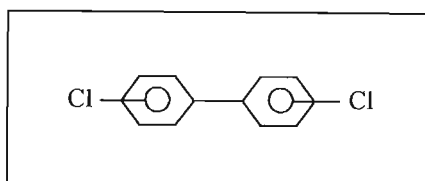
Figure 2-2: General molecular structure of a polychlorinated biphenyl

The chemical formula of PCBs is $C_{12}H_{10-n}Cl_n$ where n ranges from 1 to 10. All 209 congeners of PCBs are lipophilic and their lipophilicity increases with increasing degree of chlorination. However, they have very low water solubilities. Congeners with a lower degree of chlorination are more volatile than those with a higher degree. Pure individual PCB congeners are colourless and often crystalline. Commercial PCB mixtures are clear to light yellow oils or resins and they do not crystallize, even at low temperatures.

PCBs are practically fire resistant because of their high flash points (170–380 °C). They form vapours which are heavier than air, but are not explosive. They have low electrical conductivity, high thermal conductivity and high resistance to thermal degradation. On the basis of these properties they have been used as dielectric isolators in electrical equipment.

Investigations in many parts of the world have revealed widespread distribution of PCBs in the environment. The universal distribution of PCBs throughout the world, suggests that PCBs are transported in air (Jensen, 1966). The ability of PCBs to co-distil, volatilize from landfills into the atmosphere and resist degradation at low incinerating temperatures, makes atmospheric transport the primary mode of global distribution.

The following discussion focuses primarily on the toxicology of organochlorine compounds. It must be noted that PCBs in general cannot be regarded as homogenous since the individual congeners show diverse environmental fates and toxicities.

The toxic effects of PCBs and dioxins are very similar in nature and have been extensively documented since the discovery of their destructive nature. PCBs have several properties which make them toxicologically important. First, they are generally very resistant to both chemical and biological degradation and they are highly lipophilic. Consequently, they accumulate in food chains and human exposure occurs primarily via food. These compounds are known to be persistent and thus able to reach high concentrations both in the environment and in human tissues. There is a substantial amount of literature pertaining to the effects of these compounds. The following effects are some of the most common and well documented (Hanberg, 1996):

- Cancer and effects on behaviour and the immune system occurs after long-term exposure to relatively low doses of PCB-mixtures.

- Effects on tumour development, as well as developmental effects on reproduction, neurobehaviour, and immune function, are proposed to result from human exposure to PCBs.

- Developmental effects of PCBs on behaviour have also been reported for infants and children.

2.2 Mechanism for the formation of gaseous reaction products

2.2.1 Introduction

As with any process it is critical to understand the chemistry of the reactions occurring in the system. The chemistry of pyrolysis reactions is a very complex subject and its study and understanding is essential in explaining how the radicals are interacting to form observed reaction products.

A better understanding of pyrolysis and combustion of chlorinated hydrocarbons (CHCs) remains of considerable practical importance since each year significant quantities of toxic wastes containing chlorinated hydrocarbons are generated by chemical and allied industries. However the understanding of high-temperature chemistry and kinetics of CHCs is crude relative to that of hydrocarbons (Taylor, 1996).

Since pyrolysis of hydrocarbons has been extensively documented and the elementary reactions for these compounds are relevant to the pyrolysis of their chlorinated derivatives this section will be briefly examined. Thereafter this knowledge will be applied to chlorinated compounds with particular emphasis on the production of carbon from gas phase pyrolysis reactions.

2.2.2 Pyrolysis of hydrocarbons

2.2.2.1 Reaction families of Hydrocarbon Pyrolysis

The building blocks for overall mechanisms consist of elementary radical-forming, radical-consuming and radical interconverting reactions. Particular attention is given to homolysis, hydrogen abstraction, β-scission, addition, rearrangement, bond-forming and bond breaking processes.

The first two families are usually the important initiation and termination events. These reactions are the only ones wherein there is a net change in the number of radicals, so it is these steps that influence the total concentration of reactive free-radical intermediates.

β-scission and hydrogen abstraction steps often occur together in a chain propagation sequence. That is, a radical abstracts a hydrogen atom from the reactant to form a molecule and a new radical. This reactant-derived radical then decomposes by breaking a β bond to the radical center (β-scission) to regenerate the abstracting radical and to produce a molecule with a double bond involving the carbon atom that had been the radical center. This type of chain reaction was first explained for hydrocarbon pyrolysis by Rice and Herzfeld (1934).

2.2.2.1 (a) Homolysis

This is the most common radical-forming process. It consists of breaking of a covalent bond to form two radicals.

$$R_1 - R_2 \rightleftarrows R_1 \bullet + R_2 \bullet$$
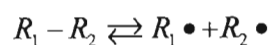
The bond dissociation enthalpy offers a guide for identifying the weakest bond in a multifunctional molecule, and hence the most facile site for homolysis or the order of homolytic liability in a closely related family of molecules (Poutsma, 2000).

2.2.2.1 (b) Molecular Disproportionation

The reverse reaction between the C-H bond in one molecule and a π bond in another molecule to produce a pair of radicals is called molecular disproportionation.

$$RH + R_2C = CR_2 \rightleftarrows R \bullet + R_2HCCR_2 \bullet$$
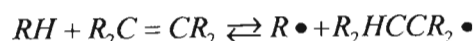
The encounter of two radicals leads not only to combination as normally the dominant process but also, if at least one contains an H substituent in the β position, a significant proportion of disproportionation in which this hydrogen is transferred to a radical center to form one saturated and one unsaturated product (Mitchell, 1993). Radical-interconverting reactions are a class of reactions where one radical is consumed whilst another is formed.

2.2.2.1 (c) Hydrogen abstraction

Hydrogen abstraction is a bimolecular process, which requires collision of two reaction partners, and is characterised by a negative change in entropy, hence its Arrehnius factors are

lower than for homolysis. This reaction is the second major contributor to the initial activation of organics under pyrolysis conditions, besides homolysis of C-C and C-X (X= Cl, Br or S) bonds to form smaller fragment radicals, is cleavage of a C-H bond by hydrogen transfer to an attacking radical (radical metathesis):

$$A \bullet + HB \rightarrow \left[A \underset{1}{H} B \leftrightarrow {}^{\delta}A^{-} \underset{2}{H} {}^{\delta}B^{+} \right] \rightarrow AH + B \bullet$$
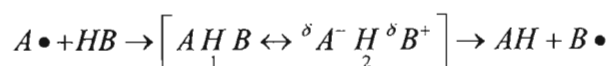
In the hydrogen abstraction transition state (1↔2), bond making and bond breaking are coupled such that the required activation energy is only a small value of the bond dissociation enthalpy of the bond being broken.

The kinetic enhancement of hydrogen abstraction by the polar effect makes possible the known phenomenon of homogenous catalysis of certain pyrolysis reactions by H-X species such as HCl, HBr or H_2S (Mitchell, 1993). This offers an advantage in systems were a near thermoneutral hydrogen transfer is rate limiting. If the medium contains comparable amounts of an H-X species, the same net transformation could be achieved by successive steps. If the activation energy of these steps were significantly lower then this offers a kinetic advantage, with the H-X serving as a non-consumed catalyst. Since X is electronegative the polar effect lowers the activation energy for hydrogen abstraction (Rice, 1934).

2.2.2.1 (d) β- Scission-addition

A well known elementary reaction at ambient temperatures is radical addition to an olefin to form an adduct radical. Radical addition is significantly exothermic because the formation of a new C-C bond over compensates for the opening of a π bond, but it entails an unfavourable entropy loss. β- Scission occurs as the temperature is increased into the pyrolysis range through the reverse reaction, since radical addition becomes thermodynamically unfavourable.

$$R - CH_2 - CHR_1 \bullet \; \rightleftarrows \; R \bullet \; + \; CH_2 = CHR_1$$
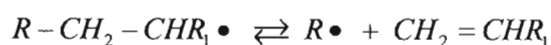
2.2.2.1 (e) Isomerisation

Isomers are compounds with the same formula but a different arrangement of atoms in the molecule and different properties. Intramolecular 1,2-shifts of hydrogen or alkyl groups in radicals are occasionally postulated but possess such a large activation barrier that is typically insurmountable compared with other radical decay pathways.

2.2.2.2 Formulation of pyrolysis reaction mechanisms

When multiple paths are available for a given type of bond-breaking reaction, the path that involves cleavage of the weakest chemical bond is expected to be the fastest path. In this light, note that C-H bonds are typically stronger than C-C bonds. The presence of a double bond or an aromatic ring can also influence the strengths of the C-H and C-C bonds. Bonds involving the carbon atom α to the unsaturated carbon atom are weaker than their aliphatic analogs because an unpaired electron on an α carbon can be delocalized over multiple carbon atoms (Savage, 2000).

Bond dissociation energies can be used to predict the important elementary steps in hydrocarbon pyrolysis. As an example consider the pyrolysis of alkylbenzene studied by Savage (2000). From Figure 2-3 we can see that the weakest bond is the bond between the α and β carbons in the alkyl chain. Thus one expects homolytic dissociation of this C-C bond to be the fastest initiation step. Moreover on expects cleavage of this C-C bond to be associated with the fastest β-scission step. Accordingly β-scission of the γ-radical is expected to be the fastest β-scission step. Examining the bond dissociation energies of the C-H bonds, one observes that the α-C-H bond is the weakest, so the fastest hydrogen abstraction steps should involve these hydrogen atoms.
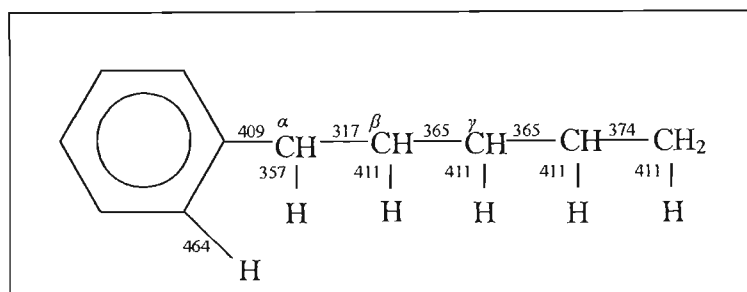
Figure 2-3: Bond dissociation energies (kJ/mol) for alkylbenzene

Kossiakoff (1943) encountered in gas phase pyrolysis, where the substrate concentration is low and at high temperatures, that unimolecular steps (β-scission and isomersiation) are favoured over bimolecular hydrogen abstraction steps. If β-scission is the faster of the two unimolecular steps, then radicals undergo successive β-scission reactions and eliminate small molecules (e.g. ethylene for pyrolysis of n-alkanes) until there are no more weak C-C bonds to break by β-scission. On the other hand, if intramolecular hydrogen abstraction (isomerisation) is the more rapid step, an equilibrium distribution of radicals will be produced prior to the β-scission decomposition step. These isomerisation steps will favour the more stable radicals and they will thereby influence the product distribution so that for

the case of n-alkane pyrolysis, less ethylene is produced and higher hydrocarbons are produced.

Poutsma (2000) showed that homolysis reactions are favoured at higher temperatures. Also since molecular disproportionation is bimolecular and homolysis is unimolecular it will be favoured by higher concentrations. Thus molecular disproportionation though generally unlikely in competition with homolysis, should be considered under circumstances where:

- The reactants or accumulating products lack weak C-C bonds but do contain favourable unsaturated reaction partners (olefins or aromatics) for this form of hydrogen transfer.
- Temperatures are low
- Concentrations of unsaturates are high e.g. in the latter stages of cracking

2.2.3 Pyrolysis of Chlorinated Hydrocarbons

2.2.3.1 Chemistry

The reaction steps outlined in section 2.2.2.1 for hydrocarbon pyrolysis are also available to the radicals in the pyrolysis of chlorinated hydrocarbons. However in chlorinated systems the initiation reactions differ due to the lower bond energy of C-Cl bond, therefore cleavage of this bond is the first step in the reaction mechanism.

Table 2-1: Comparison of the bond dissociation energy between chlorine and hydrogen bonds (Mckinnon, 1990)

Bond	Bond Dissociation Energy/ (kJ/mol)
C-Cl	242
CH_3-H	435
C_2H_5-H	410
C_6H_5-H	462

The weakness of the C-Cl bond leads to relatively high Cl atom concentration in the sooting reaction system (Starikovsky, 1998). Frenklach (1986) as well as McKinnon (1990) have shown that the formation of soot and the distribution of pyrolysis products can be explained through chlorine catalysed reaction mechanisms.

Wenpin (1992) developed a detailed kinetic reaction mechanism based upon fundamental thermochemical data, kinetic principles, transition state theory and evaluated literature rate

constant data. He used the above-mentioned data to construct a model that is able to predict the stable species concentration profiles of CH_3Cl and CH_2Cl_2 in combustion and pyrolysis environments. By performing a sensitivity analysis on the model he was able to provide insight into the effects of chlorinated hydrocarbons in pyrolysis and oxidation environments.

The analysis indicated that atomic chlorine is formed at early reaction times. The chlorine reacts very rapidly with the reactant fuel molecules, which at early times are present at high levels. The important reaction pathways at combustion temperature are abstraction of H by the Cl to form the corresponding hydrogen radical and HCl. These abstraction reactions by Cl are fast, they have Arrhenius factors usually greater than 1.0 E+13 and with relatively low activation energies, typically just a few kJ/mol. The result is a rapid, nearly catalytic production of hydrocarbon and chlorocarbon radicals early in the reaction, where there is a recycle of a significant fraction of the HCl to Cl.

The oxidative pyrolysis of methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4) was investigated by Tirey et al (1990). For the studies Tirey (1990) used tubular flow reactor operating under laminar flow conditions, coupled to a GC-MS. Data was obtained over a temperature range of 573-1273K.

This study first illustrated the dominance of the pyrolytic reaction behaviour leading to the formation of several thermally stable reaction by-products and the observation of chlorinated molecular growth reactions resulting in the formation of hexachlorobenzene, C_6Cl_6 (cy), from simple chlorinated methane precursors, $CHCl_3$ and CCl_4.

The formation of higher molecular weight compounds from the pyrolysis and combustion (and oxidative pyrolysis) of chlorinated hydrocarbons have also been reported in literature for the compounds shown in Table 2-2.

Table 2-2: Compounds that result in the formation of higher molecular weight compounds when pyrolysed

Compound	Molecular Formula
Chloroform	$CHCl_3$
Carbon tetrachloride	CCl_4
Dichloroacetylene	C_2Cl_2
Trichloroethene	C_2HCl_3
Tetrachloroethene	C_2Cl_4
Hexachloropropene	C_3Cl_6
1,3- Hexachlorobutadiene	C_4Cl_6

The fact that methyl chloride and methylene chloride did not produce any chlorinated aromatics as opposed to chloroform and carbon tetrachloride lead Dellinger and Taylor (1990) to propose that chlorine facilitates condensation reactions resulting in the formation of chlorinated aromatic species. They further suggested that the tendency to form higher molecular weight species is attributable to the propensity for chlorinated radicals to undergo reversible, addition/elimination (displacement) type molecular growth reactions. An example of these type of reaction is shown below:

$$C_2Cl_3 + C_2Cl_4 \leftrightarrow C_4Cl_7^{\bullet} \rightarrow C_4Cl_6 + Cl$$

Taylor (1999) postulated that chlorine substitution can play a major role in the rate of these molecular growth reactions through inductive destabilization of the initially formed adduct and through elimination of chlorine from the adduct. Chlorine elimination reduces the probability of the reverse decomposition of the adduct to reactants. The lower C-Cl bond energies in CHCs, versus C-H bond energies in hydrocarbons, may favour these types of molecular growth reactions (Taylor, 1999).

Tirey et al (1994) presented calculations illustrating that chemically activated displacement of Cl atoms from olefinic and acetylenic species by olefinic radicals is favoured for CHCs as compared to the similar displacement of H atoms from hydrocarbons. They proposed that this is in part responsible for the high yields of chlorinated aromatics for the more chlorinated of these species.

2.2.3.1 Effect of reaction atmosphere on the thermal destruction of chlorinated compounds

Graham (1986) examined the effect of oxygen concentration on the thermal stability of the components of a mixture of carbon tetrachloride, monochlorobenzene, trichloroethene, trichloroethylene and toluene and the formation of thermal reaction products. Thermal decomposition studies were conducted in atmospheres in which combustion oxygen was present in excess, stoichiometric and absent (pyrolysis).

Results from Graham's (1986) study indicated that decreasing the oxygen concentration increased the thermal stability of the mixture components except carbon tetrachloride. Furthermore each component was less stable in the mixture as compared to the pure compound. The number and complexity of thermal reaction products increased with decreasing oxygen concentration. In all cases, products ranged from simple chlorinated aliphatics to complex polynuclear aromatics. The majority of the identified products are the result of pyrolysis type reactions regardless of the oxygen level in the reactor, although increased numbers and amounts of partial oxidation products were observed as the oxygen concentration increased.

The thermal behaviour of these compounds may be explained by examination of possible elementary reaction mechanisms. Unimolecular decomposition of these compounds would involve a simple rupture of the weakest bond. This is, in principal, a possible decomposition mechanism for each of the compounds; however the lowest bond dissociation energy (LBDE) may be prohibitively large for some of the compounds.

Table 2-3: Energies required for cleavage of the bonds in the respective compounds (Graham, 1986).

Molecule	Bond	Value/ (kJ/mol)
Carbon tetrachloride	C-Cl	293
Chlorobenzene	C-Cl	397
	C-H	460
Toluene	C-H bond of the methyl substituent	356
Chloroethylene	C-Cl	351

On the basis of relative LBDEs Graham (1986) postulated that CCl_4 had undergone unimolecular decomposition by C-Cl bond rupture, since the decomposition profiles were essentially identical for all reaction atmospheres which is consistent for unimolecular decomposition. On the other hand, trichloroethylene, chlorobenzene and toluene, which are dependant on the reaction atmosphere, have large LBDEs but also, have electron structures to decompose by electrophilic attack by an electron-deficient radical species such as H, OH or O.

Similar results were conducted by Taylor (1998), in which he tested the effect of reaction environment on the thermal decomposition profile of several chlorinated methanes namely: methyl chloride, dichloromethane, chloroform and carbon tetrachloride.

Taylor (1998) deduced that although CH_2Cl_2 is initially more stable than CCl_4, CH_2Cl_2 becomes much more sensitive to oxidative degradation at higher temperatures, and the DE curves intersect at 750°C (99.15%). The decreasing order of stability in the absence of oxygen on the basis of the temperature for 99% destruction is

$$CH_3Cl > CCl_4 > CH_2Cl_2 > CHCl_3$$
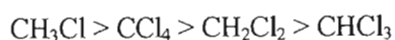
Taylor found that although CCl_4 is initially much less stable than CH_2Cl_2 the DE curves cross at a temperature of 800°C (95.5%) with CH_2Cl_2 more easily degraded at higher

temperatures. With the exception of the higher stability of CCl_4 under near pyrolytic conditions, the relative stabilities for these components vary little with change in reaction atmosphere. In contrast, the absolute thermal stability for each chloromethane component is significantly greater under pyrolytic conditions.

As a result of thermochemical considerations, one may expect the highest Cl atom reactivity with hydrogen-containing chloromethanes. The higher relative stability of CCl_4 compared with that of CH_2Cl_2 and $CHCl_3$ is consistent with this hypothesis. Furthermore, the extremely high thermal stability of CH_3Cl as a result of insufficient Cl atom concentrations is also consistent with this radical initiation mechanism. The observed reactivity of CH_3Cl, CH_2Cl_2 and $CHCl_3$ also correlates with the strength of the abstractable carbon-hydrogen bond.

2.3. Formation of carbon from gas phase pyrolysis

2.3.1 Background

The term carbon black identifies an important family of industrial carbons used principally as reinforcing agents in rubber and as black pigments in inks, coatings and plastics. It is important to note that the term "carbon" is used to describe a wide variety of solid materials, many of which contain appreciable amounts of hydrogen and other elements, which may have been present in the starting compound.

Carbon black is essentially elemental carbon. They are differentiated from bulk commercial carbons such as cokes and charcoals by the fact that carbon blacks are particulate and are composed of spherical particles. The term soot is reserved for the carbon black particles produced by combustion, although carbon blacks, generated by other processes, such as discharges and thermolysis appear to be very similar. Many grades and types of carbon black are produced commercially, ranging in size from less than 100 to over 4000   in diameter (Smith, 1964).

From a chemical point of view carbon black manufacturing processes can be classified into two categories: incomplete combustion and thermal decomposition of hydrocarbons, depending on the presence or absence of oxygen (Donnet, 1993).

Depending on the feedstock and on the quality of the product, the furnace process achieves poor carbon yields and is characterized by a high level of atmospheric emissions. While the legislation in different countries will become more stringent, it will be an increased necessity for the carbon black industry to take into account these environmental aspects.

The carbon black industry also faces problems with the availability of adequate raw materials, as highly aromatic hydrocarbons are required for the production of most carbon

blacks. While the furnace process has been adapted to meet the requirements of the rubber and plastics industries for more than 50 years, it is not certain whether this technology will be able to survive the next century. Although the partial combustion processes are able to produce carbon blacks at a very low price, satisfying the present demand, it remains that the operating conditions are limited by thermodynamic reactions (Fulcheri, 2002).

2.3.2 Industrial Processes for formation of carbon

2.3.2.1 Channel process

In this process carbon particles are produced by the incomplete oxidation of natural gas. Flames from the burning gas impinge on steel channels, where the carbon particles are deposited. These channels move over scrapers that remove carbon black, which is collected in hoppers at the bottom of the channel houses. The yield of the carbon black obtained is very low typically about 1-5%.

The particle size of channel blacks is affected by: slot width in the burner tip, tip distance from the channel, amount of ventilation, and the molecular weight of the feedstock. Natural gas was the source of hydrocarbon for channel black production; however, due to the increased cost of natural gas and more stringent environmental regulations, the production of channel blacks has been largely discontinued. Oil furnace blacks from petroleum oils have replaced the applications for channel blacks.

2.3.2.2 Oil Furnace Process

Aromatic residue oils from petroleum refineries are used for producing oil furnace blacks. In this process oil is heated to about 300°C and then atomized into the hot zone of the furnace at 1400°C. The formation of the carbon black occurs in the hot zone. The yields obtained from this process are considerably higher than that of the channel process and are of the order 35-65%.

The properties of the carbon black produced are adjusted by controlling process variables like the feedstock rate and aromaticity. Decreasing the feedstock rate increases the reactor temperature thus producing lower yields and higher surface area products. Increasing the aromaticity of the feedstock increases the degree of aggregation of carbon black.

2.3.2.3 Thermal Process

The thermal decomposition of hydrocarbon gases in the absence of a flame provides the reaction for the production of thermal blacks. In a typical process two refractory lined reactors are operated in parallel at 1300°C. When one generator is being reheated by burning a stoichiometric mixture of fuel and air, the other is injected with natural gas to produce thermal black. The effluent stream from these reactors contains 90% hydrogen, 6% methane and the remainder a mixture of hydrocarbons. Typical yields of this process are 40-50%.

2.3.3 Composition and Chemical Properties

Carbon blacks consist of 90-99% elemental carbon. Oxygen and hydrogen are the other major constituents and vary with the type of black and method of manufacture. In the following tables typical values for the respective carbon properties are shown.

Table 2-4: Typical particle sizes of commercial carbon blacks (Kinoshita, 1987)

Production Method	Raw Material	Average Particle Size/ $\times 10^{-10}$ meters
Channel Processes	Natural Gas	200-300
Furnace Process	Natural Gas, Petroleum and liquid hydrocarbons	100-800
Acetylene Process	Acetylene	350-420
Thermal Process	Natural gas and coke oven gas	1200-5000

Table 2-5: Composition of commercial carbon blacks (Smith, 1964)

Type	% Carbon	% Oxygen	% Hydrogen	% Volatile Content
High-colour channel	88.4	11.2	0.4	18
Long- Flow channel	90.0	8.7	0.8	12
Reinforcing channel	95.2	3.6	0.6	5
Semi-reinforcing furnace	99.2	0.4	0.3	1.2
Reinforcing oil furnace	98.0	0.8	0.3	1.4
Thermal Acetylene	99.5	-	0.05	0.06

The hydrogen present is residual hydrogen from the hydrocarbon raw material and is distributed throughout the particle. Since oxygen is not present in significant amounts in the reaction zone where carbon black forms, its presence is accounted for by subsequent oxidation and accordingly is confined to the surface of the particle. The oxygen and hydrogen combine with surface carbon atoms and form a variety of surface complexes. Some of the principle surface groups reported in literature are $-OH$, $>C=O$, $-COOH$, as well as aromatic hydrogen, lactones and possibly heterocyclic ether structures. Chemical properties of the carbon black skeleton are analogous to those of large polynuclear aromatic molecules.

The properties of the carbon formed depend on a number of factors however the most important being whether the carbon is formed on a surface present in the reaction zone or from the vapour phase. It is interesting to note that, although a wide variety of surface carbon can be formed, essentially only one type of carbon is formed from the vapour phase. This material is first seen as "smoke" of solid particles in the decomposing gases but it rapidly settles out, as the temperature falls, as a very light fluffy mass of black carbon that has an enormous surface area and porosity (Palmer, 1965).

2.3.4 Chemistry of carbon black formation from hydrocarbons

Due to the overwhelming literature available it is necessary to be restrictive in surveying the subject of carbon formation, thus in this review the main effort will be to assess the present knowledge concerning the phenomenology, kinetics and carbon formation from gases.

Over the years a number of theories for carbon formation have been postulated. Some of the theories are applicable to nucleation while others may be best applied to growth particles, were each process is governed by different laws (Palmer, 1965). The following is a brief description of the more common theories:

- The atomic carbon theory: Gaydon and Wolfard (1978) suggest that monatomic carbon may possibly be a significant species in nucleation.

- The C_2 Theory: Smith (1964) suggests that solid carbon results from the polymerization of C_2.

- The C_3 Theory: Cabanne (1972) supported the view that solid carbon in flames arises by condensation of carbon vapour, the main constituent of which was believed to be C_3.

- The acetylene theory: The essence of the current acetylene theory is that carbon particles are formed from acetylene by simultaneous polymerization and dehydrogenation. The pyrolysis of acetylene is particularly interesting because of its formation from other hydrocarbons.

- The surface decomposition theory: Tesner (1984) has been the principal advocate of a model for carbon particle growth that envisages it as occurring through direct decomposition of hydrocarbons on the particle surface.

Precise knowledge of the decomposition mechanism of a hydrocarbon to form carbon and hydrogen is lacking. From the routes suggested above it is not possible to pick out one and claim it is the route to soot formation. It is very probable that no universal route exists but rather a combination of many different routes. However it is generally accepted by many authors that initial decomposition of the hydrocarbon occurs by cracking and dehydrogenation to form active fragments, which rapidly recombine to form nuclei (Frenklach, 1986; Fussey, 1981; Gaydon, 1960).

In the past one of the most believed theories for soot formation was the "aromatic model". This model assumes that large polycyclic aromatic hydrocarbons (PAHs) coagulate and give rise to primary condensed particles in the gas phase. However in recent years the "polyyne model" has become more popular, purely through deductive experimental work. D' Alessio and coworkers (1992) discovered that primary soot particles do not absorb light in the visible wavelengths and concluded that soot particles are giant agglomerates of large condensed PAHs. They pointed out further that that soot inception is akin to fast polymerisation.

Tesner et al (1994) provided further evidence to D' Alessio's theory by observing that the pyrolysis of a mixture of naphthalene and acetylene produces a tenth as many particles as the pyrolysis of pure naphthalene. Since the presence of acetylene is known to promote growth of PAHs the decrease in the number density of particles rejects "the aromatic model" idea of a dominating role for PAHs in soot formation.

The most recent work rejecting mechanism of soot formation through a PAH generation stage was performed by Shurupov (2000). He conducted experiments on the isothermal pyrolysis of (1) naphthalene-benzene-helium, (2) anthracene-benzene-helium, (3) α-methyl naphthalene-helium as well as some PAH with acetylene addition, at a temperature of 1473K. The major conclusion from Shurupov's work was that during the pyrolysis of a mixture of aromatics and acetylene, it is the acetylene that generates preferably soot particle nuclei, whereas the other components are consumed by the heterogeneous growth particles. This observation is further experimental evidence contradicting the aromatic model.

Krestinin (2000) pyrolyzed methane, acetylene, ethene, diacetylene, benzene and naphthalene. From these results he was able to validate the polyyne model. This model uses the acetylene pathway to form soot particles. The pyrolysis of the above mentioned compounds yielded polymeric globules as primary soot particles. The polyyne model is based on the picture of soot formation shown schematically in Figure 2-4.
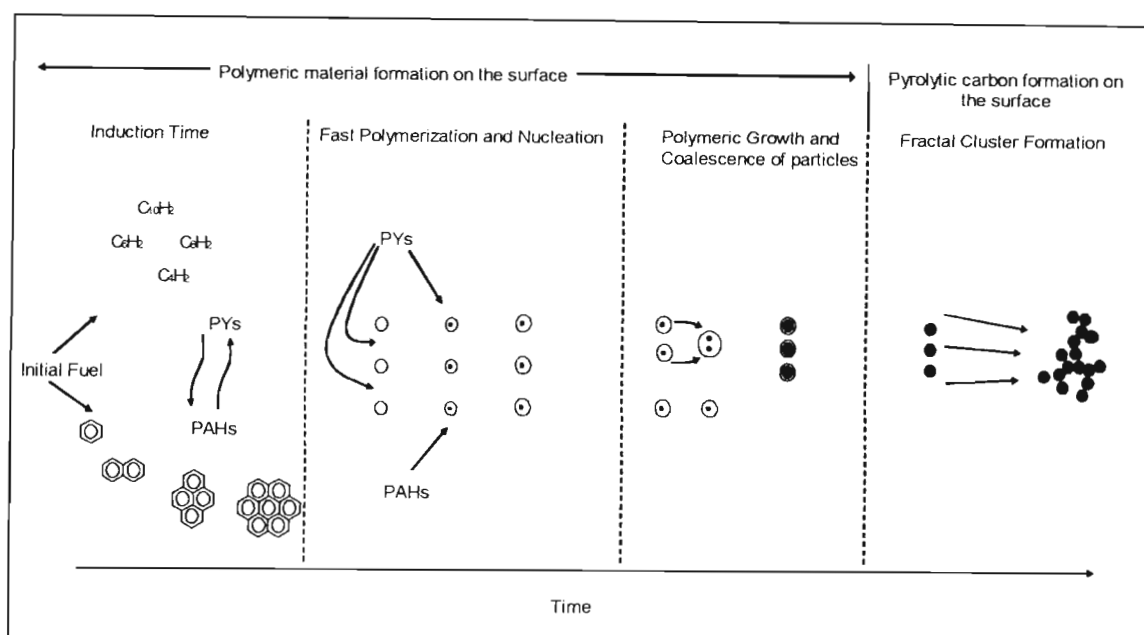
Figure 2-4: Outline of the soot formation mechanism suggested by Krestinin (2000)

During the induction time the pyrolysis of initial fuel results in the formation of polynuclear aromatic hydrocarbons and polyyne molecules. Compared to the rather slow increase in the number of aromatic rings in the PAHs the polyynes grow in a simple and fast way:

Polyyne Model: $C_{2n}H_2 + C_2H = C_{2n}+2H_2 + H$
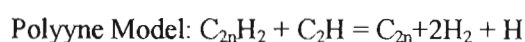
Consequently the concentrations of the polyynes (C_4H_2, C_6H_2, C_8H_2 etc) are high enough to be detected as major hydrocarbon intermediates. This together with the high reactivity of these species in polymerisation reactions suggest that polyynes can be assumed to be the gaseous precursors of soot. This forms the basis of the polyyne model.

Once the first radical nucleus reaches a critical diameter, namely the end of the induction period, the incipient particles produced from the first stage next enter the growth stage, were two processes occur simultaneously. The process consists of the interaction of the molecules of the hydrocarbon and of the radical nuclei with the extremely active surface of the growing nuclei of the carbon particles. At the same time the small spherical particles collide and coalesce into larger particles.

The final stage is called chain formation. In this stage the soot particles collide and stick however they don't coalesce instead they form chain like structures. Harris (1995) and many other authors also observed spherical units of magnitude 100-300Å attached in necklace- like chains.

2.3.5 Influence of Process Variables

2.3.5.1 Influence of Molecular Structure

Johnson and Anderson (1962) have carried out an investigation by electron microscopy on carbon formed by pyrolysis of a wide variety of hydrocarbons from 500°C to 1000°C. They observed different types of solid carbon particles formed vary from tiny isolated specks of material about 100 Å in diameter, up to large dense particles, 5000 Å in diameter, roughly spherical in shape and linked together into networks of chain-like structures.

The entire range of products, including large amounts of polymeric material at the lower temperatures used, can be produced from any of the hydrocarbons studied simply by changing three essential reaction conditions namely the pyrolysis temperature, contact times and concentration of the hydrocarbon. As these three parameters were varied they noticed a gradual transition from one type of particle to another with no sharp differentiation between particular types at any stage. The general conclusion was that the structure and composition of pyrolytic carbons depend little on the nature of the starting compound provided that they only contain carbon and hydrogen.

2.3.5.2 Presence of oxygen

The presence of small amounts of oxygen and water vapor in the decomposing gases largely suppresses the formation of gaseous carbon, (Palmer and Cullis, 1965).

2.3.5.3 Influence of Additives

Determinations have been made of the influence of a very large number and variety of additives to the fuel. The observed effects are generally quite small. Thus for example, addition of acetylene, various olefins, or various paraffinic hydrocarbons has little or no effect on carbon formation in the methane diffusion flame. However benzene addition produces an enhancement and naphthalene promotes carbon formation very strongly. Chlorine compounds have a smaller but qualitatively similar effect, the reduction in carbon formation being directly dependant on the amount of combined chlorine in the additive.

2.3.6 Carbon formation from chlorinated hydrocarbons

2.3.6.1 Chemistry of carbon formation

It has been well documented that the amount of soot produced in the pyrolysis of chlorinated hydrocarbons is larger than that formed from the pyrolysis of normal hydrocarbons. The high sooting trend of chlorinated hydrocarbons is again attributed to a weaker C-Cl bond compared with a C-H bond (See Tables 2-1 and 2-3).

According to Frenklach's (1986) results, chlorine favors the formation of species considered as potential precursors of soot. To exactly see how the chlorine achieves this, consider the mechanism for methyl chloride pyrolysis suggested by Weissman (1984).

$$CH_3Cl = CH_3 + Cl \qquad (2\text{-}2)$$

$$Cl + CH_3Cl = HCl + CH_2Cl \qquad (2\text{-}3) \qquad \text{Formation of } CH_3 \text{ and } CH_2Cl$$

$$Cl + CH_4 = HCl + CH_3 \qquad (2\text{-}4)$$

$$CH_3 + CH_3 = C_2H_6 \qquad (2\text{-}5)$$

$$CH_2Cl + CH_2Cl = 1,2\text{-} C_2H_4Cl_2 \qquad (2\text{-}6) \qquad \text{Recombination reactions}$$

$$CH_3 + CH_2Cl = C_2H_5Cl \qquad (2\text{-}7)$$

$$C_2H_5Cl = C_2H_4 + HCl \qquad (2\text{-}8)$$

Decomposition of reaction

$$1,2\_ C_2H_4Cl_2 = C_2H_3Cl + HCl \qquad (2\text{-}9) \qquad \text{products by HCl elimination.}$$

$$C_2H_3Cl = C_2H_2 + HCl \qquad (2\text{-}10)$$

$$Cl + C_2H_6 = HCl + C_2H_5 \qquad (2\text{-}11) \qquad \text{Dehydrogenation driven by}$$
hydrogen abstraction reactions.

$$C_2H_5 = C_2H_4 + H \qquad (2\text{-}12)$$

$$H + HCl = H_2 + Cl \qquad (2\text{-}13)$$

$$Cl + C_2H_4 = HCl + C_2H_3 \qquad (2\text{-}14)$$

$$C_2H_3 = C_2H_2 + H \qquad (2\text{-}15)$$

Weissman (1984) suggested that the C_2H_3 formed from reaction (2-14) leads to C_2H_2 via reaction (2-15) and the formation of aromatics comes from the addition of C_2H_3 and C_2H_2. Thus the observed higher sooting tendency of methyl chloride compared with methane is explained by the chlorine-catalyzed formation of C_2H_3 and C_2H_2, which are soot precursors.

Frenklach (1986) observed that the general trend for chlorinated hydrocarbons with a H:Cl ratio of one are the sootiest example CH_2Cl_2 and $C_2H_2Cl_2$. Their soot yields are large, comparable to the yields in the pyrolysis of aromatic hydrocarbon and the maximum values are obtained at lower temperatures. The above statement is verified by the data obtained by Frenklach (1986) which clearly showed the higher sooting tendency of chlorinated hydrocarbons. The more hydrogenated CHC's (CH_3Cl and C_2H_3Cl) are poor sooters, whilst less hydrogenated CHC's ($CHCl_3$, CCl_4 and C_2HCl_3) soot at remarkably high temperatures (Frenklach, 1983). The partial reason for this trend is because the more hydrogen present in the system will rapidly react with the chlorine radicals to form hydrogen chloride. The absence of chlorine from the reacting system means that it cannot catalyze reactions leading to soot formation.

Further the important role of CHCl radical leading to C_3H_3 through reaction (2-16) was suggested.

$$CHCl + C_2H_2 \rightleftharpoons C_3H_3 + Cl \qquad (2\text{-}16)$$
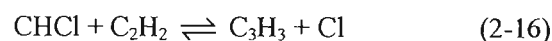
Rapid formation of C_3H_3 initiates an efficient pathway to soot, because the propargyl radical recombination is considered to be a dominant pathway to the first aromatic ring formation.

2.3.6.2 Effect of the hydrogen to chlorine ratio on the sooting propensity

The action of hydrogen additives is apparently related with the effective formation of H atoms and further reactions. The thermoneutral reaction below gives fast generation of H-atoms

$$\dot{C}l + H_2 \rightleftharpoons HCl + H \qquad (2\text{-}17)$$

These H atoms which in turn may react via:

$$\dot{H} + C_xCl_y \rightleftharpoons HCl + C_xCl_{y-1} \qquad (2\text{-}18)$$
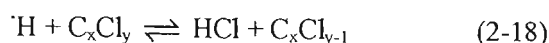
Otherwise the small additive concentrations of H_2 act as promoting factor through the binding of two Cl-atoms and increasing of C/Cl ratio to a more favourable magnitude (Starikovsky 1998).

For large hydrogen concentrations [H]>>[Cl] a soot suppressing occurs. If H_2 is in excess the formation of soot precursors cannot compete with the faster reactions. Starikovsky (1998) suggested that one of the fastest reactions' which would occur was the formation of CH_4 via the reactions:

$$CCl + H \rightleftharpoons CH + Cl \qquad (2\text{-}19)$$

$$CH + H_2 \rightleftharpoons CH_2 + H \qquad (2\text{-}20)$$

$$CH_2 + H_2 \rightleftharpoons CH_3 + H \qquad (2\text{-}21)$$

$$CH_2 + H_2 \rightleftharpoons CH_4 + H \qquad (2\text{-}22)$$
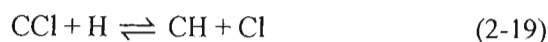
As a result a significant part of carbon converts to CH_3 and CH_4 during the residence time for the experiments, which means that there is not a sufficient amount of reaction time for soot growth.

Frenklach (1989) found that the pathway to soot from chlorinated methanes and ethylenes with a high H/Cl ratio was found to proceed via the formation of C_2H, C_2H_2 and C_2H_3. For chlorinated hydrocarbons with a low H/Cl ratio, it was concluded that the formation of C_2 and its contribution to soot formation becomes significant at high temperatures. Frenklach (1989) also showed that the sooting tendency and PAH production increased with escalating Cl/H ratio. Based on kinetics analysis and modelling he attributed this trend to the enhanced, Cl-catalysed molecular degradation that promotes the formation of aromatic ring compounds, and the large concentration of Cl atoms that accelerates the abstraction of hydrogen from stable PAH molecules, thus activating them for further growth. In terms of the soot formation mechanism discussed above, the further growth could include reactive coagulation involving aryl radicals as well as addition of acetylene to aryl radicals.

Chapter 3: Available technologies for waste destruction

There are a number of waste destruction technologies that are available and operating on a commercial scale throughout the world. However, one must realise that there are specific limitations to each of these processes and hence an opportunity for other more effective technologies to emerge.

In order to assess these technologies they will be discussed according to the universal criteria as stipulated by the United Nations. The following table summarizes the technologies that will be discussed in detail. During the ensuing discussion we will expose the limitations of the technologies shown in Table 3-1.

Table 3-1: Summary of current waste destruction technologies

Technology	Feed Material	Operating Conditions	% DE	Advantages	Disadvantages
Rotary Kiln Incineration	Dichlorobenzene, tetrachlorobenzene and also PCBs	1000°C – 1200°C	*99.9999	- Ability to handle variety of solid and liquid wastes - High capacity: 250-500 kg/h	- Expensive to build and maintain -Releases dioxins but within the limits
Liquid Injection Incineration	Oils and chlorinated solvents (CCl_4, $CHCl_3$, CH_3Cl, CH_3CCl_3)	1350°C 1.3 seconds	*99.99	- Well established technology - Meets most of the performance criteria	- Does not satisfy the limits for dioxin production
Argon Plasma Arc	CFCs and halons	2500°C 20ms	99.9998	- Low emissions of dioxins - Low mass emissions of gaseous pollutants	- Feed pretreating required - Liquid effluent discharged
Inductively Coupled Radio Frequency Plasma	CFCs	2000°C 2 seconds	*99.99	- Good reliability - Low dioxin emission	- High energy consumption (1.28 kWh/ kg feed)
CO_2 Plasma Arc	PCB and trichlorobenzene	1300°C – 3500°C	*99.9999	- High DREs achieved	- High energy consumption - Emission of particulates higher than limit
Solvated Electron	Carbon tetrachloride and		*99.99	- Simple process	- Process expensive

Decomposition	CFCs			- High DEs achieved	- Safety concern
Gas Phase Chemical Reduction	CFCs: PCBs and chlorobenzene	$850^{\circ}C - 900^{\circ}C$	*99.9999	- Capable of handling a variety of inorganic chemicals - Low pollutant emissions	-High feed concentrations required. - Expensive
Gas Phase Catalytic Dehalogenation	PCBs, CFCS	$400^{\circ}C$	*99.9998	- Low energy consumption - Low mass emissions	- Production of liquid effluents - Expensive

* Indicates destruction and removal efficiency

3.1 Criteria for Technology Screening

In the past many countries have had their own internal standards for assessing the performance of waste destruction technologies, prior to being allowed to operate on a commercial scale. Most of these countries had large amounts of stockpiled waste and desperately needed to get rid of their waste. Hence the laws governing waste destruction were extremely lenient. Although developing countries did not have large amounts of wastes they also had relaxed waste laws because of their limited resources. Because of these poor waste destruction laws many countries are using equipment that are ineffective in their respective waste destruction applications, the results of which are the production of materials that are more toxic than the initial starting material and the production of less harmful by-products in exceedingly dangerous quantities.

In the early 1980's The United Nations Environment Programme (UNEP) recognized the need for a unified set of laws to stringently control waste destruction. In April of 2002 they issued their latest report evaluating existing waste destruction technologies. Of the 45 technologies evaluated only 16 met their criteria. These technologies were assessed according to the following criteria:

1. Destruction Efficiency (DE) or Destruction and Removal Efficiency (DRE)

2. Emissions of dioxins and furans

3. Emissions of other pollutants

4. Technical capability

The first three criteria refer to the technical performance of the equipment and are used as a measure of the potential impact on human health and the environment. The technical capability criterion indicates the extent to which the technology has been demonstrated to be able to dispose of their respective wastes effectively and on a commercial scale.

These criteria are very important as they serve as a guideline for assessing the performance of, and in addition a comparison between, existing technologies and pyrolysis using induction heating in the global arena.

3.1.1 Destruction Efficiency (DE) and Destruction and Removal Efficiency (DRE)

The DE is determined by subtracting from the mass of a chemical fed into a destruction system during a specific period of time, the mass of that chemical that is released in stack gases, fly ash, scrubber water, bottom ash, and any other system residues and expressing that difference as a percentage of the mass of the chemical fed into the system. In mathematical terms the DE is defined as:

$$DE = \frac{Moles_{in} - \sum\limits_{Allstreams} Moles_{out}}{Moles_{in}} \quad \dots\dots(3\text{-}1)$$

The DRE has the same equation except it only considers the reactants escaping in the stack gases. These terms are a measure of how completely a particular technology destroys a contaminant of interest. The DE is a more comprehensive measure of destruction than DRE, because the DE considers the amount of the chemical of interest that escapes destruction by being removed from the process in the stack gases together with all other residue streams. Most references citing performance of destruction processes only provide data for stack emissions and thus, generally, data is only available for DRE and not DE.

3.1.2 Emissions of Dioxins and Furans

Any high temperature process used to destroy waste has the potential to form polychlorinated dibenzo-paradioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) as by-products. These substances are among the products of incomplete combustion that are of greatest concern for potential adverse effects on public health and the environment.

The internationally recognized measure of the toxicity of these compounds is the toxic equivalency factor (ITEQ), which is a weighted measure of the toxicity for all the members of the families of these toxic compounds. For purposes of screening destruction technologies, the maximum concentration of dioxins and furans in the stack gas from destruction technologies are:

- 0.5 ng-ITEQ/Nm^3 for foams

- 0.2 ng-ITEQ/Nm^3 for concentrated sources

3.1.3 Emissions of Acid Gases, Particulate Matter and Carbon Monoxide

Acid gases are generally formed when wastes are destroyed and these must be removed from the stack gases before the gases are released to the atmosphere. The concentration limits for acid gases shown in Table 3-2 have been set universally by the UNEP.

Table 3-2: Concentration limit for the release of acid gases in stacks

Compound	Maximum concentration/ (mg/Nm^3)
CO	100
HBr/Br$_2$	5
HCl/ Cl$_2$	100
HF	5
Total suspended particulate (TSP)	50

Carbon monoxide is generally released from incinerators resulting from incomplete combustion and may be released from some waste destruction facilities because it is one form by which the carbon content of the waste can exit the process. Carbon monoxide is a good measure of how well the destruction process is being controlled in a combustion environment.

3.1.4 Technical Capability

As well as meeting the above performance requirements it is necessary that destruction technologies have been demonstrated to be technically capable at an appropriate scale of operation. In practical terms, this means that the technology should be demonstrated to achieve the required DE while satisfying the emissions criteria established above. The processing capacity of an acceptable pilot plant or demonstration plant was set by the UNEP to a value of no less than 1.0 kg/hr of the substance to be destroyed.

3.2 Commercially Operating Technologies

The following is a comprehensive assessment of technologies that are currently in commercial use for the destruction of a variety of wastes. These technologies have been screened by the UNEP task force under the criteria mentioned in section 3.1 and have found to be suitable for operation. The following discussion is a summary of the information composed by UNEPs technology and economic assessment panel in April 2002.

The technologies will be discussed under three sections namely:

- Incineration Technologies
- Plasma Technologies
- Non-Incineration Technologies

3.2.1 Incineration Technologies

Incineration is basically burning a compound in an excess of air. A range of 700°C-760°C is normally required for combustion and most general-purpose incinerators have an operating temperature between 760°C and 1100°C (Corey, 1969). However high performance incinerators designed specifically to destroy stable organic compounds (e.g. PCBs) operate at higher temperatures, commonly at 1200°C or higher.

Atmospheric emissions from incinerators are classified into:
- Particulates e.g. fly ash, smoke
- Combustible gases e.g. carbon monoxide, hydrocarbons and partially oxidised hydrocarbons.
- Non-combustible gases e.g. nitrogen oxides and hydrogen halides

One of the serious problems with incinerators is the production of toxic PCDDs and PCDFs. The production of these carcinogenic compounds can be minimised to trace amounts by incinerators that are well designed. A good incineration facility should be capable of high temperatures, adequate residence times (1 to 2 seconds), good mixing and have an excess of oxygen (Niessen, 1978). However, the very large volumes of gases produced by incinerators result in significant emissions of dioxins and furans even if their concentrations are low. The emission of dioxins and furans from incinerators is the principal reason why their use as a means of destruction of hazardous waste continues to be criticized (Costner, 1998).

Different classes of wastes require incinerators of different design. The ensuing discussion focuses on two well recognised incinerator designs.

3.2.1.1 Rotary Kiln Incineration

Rotary kiln incinerators are refractory-lined rotating cylindrical steel shells mounted on a slight incline from horizontal. Capable of handling both liquid and solid wastes, the rotation of the shell enhances mixing and the inclination causes ash or molten slag to fall out. Most rotary kilns are equipped with an afterburner that ensures complete destruction of exhaust gases. Hydrocarbon fuels, such as natural gas, fuel oil or high calorific liquid waste are

typically used as an energy source. Rotary kilns have been used to destroy all forms of hazardous waste (gas, liquid, solids, including sludge).

Because of their flexibility, rotary kilns are most frequently incorporated into the design of commercial incinerator facilities. Their operating permits usually restrict the quantity of chlorine-containing waste.

Rotary kilns operating with afterburner temperatures of 1000-1200°C have demonstrated DREs in excess of 99.9999% destroying refractory compounds such as PCBs, dichlorobenzene and tetrachlorobenzene. A typical kiln had a total feed of 7,758 kg/h of which 956 kg/h was refractory feed and the flue gas volume was reported at 78,500 Nm^3/h. It is reported that such an incinerator could process 250-500 kg/h of CFCs.

3.2.1.1 (a) Technical capability

Rotary kilns are widely used in developed countries for the incineration of hazardous wastes, including chlorinated solvents (CCl_4, $CHCl_3$, CH_3Cl, CH_3CCl_3), and toxic waste, such as PCBs. In Europe and Japan they have been used to destroy CFCs. Destruction costs for the incineration of ozone depleting substances (ODS) are expected to be in the $US 3-5/kg range for CFCs and greater than $US 7/kg for halons.

3.2.1.1 (b) Advantages

The principal advantage of the rotary kiln is its ability to handle a wide variety of liquid and solid wastes, so they can handle both foams and concentrated sources. Furthermore, even though their capacity to handle CFCs is limited to 1% of total feed as fluorine, the resulting capacity for CFCs is still quite high.

3.2.1.1 (c) Disadvantages

Rotary kilns are very expensive to build and maintenance costs are high, so it is unlikely that new rotary kilns will be built with the intention of destroying ODS only. The capital expense could be justified, however, where there are opportunities to destroy a variety of hazardous waste materials. Some kilns have reported PCDD/F levels exceeding 0.3 ng/Nm^3, which satisfies the screening limit for foams but not for concentrated sources.

3.2.1.2 Liquid injection Incineration

3.2.1.2 (a) Process Description

Liquid injection incinerators are usually single-chamber units with one or more waste burners into which the liquid waste is injected, atomized into fine droplets and burned in suspension. Tangential firing is frequently used to promote turbulent mixing. Problems of flame stability may result when volumes greater than 40% of CFCs or other ODS are injected into the burner. These incinerators are able to handle a wide range of liquid or vapour wastes and have no moving parts. Liquid injection incinerators are limited to treating wastes that can be pumped and atomized through the burner and are therefore susceptible to plugging if liquids with significant ash are used.

The DRE for a liquid injection incinerator operating at 1350°C is reported to exceed 99.99%. A total feed of between 110 and 220 kg/h of liquid waste was being fed to the unit, of which about 11 kg/h was CFC. An average flue gas volume of 3,200 Nm^3/h was estimated and reported emissions of pollutants are tabulated below.

3.2.1.2 (b) Technical capability

Liquid injection incinerators are generally located on manufacturing sites to dispose of wastes such as oils, solvents, including chlorinated solvents (CCl_4, $CHCl_3$, CH_3Cl, CH_3CCl_3), and wastewater. Liquid injection incinerators have also been used by some hazardous waste destruction service providers.

Asahi Glass Company operates a liquid injection incinerator at its Chiba Plant in Japan. The plant incinerates waste CFCs and HFCs along with waste oil and wastewater. The process performance data is summarized in Table 3-3.

Table 3-3: Performance Data for Liquid Injector Incineration

Operating Conditions and Destruction Efficiency		Atmospheric Emissions	
Total Feed/ (kg/h)	110 to 220	PCDD/F / (ngITEQ/Nm^3)	<0.52
CFC Feed/ (kg/h)	11	HCl/ (mg/Nm^3)	<10
Temperature/ °C	1350	HF/ (mg/Nm^3)	<1
Residence Time/ s	1.3	Particulates/ (mg/Nm^3)	< 23
DRE/ %	>99.99	Gas Volume/ (Nm^3/h)	21

3.2.1.2 (c) Advantages

Liquid injection incineration is an established destruction technology with a proven track record in ODS destruction. All of the performance criteria are met with the exception of PCDD/PCDF emission. If properly designed, all of the performance criteria would be expected to be met. Costs are expected to be in the lower end of the range for ODS destruction technologies.

3.2.1.2 (d) Disadvantages

The particular incinerator for which performance data was reported did not meet the screening limit for PCDD/PCDF emission, although there is a strong likelihood that a unit with a properly designed gas cleaning system incorporating a rapid quench operation would satisfy this criterion. The technology is primarily designed for the destruction of liquid wastes, although it is possible that the feed system could be modified to handle liquefied gases. The most serious disadvantage is the relatively high rate of emissions of pollutants given the very modest rate of ODS destruction.

3.2.2 Plasma Technologies

Plasma is a form of matter in which many of the electrons wander around freely among the nuclei of the atoms. Plasma has been called the fourth state of matter, the other three being solid, liquid, and gas.

An atom that has lost some of its electrons, thereby attaining an electric charge, is an ion. When a gas is subjected to heat or an electric field, some of its atoms become ions and the gas is said to be ionized. An ionized gas, unlike a gas in its normal condition, can conduct electrical current to a limited extent. If the heat or electric field becomes extreme, many of the atoms become ions. The resulting super-ionized gas is a plasma, which can conduct a large and sustained electric current. This high temperature ionized conductive gas can be created by the interaction of a gas with an electric or magnetic field. Plasmas are a source of reactive species, and the high temperatures promote rapid chemical reactions.

Plasmas at atmospheric pressure can be divided into non-equilibrium and thermal plasmas. Thermal plasma is the main method for waste destruction. In thermal plasmas, the electrons, ions and neutral particles are at close to the same temperature, typically between 5000°C and 30 000°C. The high temperatures lead to very rapid chemical reactions. Such plasmas are often used for the destruction of concentrated streams of hazardous chemicals, including CFCs and halons.

The ionization of a gas to form a plasma is not a combustion process. Electrical energy is converted directly to thermal energy. Applying reaction heat with plasma technology renders it possible to control heat and the chemical environment independently. For example, it is possible to heat a reducing gas to a high temperature without the use of oxygen, or to obtain an oxidizing environment without the introduction of any fuel. Thermal plasmas can be generated by passing a DC or AC electric current through a gas between electrodes, by the application of a radio frequency magnetic field without electrodes, or by the application of microwaves.

During the past decade, thermal plasma technology has evolved as one of the more promising innovative technologies for the thermal destruction of hazardous wastes. The current interest in applying plasmas to the destruction of hazardous wastes is related to the availability of both DC and RF plasma torches in the power range up to 1.0 MW.

3.2.2.1 Argon Plasma Arc

3.2.2.1 (a) Process Description

PLASCON is a plasma process. Argon is used as the plasma gas since it is inert and does not react with the torch components. Waste is rapidly heated in the reaction chamber to about 2500°C, where pyrolysis occurs. Steam is added together with the waste at the injection manifold; the oxygen ensures that any carbon formed during pyrolysis is converted to carbon dioxide, and the hydrogen prevents formation of CF_4, which is a strong greenhouse gas.
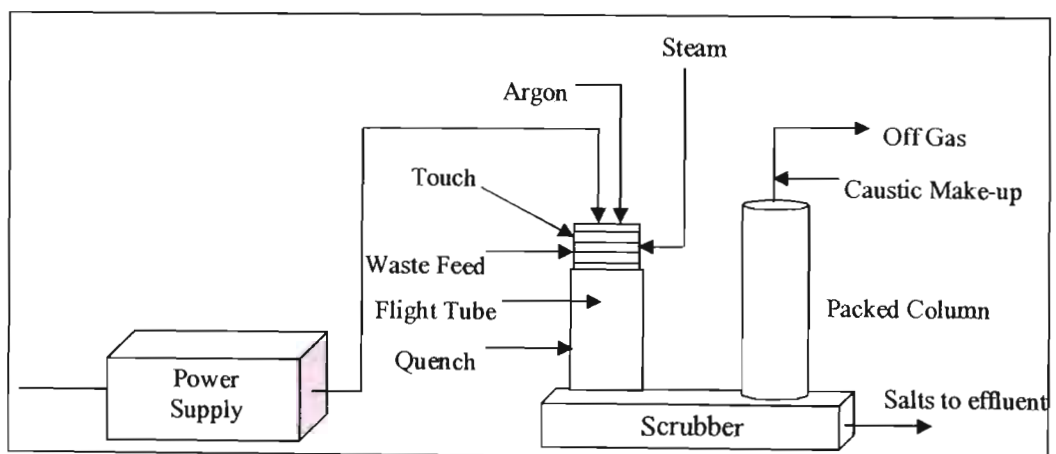
Figure 3-1: Schematic of the PLASCON process

The use of steam rather than oxygen gives more thorough destruction for a given feed rate, since the thermodynamic mixing temperature is higher. Pyrolysis is followed by rapid alkaline quenching from 1200 °C to less than 100 °C. Such rapid quenching limits the formation of dioxins and furans. The cool gas from the quench is further scrubbed with alkaline liquor in a counter-current packed column to neutralize HCl and other acid gases. The off-gas from the column consists mainly of argon and CO_2.

Key advantages of this process are the very high destruction efficiencies and negligible dioxins/furans emissions demonstrated on a commercially operating system. A destruction efficiency of 99.9998% has been achieved at destruction rates of 120 kg/hr and an electrical power of 150 kW.

Table 3-4: Typical emissions from the PLASCON process

Pollutant	Concentration/ (mg/Nm^3)	Mass Emission/ (mg/h)
PCDD/ PCDF	6×10^{-9}	2×10^{-7}
HCl/ Cl_2	1.7	65
HF	0.23	9
HBr/ Br_2	<4.0	<150
Particulates	<10	<400
CO	96	3700

3.2.2.1 (b) Advantages

The major advantage of this technology is that it is a non-incineration technology that has demonstrated high destruction efficiency of both CFCs and halons on a commercial scale for several years. It has also demonstrated very low emissions of PCDD/PCDFs. Mass emissions of pollutants are very low because of the relatively low volume of flue gas produced by the process.

3.2.2.1 (c) Disadvantages

One disadvantage is that the recovered ODS must be pretreated to remove oil before destruction. In the current process, the halide salts formed by the neutralization of the acid gases formed are released as a liquid effluent to the environment.

3.2.2.2 Inductively Coupled Radio Frequency (ICRF) Plasma

3.2.2.2 (a) Process Description

Gaseous CFCs and steam are fed through the plasma torch where temperatures of 10 000°C are achieved in a 185 kW inductively coupled radio frequency torch. The gases enter directly into the destruction reactor maintained at about 2000°C for about 2 seconds. Subsequently, the gases are cooled and scrubbed with caustic solution to remove acid gases. One advantage claimed for the RF plasma over DC plasma is the elimination of electrodes that are known in DC plasmas to be subject to corrosion. The RF plasma has a slower gas flow rate and a larger plasma flame that results in higher residence time. The ICRF plasma process has demonstrated a DRE exceeding 99.99% while destroying CFC at a rate of 50-80 kg/h.

Table 3-5: Typical emissions from the ICRF plasma process for a volumetric flowrate of 20Nm³/h

Pollutant	Concentration/ (mg/Nm³)	Mass Emission/ (mg/h)
PCDD/ PCDF	0.012×10^{-6}	0.3×10^{-6}
HCl/ Cl$_2$	4.8	100
HF	2.4	50
HBr/ Br$_2$	2.4	50
Particulates	4.8	100
CO	4.8	100

3.2.2.2 (b) Technical capability

Based on these pilot plant results, a demonstration plant was constructed at Ichikawa City Plasma temperatures of 10 000°C were achieved in a 185kW inductively coupled radio frequency torch. The equipment for the demonstration plant was essentially the same as that used in the pilot plant except for the electric power supply which was 132kW. A commercial plant has operated since 1995 and over 300 MT of CFCs, HCFCs and HFCs have been destroyed.

3.2.2.2 (c) Advantages

The process has been demonstrated on a commercial scale to achieve high destruction of CFC and low emission of pollutants. As noted above, the elimination of electrodes may lead to better reliability than plasma arc processes. Also, the ICRF plasma does not require argon

and may cost less to operate than the PLASCON process. Finally the low volume of gas produced by the process results in low levels of mass pollutants emission.

3.2.2.2 (d) Disadvantages

One key disadvantage is the high energy consumption required for plasma generation. The nominal power output is 100kW, with a plasma energy consumption of 1.28kWh/ kg feed.

3.2.2.3 CO_2 Plasma Arc

3.2.2.3 (a) Process Description

A high temperature plasma is again generated by sending a powerful electric discharge into an inert atmospheric gas. Once the plasma field has been formed, it is sustained with ordinary compressed air or certain atmospheric gases depending on desired process outcomes. The temperature of the plasma is well over 5000 °C at the point of generation into which the liquid or gaseous waste is directly injected. The temperature in the upper reactor is about 3500 °C and decreases through the reaction zone to a precisely controlled temperature of about 1300 °C.

The PARCON technology destroys hazardous organic compounds by a three-step process. The waste is first decomposed in the plasma field, leaving only the constituent atoms. The atoms are then chemically reacted with oxygen in a turbulent atmosphere below the reactor, creating new molecules with predicted and known elements. The gas comprised of the newly formed molecules is then quickly cooled to 70 °C, preventing the atoms form reorganizing into dioxins and furans. Conventional chemical scrubbing then cleans the exit gas. A special feature of the process is the use of CO_2, which is formed from the oxidation reaction, as the gas to sustain the plasma. The process can be arranged to compress and recover surplus CO_2 for sale.

The DRE for destruction of PCB and trichlorinated benzene is reported to exceed 99.9999%. The feed rate of these refractory compounds was 8 kg/h during the demonstration project and the flue gas volume is reported as 3.1 Nm 3 /h.

3.2.2.3 (b) Technical capability

To date the featured product has been the PARCON 125, a transportable waste treatment facility that destroys hazardous gases and liquids at a rate of up to 12.5 kg/h. The PARCON

125 is ideal for demonstrations, pilot projects and small commercial applications. Plasma Environmental Technologies have developed, tested and patented advanced versions of PARCON that offer greater capacities. The PARCON process is applicable to ODS liquids and gases only.

3.2.2.3 (c) Advantages

The PARCON process has demonstrated high DREs with refractory compounds at a reasonably high demonstration rate. Mass emission rates of the pollutants of interest are low, primarily because of the low volume of flue gas produced by the process.

3.2.2.3 (d) Disadvantages

The process has not yet been demonstrated on a commercial scale. The emission of particulates violates the screening limit of 50 mg/Nm^3 but a commercial system would include a properly designed gas cleaning system and there is little likelihood that the screening limit could not be satisfied. Another disadvantage is the high energy consumption required for the plasma generation.

Table 3-6: Performance data of the CO$_2$ Plasma Arc Process

Process conditions		Air Emissions	
ODS Feed rate/ (kg/h)	50	PCDD/F / (ngITEQ/Nm^3)	0.013
POHC	PCB, TriCB	HCl/ (mg/Nm^3)	17.3
DRE/ %	>99.99	HF/ (mg/Nm^3)	4.4
		Particulates/ (mg/Nm^3)	220
		CO/ (mg/Nm^3)	31
		Gas Volume	3.1

3.2.3 Non-Incineration Technologies

3.2.3.1 Solvated Electron Decomposition

3.2.3.1 (a) Process Description

The process is a batch process involving two simple vessels; one a heated reaction vessel and the other refrigerated ammonia recycle vessel. The ODS compounds are decomposed in the

reaction vessel with liquid ammonia and metallic sodium. The process operates at atmospheric pressure. It is expected that this process would produce no dioxins and furans since it does not involve oxidation and operates at relatively low temperatures. No atmospheric emissions result from the decomposition of the original ODS material. Only non-toxic waste products are formed: sodium chloride, sodium fluoride, biodegradable organic compounds and water. Methane and ethane are also produced as by-products. Metallic sodium is consumed in the process and is the major component of operating cost. About 95-98% of the ammonia is recycled and hence does not contribute much to the operating cost. The process was demonstrated on a pilot scale to destroy carbon tetrachloride, several CFCs, HFCs, refrigerant blends and halons at greater than 99.99% efficiency.

3.2.3.1 (b) Technical capability

Commodore Advanced Sciences developed a process for the destruction of ODS in the early 1990s based on solvated electron solutions formed by dissolving metallic sodium in ammonia. A US patent for the process was issued in 1995. While developed specifically for ODS destruction, the process has never been commercially applied to ODS destruction because of lack of demand. It has been applied successfully to PCB destruction and is currently being applied to the destruction of chemical warfare agents. Finally, operating cost is heavily dependent on the cost of metallic sodium and is reported to exceed $US 7/kg of CFC.

3.2.3.1 (c) Advantages

A major advantage of the process is its simplicity and its low operating temperature. It offers high destruction efficiency and very low emission of pollutants, particularly PCDD/PCDFs.

3.2.3.1 (d) Disadvantages

A disadvantage is the lack of demonstration of ODS destruction on a commercial scale, although there appears to be little doubt that the process could be successfully applied for that purpose. Handling metallic sodium presents safety issues and requires careful attention to operating procedures. Finally, the process appears to be very expensive to operate compared to other ODS destruction technologies.

Table3-7: Performance data for Solvated Electron Decomposition

Process conditions		Air Emissions	
CFC Feed rate/ (kg/h)	50	PCDD/F / (ngITEQ/Nm^3)	0.001
		HCl/ (mg/Nm^3)	0.1
DRE/ %	>99.99	HF/ (mg/Nm^3)	0.1
		Particulates/ (mg/Nm^3)	11
		CO/ (mg/Nm^3)	11
		Gas Volume/ (Nm^3/h)	80

3.2.3.2 Gas Phase Chemical Reduction (GPCR)

3.2.3.2 (a) Process Description

The GPCR technology involves the gas-phase chemical reduction of organic compounds by hydrogen at temperatures of 850°C to 900°C. In contrast to conventional incineration technologies, the GPCR technology uses hydrogen to break down the bonds that hold the molecule together. The technology consists of three main components:

> ➢ The front end system which heats contaminated solids, liquids or gases, renders the contaminants into a gaseous form.
> ➢ The GPCR reactor, in which the gaseous contaminants are heated electrically to the reaction temperature and then broken down in less than a second by hydrogen into methane and acid.
> ➢ The gas scrubbing system, which removes acid from the methane-rich gas product.

Halogenated hydrocarbons such as CFCs are chemically reduced to methane, hydrogen chloride and hydrogen fluoride. The methane is recovered and reused as a fuel for system components, while the acids are neutralized with caustic or lime.

3.2.3.2 (b) Technical capability

Eco Logic have developed and commercialized the ECO LOGIC Gas-Phase Chemical Reduction process. The proprietary process is a non-incineration technology suitable for destroying organic wastes in all matrices including soil, sediment, sludge, high-strength oils, watery wastes and bulk solids such as electrical equipment. While Eco Logic has no experience with ODS, the company has destroyed PCB waste and chlorobenzene waste on a

commercial scale to DREs exceeding 99.9999%. Eco Logic has also destroyed PCB, DDT and hexachlorobenzene waste on a commercial scale to DREs exceeding 99.9999%. The GPCR process is reported to destroy ODS at a cost in the range of $US 3-5//kg. The DRE for a GPCR process designed to destroy 25 kg/h of CFC would exceed 99.9999%. The reported volume of flue gas is 156 Nm^3/h and emissions of pollutants are tabulated in Table 3-8.

3.2.3.2 (c) Advantages

The major advantages of this process are that it is essentially indiscriminant with regard to the nature of the organic waste that it can destroy and that it achieves very high destruction efficiencies. The process achieves among the lowest emissions of pollutants due both to very low concentrations of pollutants in the flue gas and also a very low flue gas volume.

3.2.3.2 (d) Disadvantages

The major drawback is the lack of experience on any scale in destroying ODS, although the process has been proven on refractory compounds such as PCBs. Although Eco Logic claims that the process does not preclude recovery of acids, this feature has not yet been commercialized.

Table 3-8: Performance data for ECO LOGIC Gas-Phase Chemical Reduction process.

Process conditions		Air Emissions	
POHC Oil Concentration	48-54% PCBs	PCDD/F / (ngITEQ/Nm^3)	0.015
DRE/ %	99.99999	HCl/ (mg/Nm^3)	0.1
		HF/ (mg/Nm^3)	0.1
POHC Oil Concentration	25-33% CBs	Particulates/ (mg/Nm^3)	0.5
DRE/ %		CO/ (mg/Nm^3)	1.1
		Gas Volume/ (Nm^3/h)	156

3.2.3.3 Gas Phase Catalytic Dehalogenation

3.2.3.3 (a) Process Description

Hitachi Ltd. of Tokyo, Japan has developed a process in which CFCs are destroyed over a proprietary metal oxide catalyst at 400°C at atmospheric pressure. The HCl and HF produced are absorbed in a lime solution.

The DRE reported for disposing of CFC-12 exceeded 99.99%. A flue gas volume of 15 Nm^3/h was estimated for a system destroying 10 kg/h and estimates of the emissions are tabulated in Table 3-9.

3.2.3.3 (b) Technical capability

The Hitachi process has been demonstrated to successfully destroy CFCs and a similar process has been commercialized for perfluoro-carbon (PFC) decomposition as well as PCB destruction. Commercial destruction of PFCs has demonstrated a destruction efficiency exceeding 99%, and destruction of PCBs has demonstrated a destruction efficiency of 99.9998%. It is claimed that no dioxins or furans are produced in the process, although the process operates at a temperature that would generally result in the formation of PCDD/PCDFs.

Hitachi estimates operating costs of about $US 2-3/kg CFC-12 but when depreciation and other fixed costs are applied the destruction cost is more likely to be in the range $US5-7/kg. Capital costs were estimated at about $US 250,000 for a 1 kg/h system and $US 1 million for a 10 kg/h system.

Table 3-9: Performance data for Hitachi Process

Process conditions		Air Emissions	
ODS Feed rate/ (kg/h)	1	PCDD/F / (ngITEQ/Nm³)	<0.01
		HCl/ (mg/Nm³)	1.0
DRE/ %	>99.99	HF/ (mg/Nm³)	<0.5
		Particulates/ (mg/Nm³)	2
		CO/ (mg/Nm³)	13
		Gas Volume/ (Nm³/h)	15

3.2.3.3 (c) Advantages

It is very efficient in destroying CFCs and it is claimed that no dioxins or furans are produced in the process. The process operates at significantly lower temperatures than incineration processes, so energy input would be considerable lower. Most importantly, mass emissions are very low due to the very low flue gas volume.

3.2.3.3 (d) Disadvantages

The destruction cost using this process appears to be higher than many other destruction technologies. Halide salts produced from the acid gases would need to be discharged as a liquid effluent for this process.

Chapter 4: Core Concepts

The technology of pyrolysis using induction heating involves two major concepts. These are induction heating and thermal transparency, and will be discussed accordingly in this chapter.

4.1 Introduction to radiation

The following section provides a brief introduction to radiation. This will form the background for the ensuing discussion pertaining to the concept of thermal transparency.

Heat is the transfer of kinetic energy from one medium or object to another, or from an energy source to a medium or object. Heat is simply energy in motion due to a difference in temperature. The mechanisms by which heat transfer occurs can be grouped into three broad categories:

> **Conduction:** Transfer of energy occurs through direct contact. Where a temperature gradient exists heat energy will flow from the region of high temperature to a region of low temperature. Conduction occurs through either molecular interaction or by free electrons.

> **Convection:** Heat transfer due to convection involves the exchange of energy between a surface and an adjacent fluid when a temperature difference exists between the fluid and the surface.

> **Radiation:** It is the transfer of heat from one body to another, not in contact with it, by means of wave motion through space. The unique property of radiation is that it does not require an intervening medium. The maximum amount of radiant energy transfer occurs in a vacuum. Radiation travels at the speed of light, having both wave and particle like properties.

A simple example of heat radiation is the effect of infrared energy as it strikes a surface. Infrared energy is an electromagnetic field that is capable of transferring energy from a source such as a fireplace to a destination, such as surfaces within the room. A unique aspect of radiation is that both the amount of radiation and the quality of radiation depend upon the temperature (Welty, 1984). The color of incandescent objects changes with temperature. The changing optical properties of radiation with temperature are of paramount importance in determining the radiant energy. For the purposes of our current discussion we are interested

in a class of radiation that has a wavelength between 0.1 to 100μm, it is termed thermal radiation.

It is rare in actual situations that only one mechanism, e.g. conduction, be responsible for the transfer of energy. However, in certain instances, certain modes of heat transfer can be eliminated from the overall mechanism. Edwards (1981) stated that radiation can be ignored when two conditions are satisfied:

> In a fluid that is highly opaque to the source spectrum. In such a fluid the radiation is merely a contributor to the thermal conductivity e.g. water

> A fluid that is perfectly transparent to the source spectrum is termed diathermanous. In such a fluid there is no physical mechanism by which it can absorb radiation passing through it. It follows from thermodynamics that such a medium cannot emit radiation either and therefore cannot be heated or cooled by radiation.

4.2 Thermal Transparency

4.2.1 Introduction

To our knowledge the concept of thermal transparency was first reported by Matovich (1977) in which he used nitrogen gas as an inert blanket in his fluid wall reactors. He stated that simple inert molecules like (N_2, Ar) were transparent to radiation. Welty (1984) later found that nonluminous gases, inert gases and diatomic gases of symmetrical composition (e.g. O_2, N_2 and H_2) are considered transparent to thermal radiation. The determination of the absorption and emission of radiation from gases is very difficult, as it involves a number of variables namely: temperature, composition and density of the gas, as well as the geometry of the gas molecules.

In the pyrolysis system heat is generated in a graphite tube, which then radiates this energy out as photons. The feed gas flowing through the tube, which consists of argon and the respective chlorinated hydrocarbon, then absorbs these photons, which are basically discrete packages of energy.

Pillay (2001) recorded exit temperatures not exceeding 50°C for a stream of argon gas passing through a graphite reactor at 1000°C. It is important to state that the temperature of the gas was measured at the exit of the system, approximately 1.5m away from the graphite reactor. The significance of this statement will be validated in the subsequent discussion. To explain the experimental observation Pillay (2001) postulated that the argon was transparent to the radiation emitted from the graphite tube, in the sense that it absorbs a very small

portion of emitted energy such that no significant temperature increase occurred. Similar observations were made during experiments conducted in a slightly modified system to that of Pillay (2001). These observations were extremely perplexing in view of the fact that if argon was indeed transparent to radiation then this would provide a greater driving force for convection and conduction thus causing the gas to heat up.

In the subsequent discussion the subject of thermal transparency will be clarified through modelling coupled with experimental work.

4.2.2 Effect of radiation on Argon

Prior to the system being modelled some calculations were undertaken to determine whether argon was in fact transparent to radiation. These calculations were based on the principle of quantization of energy (Atkins P. W, 1993). The quantization of energy simply means that the energy of an electromagnetic oscillator is limited to discrete values. In particular the permitted energies of an oscillator of a set frequency are limited. Translation of these classical definitions in terms of molecular considerations implies that every compound requires a specific amount of energy or rather excitation energy to move to an excited state.

Faraday and Kuppermann (1963) conducted experiments to determine the lowest excitation energy of argon; they reported a minimum value of 12eV. In order to determine if the energy of the photons is sufficient to exceed the threshold value and thus excite the gas, two simple calculations were performed. These methods have been used because the exact frequency of the photons emitted from the graphite reactor cannot be measured directly.

Calculation 1)

The first method assumes that the frequency of the photons in the reaction zone is equivalent to that of red light. This assumption is reasonable since the reaction zone glows red when heated.

Energy of a photon: $E = (hc)/\lambda$ ......where c = Speed of light

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ h = Planck's constant

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ λ = Wavelength

Wavelength of red light $\simeq$ 630nm

Energy of photons = $(4.136 \times 10^{-15} \text{ eV.s}) \times (3 \times 10^8 \text{ ms}^{-1}) \div 630 \times 10^{-9} \text{ m}$
$\qquad\qquad\qquad\quad = \underline{1.969\text{eV}}$

Calculation 2)

This method uses the principle of Wien's Displacement Law that gives the maximum intensity possible for a specific temperature.
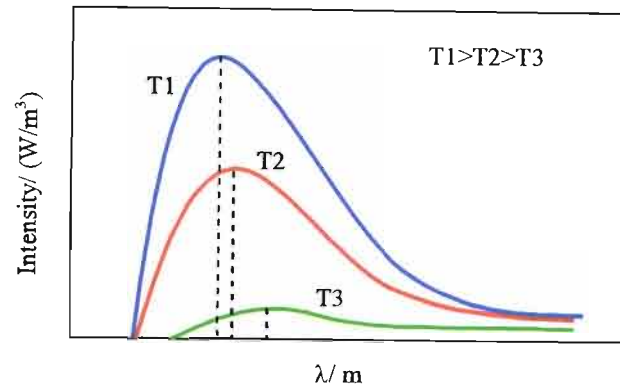
Figure 4-1: Intensity distribution for continuous spectrum radiation from an ideal radiator

From Figure 4-1 we can see that each curve has a peak wavelength where the emitted power is most concentrated

Wien's Displacement Law: $\lambda_{max}T$ = constant = 2.90 x 10^{-3} m.K

Operating Temperature of Reactor: 1273.15K

λ_{max} = 2.278 x 10^{-6} m or 2278nm (infrared region of the spectrum)

Energy of photons = (4.136 x 10^{-15} eV.s) x (3 x 10^{8} ms^{-1}) ÷ 2.278 x 10^{-6} m
= 0.5447eV

It is clear to see from both methods that the energy of the photons emitted from graphite tube appears to be considerably lower than that required by the argon gas and thus is not absorbed by the gas.

The explanation for this phenomenon can be attributed to the structure of the molecule. Argon is a monatomic gas and thus only has translational energy (kinetic energy), whilst methylene chloride (CH_2Cl_2) is a complex molecule capable of translational, vibrational and rotational motion. Each of these three motions has a certain amount of energy associated

with them. The principle of equipartition of energy states that each velocity component has on average an associated kinetic energy per molecule of $\frac{1}{2}kT$ (Young H D, 2000). In this equation k represents the Stefan-Boltzmann constant and T the temperature.

The number of velocity components needed to describe the motion of a molecule completely is called the degrees of freedom. A monatomic gas has three degrees of freedom, thus giving a total average kinetic energy per molecule of $3(\frac{1}{2}kT)$, whilst CH_2Cl_2 has many degrees of freedom. The vibrational motion of molecular bonds are not rigid, they can stretch and bend resulting in vibrations that lead to additional degrees of freedom and energies. Thus due to these additional energies polyatomic molecules are able to absorb more energy in the form of radiation rather than simple inert molecules.

4.2.3 Modelling

There was a two fold purpose for modelling the flow of argon through the system. The first was to explain the experimental observation that argon was still essentially "cold" after being exposed to a reactor at 1000°C. The second purpose was to determine whether convection and conduction were important modes of heat transfer.

The flow of argon was modelled starting from the point where it entered the reactor, through the reaction zone until if finally exited the reactor. The system was described by combined momentum, heat and mass balances. These balances were represented by complex partial differential equations that could be solved using Matlab. However this would have required extensive code and a large amount of computational power. Therefore the system was modelled using a computational fluid dynamics (CFD) package called Femlab.

A detailed discussion is given in Appendix A concerning the model. The basic assumption of the model was that only convection and conduction were present and radiation was ignored.

The simulation shown in Figure 4-2 illustrates that within a centimetre argon heats up. Earlier we stated that in our initial experiments the temperature of the gas was measured at approximately 1.2m away from the graphite reactor. From these heat transfer simulations it is clear that this was a critical mistake as the gas was able to cool significantly within a couple of centimetres after exiting the hot graphite reactor.

This simulation showed that although argon is transparent to the radiation from the graphite reactor it still heated up through convection and conduction. Figure 4-2 clearly shows that the argon heats up to the reactor temperature of a 1000°C within a centimetre after entering the hot reaction zone and then cools down rapidly after exiting the hot zone.
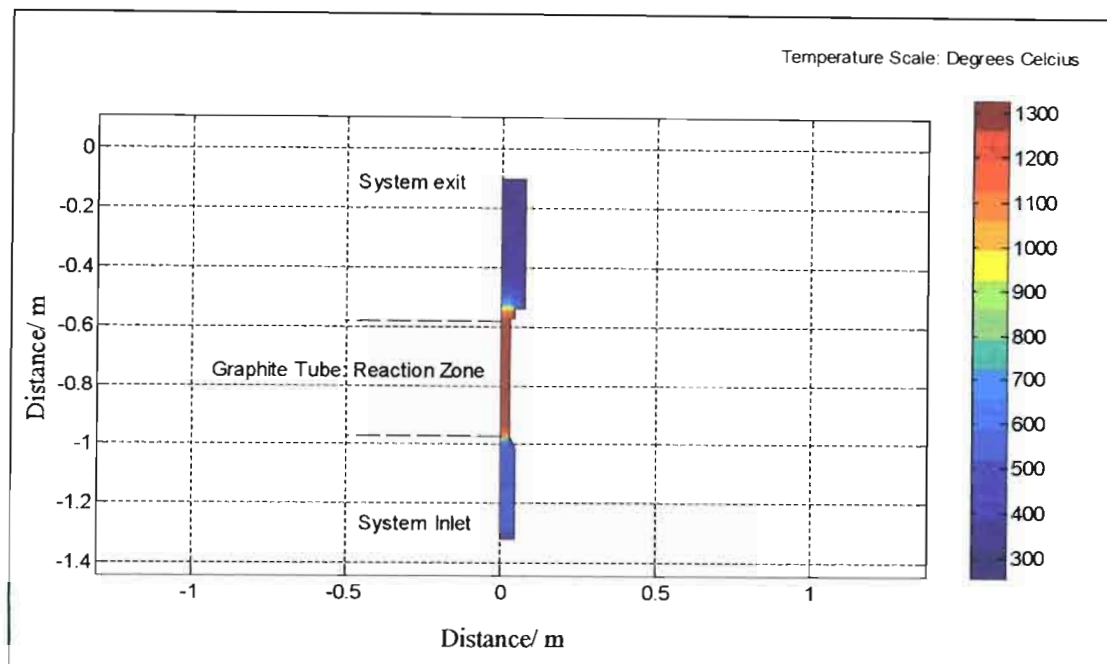
Figure 4-2: Simulated temperature profile obtained from the Femlab model for the flow of argon through the pyrolysis reactor

4.2.4 Additional Experiments

It was apparent from the Femlab model that the initial experiments, to determine if argon was heating up, were incorrect in approach. In order to verify the results obtained from the simulations certain changes were made to the initial temperature measurements. The major change was the relocation of the thermocouple to the exit and also within the graphite reactor. Measuring the temperature of the gas in the hot graphite reactor was extremely complex. The first difficulty experienced was in shielding the thermocouple from the radiation for a sufficient period of time in order to get a true reading of the argon temperature and not simply the radiation. The actual measuring of the temperature was also a problem since the geometry of system did not permit easy access to the graphite tube. The difficulties are more visibly seen in Figure 5-15.

After a few experiments were performed it became clear that the above mentioned complications were too extreme. Consequently these experimental complexities would result in a lack of confidence in the results obtained. Thus it was decided to replicate the conditions in a tube furnace, and perform the necessary temperature measurements. As can be seen in Figures 4-3 and 4-4 these experiments allowed for much better shielding of thermocouple from radiation, thus improving the validity of the results.
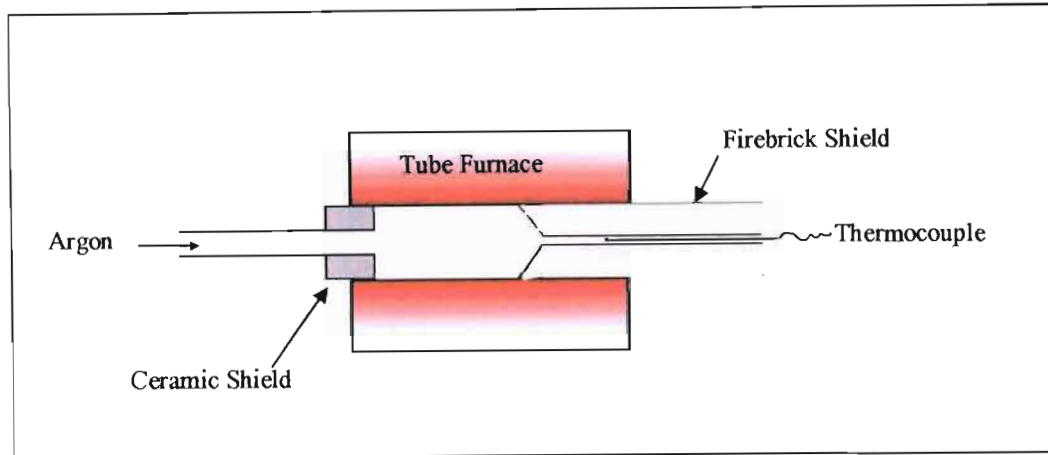
Figure 4-3: Alternative experimental setup used for argon temperature measurements.
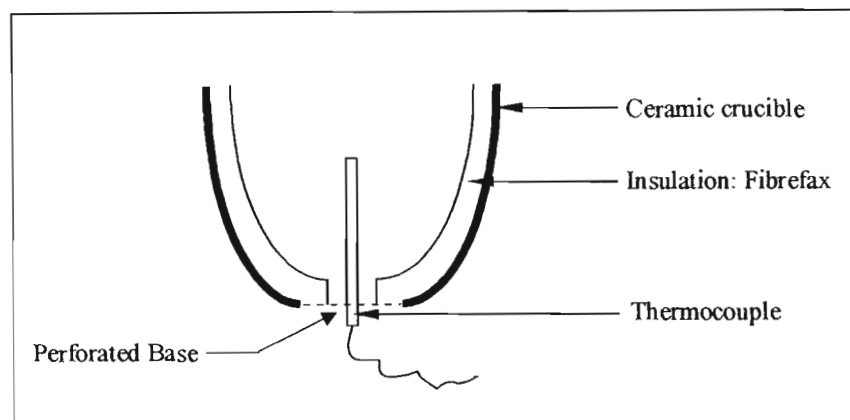
Figure 4-4: Additional protection used to shield the thermocouple from radiation emitted from the hot walls

Figure 4-5 clearly demonstrates the effectiveness of the thermocouple shielding since the maximum temperature rise of the thermocouple was only 2°C with no argon flow.
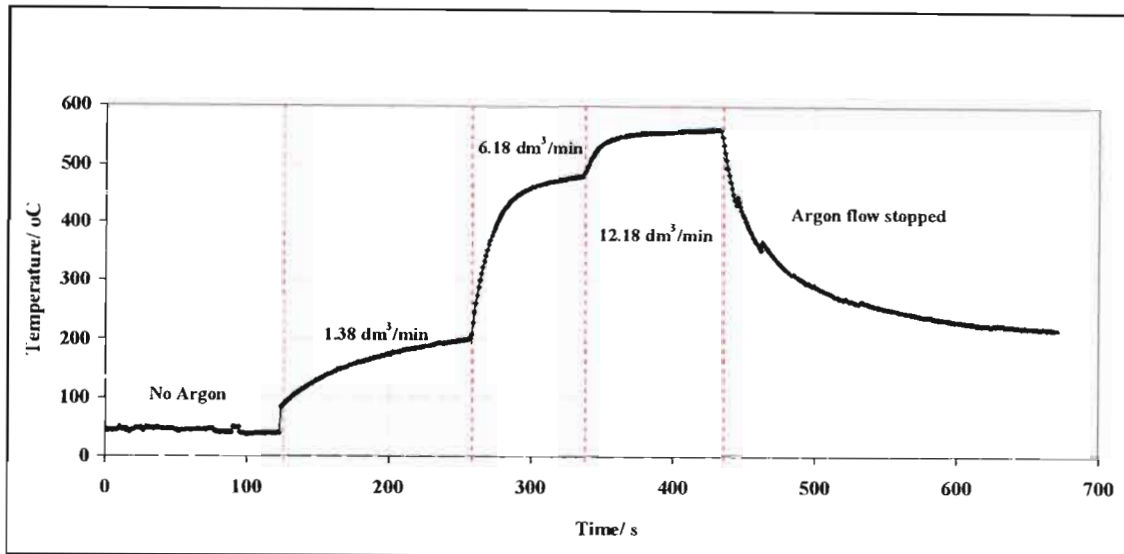
Figure 4-5: Variation of argon temperature with flowrate in a tube furnace at a 1000°C

In addition it also shows that argon does heat up through conduction and convection thus verifying the results obtained from the Femlab model for the pyrolysis reactor. The temperature measurements do not show the argon temperature reaching 1000°C because they were designed to only prove that argon heats up. Although the radiation shielding for the thermocouple works well it is only effective for a short period of time. The temperatures are not very accurate since the flow of argon over the thermocouple is not perfect.

These additional experiments were successful in proving experimentally that although argon is transparent to radiation it still heats up through the other 2 modes of heat transfer namely convection and conduction.

4.3 Induction Heating

4.3.1 Introduction

Induction heating is a means of raising the temperature of a conductive material by the transfer of electrical energy from a high frequency current carrying conductor, usually referred to as a heating coil. This coil sets up a field of magnetic flux that energises the material to be heated in such a way that current is caused to flow. The resistance of the work to this flow, or its inability to carry the induced current, causes an immediate heating action to take place (Curtis, 1944).

This type of heating has been used for more than 50 years for commercial applications. It has been traditionally used to heat metal parts in applications such as soldering, brazing, hardening and melting of metals (Stansel, 1949). The method of induction heating provides a

fast and consistent heat supply for manufacturing applications, which involve bonding or changing the properties of metals or other electrically conductive materials.

4.3.2 Principles of Operation

The basic components of an induction heating system are:

- Alternating current power supply
- Induction Coils with cooling coils
- Electrical conductive workpiece

The induction coils are normally manufactured of copper. The conductivity of the coils should be high thus the percentage of copper should be at least 90%. A copper that contains alloys will lower its conductivity and hence detract from the heating efficiency of the coil.

When an induction unit is switched on the power supply sends an alternating current through the coil, which generates a magnetic field. When the workpiece is placed within the coil and enters the magnetic field, eddy currents are induced in the opposite direction within the workpiece. This generates precise amounts of clean localised heat without any physical contact between the induction coils and the workpiece.
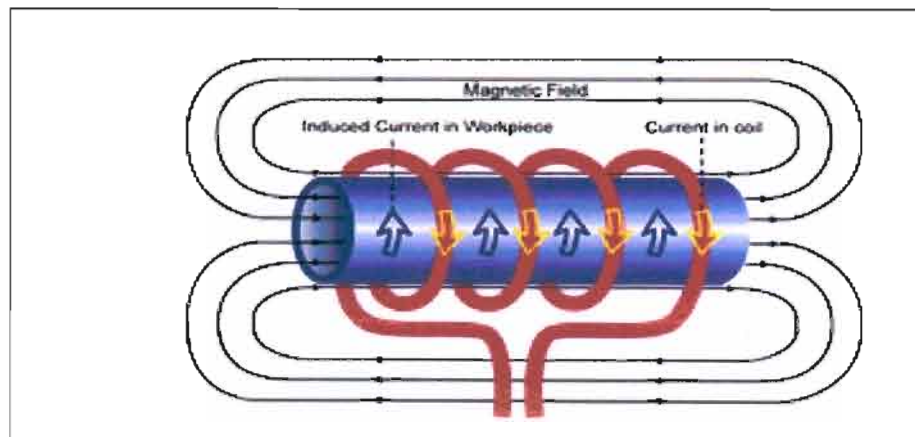
Figure 4-6: Pictorial representation of the principles of induction heating

The power that the current develops depends on several factors, these include:-

   a) The kilowatt rating of the induction heater.

   b) The electrical resistivity of the work piece.

   c) The configuration of the work coil and its relationship to the work piece.

In Figure 4-7 we can see the relationship between the frequency of the alternating current and the depth to which it penetrates in the workpiece.

Frequency/ Hz	
1 000 000	Surface heating metal strip, wire etc
500 000	
100 000	Surface heating of metals
50 000	
10 000	
1000	Deep heat penetration melting
	Low Temperature heating
60	
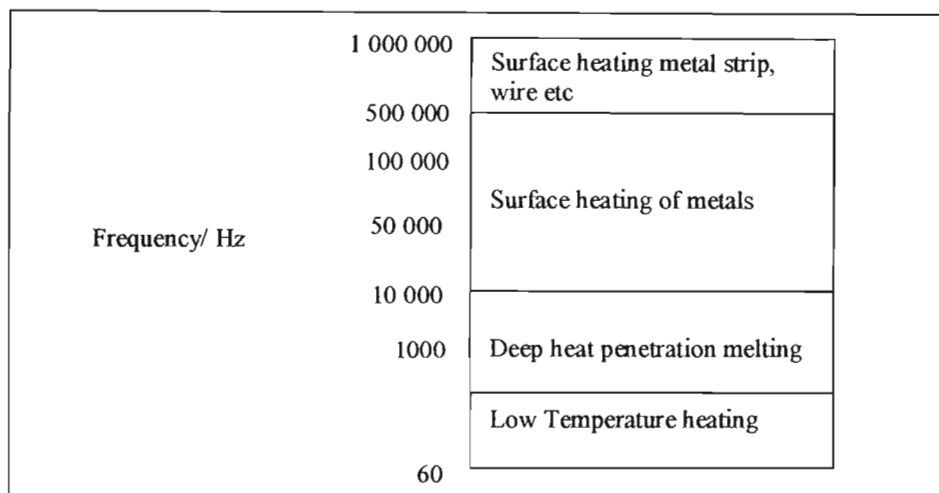
Figure 4-7: Typical frequencies for various heating applications (Curtis, 1944)

Low frequencies are effective for thicker materials requiring deep heat penetration, while higher frequencies are effective for smaller parts or shallow penetration.

Power levels and heating times are closely related to the characteristics of the workpiece and the design of the induction coil. Induction coils are water cooled and vary considerably in shape according to the application.

4.3.3 Application of induction heating to the pyrolysis reactor

Applying these induction principles to the pyrolysis system can be seen in Figure 4-8
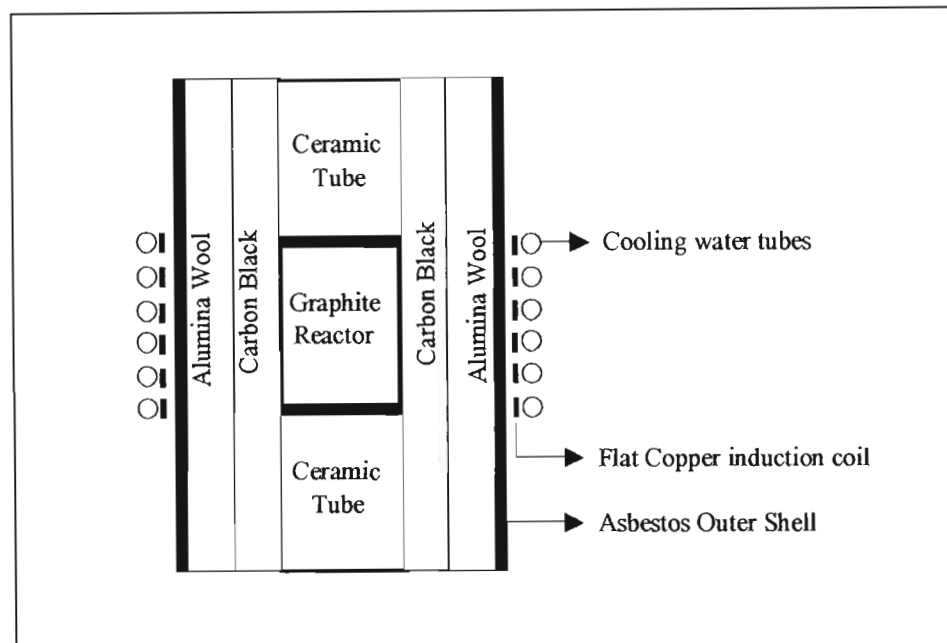
Figure 4-8: Induction heated pyrolysis reactor

The graphite tube is the workpiece and the induction coils are the flat copper coils. The alternating current flowing through the copper induction coils generates an alternating magnetic field that produces a current in the graphite tube. The graphite tube then heats up and starts to emit photons to heat up the contents contained within it.

4.3.4 Advantages over traditional heating systems

• Faster Cycle Time

Heat is developed directly and instantly inside the workpiece, allowing a much quicker startup than other industrial heating systems. Heating process times can be dramatically reduced.

• Selective Heating

Induction heating is highly directional which means that the workpiece can be heated

without affecting surrounding areas. The power input is precisely controlled to achieve the exact temperature profile required for slow or fast heating.

- Environmentally Sound

Induction heating is a clean, non-polluting process. It produces no harmful emissions, exhaust gases, smoke, loud noise or waste heat to alter the surrounding environment.

- Increased Profitability

This energy efficient process converts up to 95% of the energy expended into useful heat to reduce utility costs. Standby losses are also reduced to a minimum since the heat is only "on" when actually performing its intended task.

- User-Friendly

Working conditions are improved with the absence of smoke, fumes, noise and extraneous heat produced by furnaces or other industrial heating systems.

Chapter 5: Equipment

Introduction

The primary goals that were set down as the foundation to achieve an overall optimised experimental system were:

> → Adequate control over process variables
> → Accurate identification and quantification of all major products
> → Identification of minor products
> → Trapping all reaction products
> → Closure of the mass balance

This chapter deals with the design and development of the pyrolysis system together with techniques employed to achieve the primary goals. During this research and development stage of the project the system was improved upon continuously as knowledge increased regarding the process and the equipment. By describing the difficulties encountered and the goals achieved through design modifications it will be attempted to explain how and why the final design was employed to extract useful data for the destruction of chlorinated hydrocarbons.

5.1 Design Methodology

Before any improvements could be made to the existing system the experimental setup had to be studied. The most efficient way to study the system was to perform experimental runs on it, so as to establish where the problems lay. However due to the previous research done on the system it was postulated that the system was severely damaged and could not be operated (Pillay, 2001). Thus the entire system, both internally as well as externally, had to be stripped and carefully inspected for defective parts.

The following problems were observed:

- The carburettor feed system and the collection system had been removed.
- Gaskets on the inlet and exit of the reactor were worn.
- Thermocouples monitoring the reactor and product temperatures were broken.
- The ceramic that provided insulation as well as support for the graphite reactor was severely damaged.

Figure 5-1: Showing the extent of the damaged ceramic used in the feed zone

- The water filter for the induction unit had become extremely dirty and was impeding flow through it.
- The pump supplying cooling water to the induction coils was extremely noisy and was above the noise limit for a safe working environment.
- The insulating layer, made up of carbon black and fibre fax, was excreting droplets of yellow and red liquid. This liquid was found to combination of toxic chlorinated hydrocarbons and some oxygenated derivatives. The presence of these compounds is probably due to contamination of these insulating layers with feed as well as products due to improper operation of the unit.

Figure 5-2: Picture of the contaminated insulating layers in the pyrolysis reactor

- The exit pipe and the carbon catchpot were severely corroded.

From the above-mentioned problems the most challenging was finding a ceramic with the required properties namely: capable of withstanding a temperature of 1000°C and having the correct dimensions. In order to conduct preliminary testing the damaged ceramics were replaced with the same ceramic material that was originally used. However in the final design new ceramics were manufactured in accordance with the modified design specifications.

Once all the problems were fixed and the system was fully operational a few experimental runs were performed. From the results obtained and also from the general operation of the equipment it became apparent that a number of changes could be made to the system to improve it. Each section of the experimental setup was studied and the appropriate changes made in order to achieve a suitable design to increase the efficiency as well as the capability of the system.

When each section was analysed the following questions were used as the basis to achieve an optimised design:

1. What purpose does it serve?

2. How does it work?

3. How efficient is it?

4. What are its limitations?

5. How can it be improved?

6. Does it contribute to a safe working environment?

5.2 Design Development

The following sections discuss each aspect of the experimental configuration, with respect to the design methodology discussed in Section 5.1.

5.2.1 Feed System

The purpose of the feed system was to vaporise the liquid reactants and transfer this vaporised feed into the reactor without condensation. In addition to this it must allow for adequate control over the feed concentrations and residence times over a wide range.

5.2.1.1 Previous feed system
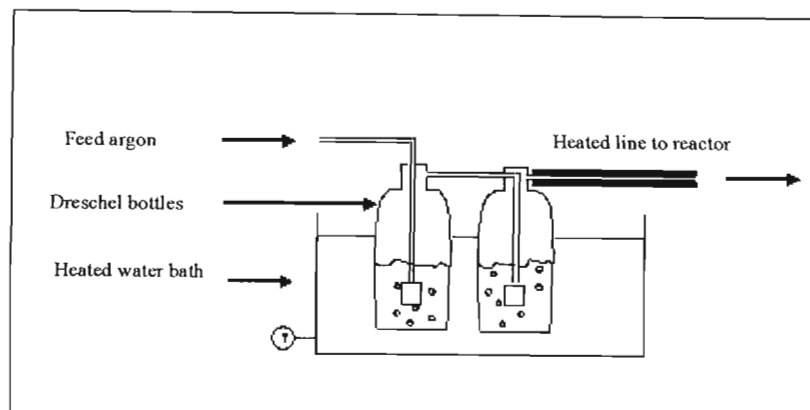
Figure 5-3: Feed system used in the original experimental setup

5.2.1.1 (a) Description

The old feed system was a carburettor type design. It consisted of saturating argon with the reactant and then passing this mixture through a heated line into the reactor. The saturation of the argon was accomplished by passing the argon through a pair of heated dreschel bottles. Changing the waterbath temperature as well as the argon flowrate varied the feed concentrations.

5.2.1.1 (b) Experimental Observations

This design worked reasonably for low boiling compounds (BP~40°C) however failed for higher boiling compounds (BP~200°C) since the waterbath was limited to a maximum temperature of 100°C. This imposed restrictions on the feed concentrations since only very small feed concentrations could be tested for high boiling compounds.

Control over the waterbath temperature was maintained to within 3°C of the set point temperature. However even such small variations in temperature caused a significant change in the feed concentration due to the volatile nature of low boiling reactants. This meant that for a specific run variations in the feed composition were constantly occurring which in turn affects the results since the feed composition is an important process variable.

The 2.2m feed line to the reactor was heated by insulated nichrome wire. This type of heating restricted the feed line temperature to approximately 100°C and this meant condensation occurred in the feed line for higher boiling point compounds. In addition this type of heating is problematic, as there are constant burnouts and breakage in contact.

One of the major disadvantages of this type of feed system was the fact that the dreschel bottles could only be half filled, to ensure sufficient vapour space, which meant that the remainder of the space was occupied by air. This compromises the whole principle of pyrolysis as it allowed oxygen into the system.

5.2.1.2 Design 1
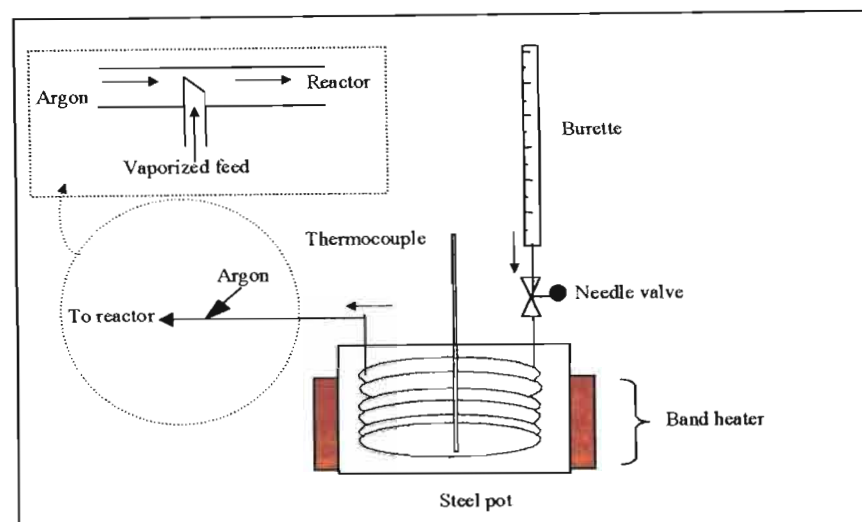
Figure 5-4: Burette type feed system

5.2.1.2 (a) Description

The new system was located as close as possible to the reactor in order to minimise condensation in the feed line. The entire system was located on top of the reactor thus reducing the feed line from 2.2m to 0.2m.

In the above arrangement the reactants were placed in a 50ml glass burette and passed through stainless steel coils contained within a mild steel pot. An external band heater was used to heat the pot and hence the coils. The band heater was capable of reaching a maximum temperature of 650°C at 1.1kW and thus it was contemplated that most liquid reactants would be easily vaporised. A needle valve was used to set the desired flowrate of the reactants from the burette.

Since the burette provided a very small driving force a vacuum was created in order to draw the reactants through the system. As we can see from the exploded view in Figure 5-4 the reactant feed tube was cut at a 45 degree angle and inserted half way into the argon line. The argon stream flows over the protruding reactant tube, which creates a vacuum that draws the reactants into the argon feed stream. The principle is similar to that of a compressed air vacuum pump.

5.2.1.2 (b) Experimental Observations

Due to the toxic nature of the reactants the system was tested using methanol. The conditions during these trials were similar to the actual experimental conditions namely: same boiler temperature, argon flowrate and reactant flowrate. To prevent contamination of the reactor internals with methanol the exit line from the boiler was not connected to the reactor during these tests. Venting the exit line from the boiler to the atmosphere also allowed us to ensure that there was complete vaporisation.

During the trials an immediate problem noticed was that the feed flowrate through the burette was continually changing. This posed a significant problem because an irregular liquid flowrate meant that the feed composition to the reactor was constantly changing.

The second major problem encountered was with the vacuum type system that was designed (Figure 5-4). The vacuum created by this setup was extremely small and was not enough to pull the reactants into the reactor. In some cases bubbles were noticed in the feed burette, which signified that some of the argon was flowing through the coils. A suitable vacuum could only be created at very high argon flowrates; however this was unsuitable as it imposed a severe restriction on residence times.

It was clear that this type of setup failed in respect to providing sufficient control over feed concentration and residence times.

5.2.1.3 Design 2
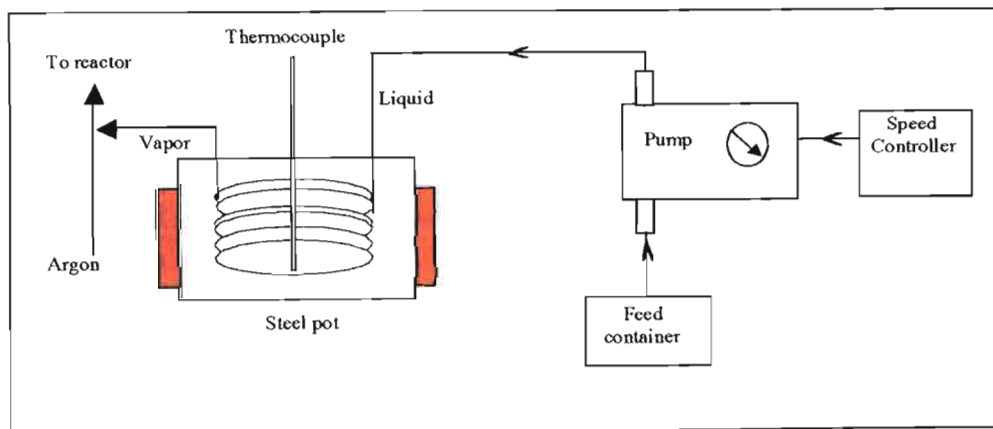
Figure 5-5: Pump feed system

5.2.1.3 (a) Description

The system was exactly the same as design 1 except the burette was replaced by a pump. The pump was an Alldos dosing pump, Primus Series, Type M, capable of a maximum output of 75 l/hr. The calculated output range needed was considerable lower than this, thus a speed controller was implemented in order to decrease the speed of the motor. Controlling the speed of the motor meant that the pump characteristic curve could be changed and thus allow for finer control at lower flowrates. (See Appendix B)

5.2.1.3 (b) Experimental Observations

The new vaporization system was again tested using methanol except it was not connected to the reactor. This was done in order to check if all the liquid was been vaporized. The boiler was set at a temperature of 200°C and a liquid flowrate of 15 ml/min. Vapour exited the reactor during the first 5 minutes, after which a combination of liquid and vapour exited. It was clear that there was poor heat transfer between the coils and the pot. The poor heat transfer meant that although the coils were initially hot, they soon cooled and could not heat up fast enough to continue vaporising the incoming liquid.

One major incident that occurred during the run was the resultant drop in temperature readings when the speed controller for the feed pump was turned on. The speed controller affected the temperature readings quite noticeably by approximately halving the true temperatures. The plug point for the speed controller was taken from the same line as for the computer, since the controller converts single-phase power into three-phase power, to satisfy the three phase pump, it was interfering with the pc card. Taking this into account a different power circuit was used for the controller. Further testing showed that this modification reduced the speed controller effect to within 5°C.

The problem was eventually solved by using a combination of the following actions:

- Taking the power source of the speed controller from a completely different circuit.
- Housing the speed controller in a perspex box away from the computer.
- Covering the perspex box with aluminium tape.
- Covering the cords of the speed controller with aluminium tape and earthing them.

5.2.1.3 (c) Solutions explored for poor heat transfer

In light of the above experimental observations it was decided to fill the space between the coils and pot wall with a heat transfer medium. Considerable research was performed in order to acquire a heat transfer medium capable of withstanding the high temperatures

(650°C), however no feasible medium could be found. Thus the feed system required further modifications. The following modifications were investigated:

Table 5-1: Possible modifications that were investigated to solve the vaporisation problem

Solution	Possible Problem
1. Remove the coils and allow the feed to vaporize through direct contact with the hot pot thus rendering the need for a heat transfer medium obsolete.	The chlorinated compounds could attack the mild steel pot.
2. Constructing the coils out of a highly conductive material, e.g. copper, as opposed to steel.	The higher conductivity materials are less resistant to attack by the chlorinated reactants.
3. Make the coils an exact fit to the inner diameter of the pot thus allowing for heat transfer through conduction.	Ineffective due to expansion of the steel at the high temperatures.
4. Insulating the pot with 50mm layer of alumina wool to minimise heat losses and increasing the pot temperature.	This could cause degradation of the feed before entering the reactor.

5.2.1.4 Design 3
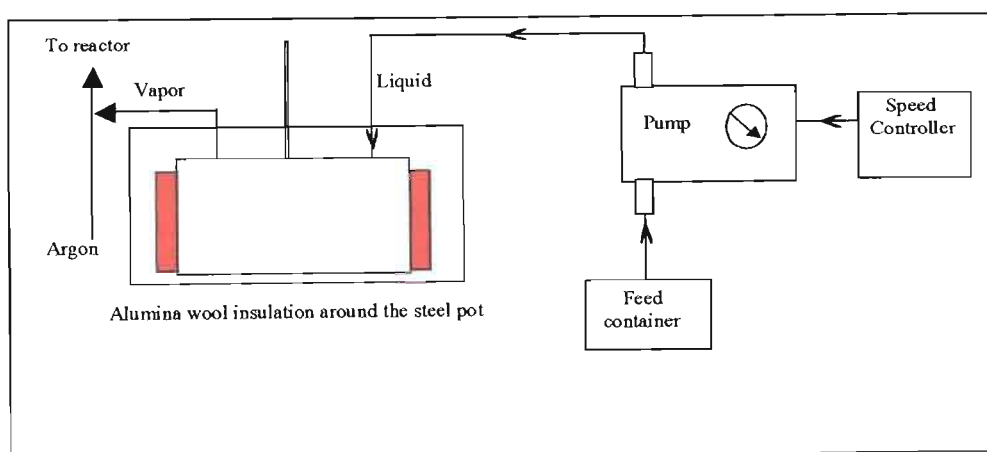
Figure 5-6: Modified pump feed system

5.2.1.4 (a) Description

After considering the possibilities, listed in Table 5-1, it was decided that a combination of options 1 and 3 would be the most feasible solution. Thus the coils were removed from the pot and the entire pot was insulated with alumina wool.

5.2.1.4 (b) Experimental Observations

After a couple of runs the inside of the pot was inspected. Corrosion was apparent on the surface of the wall, with the appearance of a brown layer. It was uncertain whether the reactants were cracking in the vaporization vessel and thus the chloride radicals were attacking the metal to from iron chloride. However after consulting some literature it was found that iron chloride was a greenish compound, which meant that the brown layer was infact a layer of rust. For rust to form some moisture had to be present in the boiler.

A reasonable explanation is that moisture could have entered the system during the conditioning of the graphite reactor. During the conditioning of the reactor, the moisture trapped in the graphite tube is removed by heating and holding a temperature of 1000°C in the tube until all the moisture is removed. Depending on the exposure of the graphite tube to the atmosphere, or any other source containing moisture, large amounts of moisture can be present. It was realistic to assume that the boiler was exposed to this hot moisture, for long periods, and thus corroded.

As a safeguard it was decided that a suitable coating would be applied to the inner surface of the pot, to provide protection against degradation. Two coatings were tried namely: a nickel-chromium coating and a teflon coating. Both coatings proved ineffective since they had worn away after a run using dichloromethane. The only coating that would have been able to adequately withstand the high temperatures and the nature of the reactants was a ceramic coating. However this would be impose severe limitations on the heat transfer.

Another option explored was to manufacture the pot out of a more suitable material instead of mild steel. Consultations with steel manufacturers revealed that 304-stainless steel was the most suitable material for transport of chlorinated hydrocarbons but at high temperatures (>60°C) the stainless steel would be attacked by the chlorinated hydrocarbons, probably more harshly than the mild steel.

Since degradation of the pot was minor it was decided to machine away the corroded layer and continue experiments using the existing pot. However the following precautions were taken:

- The pot was purged with argon before: (1) heating the pot (2) allowing the reactants to enter.

- The boiler was removed from the system during the conditioning of the graphite tube.

The precautions that were taken proved to be effective in preventing further degradation of the boiler for the duration of the experiments.

5.2.2 Feed Zone

When the reactor was stripped, to replace the damaged internals, trails of liquid droplets were found at the top ceramic section. The last run that was performed was with the feed chemical trichlorobenzene (BP: 212 °C). The appearance of the droplets suggested that some condensation had occurred in the feed section. This implied that the feed section was too long and at a temperature significantly lower than the boiling point of trichlorobenzene. The distance from where the hot gases entered the reactor to the actual reaction zone was approximately 45cm, this portion of the reactor was not heated and remained slightly above room temperature Although low boiling compounds (BP~40°C) are impervious to this "cold zone" other higher boiling compounds like trichlorobenzene are significantly affected. This "cold zone" is an ideal environment for condensation of these higher boiling compounds.

An easy solution to this problem would have been to put electrical heating elements around the feed zone and thus maintain the desired temperature. However since induction heating is used the presence of any electrical elements would be ineffective and extremely dangerous. Electrical elements are conductive and when they are placed in the feed zone they are exposed to the electromagnetic radiation generated by the induction unit, thus causing them to heat up at a tremendous rate.
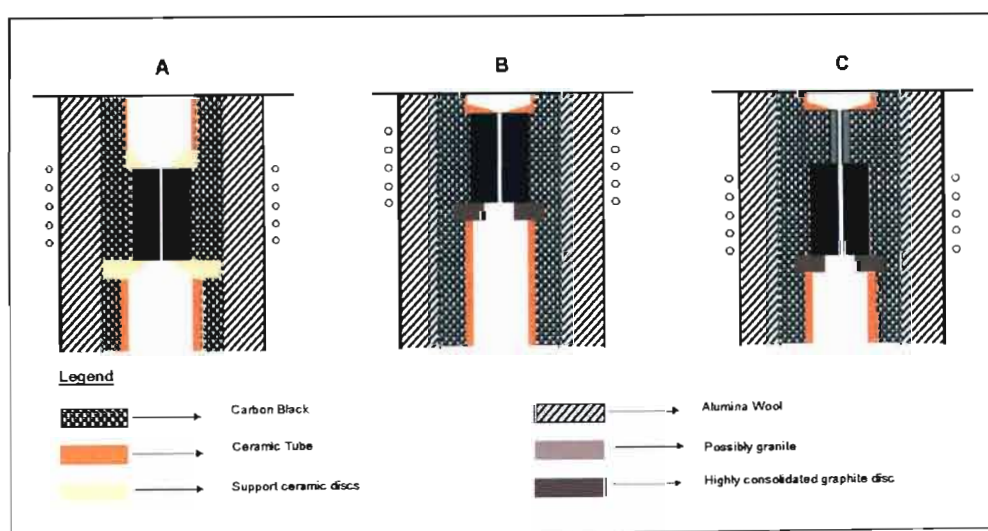
Figure 5-7: Showing the different designs that were investigated for the reactor internals

The next logical step was to try and shorten the feed zone to a minimum, thus leading from the original design A in Figure 5-7 to design B. The ceramic tube at the inlet was shortened to 5cm and the induction coils moved accordingly. This was done under the assumption that the steel top sealing the reactor would not be affected by the electromagnetic radiation from the induction coils, since the radiation would be concentrated in the reaction zone. However it was found that the steel top was affected by the electromagnetic radiation and thus heated up. This posed a serious problem since metal is much more conductive than the graphite and thus heated up very rapidly. The observed temperature of the graphite was 40°C after 5 minutes whilst the metal was at 300°C.

In order to determine exactly where the steel lid would not be affected by the electromagnetic radiation a steel rod was lowered into the reactor and the temperature monitored. By changing the distance away from the induction coils and monitoring the corresponding temperature change, the temperature profiles for steel at varying distances away from the induction coils could be determined. The results indicated that a distance of 40cm away from the reaction zone (and hence the last induction coil) provided a temperature profile only slightly lower than that of the graphite. This was clearly unacceptable since the reactants would breakdown before reaching the reaction zone.

The only viable method to heat up the feed zone was to take advantage of the fact that induction was used to heat the reactor. This was accomplished by tapping into the electromagnetic radiation using a tube with a small percentage of conductive materials.

Table 5-2: Composition of the feed zone tube as determined using an Energy dispersive x-ray spectroscopy (EDS)

Element	Weight Percentage
Carbon	15.49
Oxygen	39.23
Sodium	0.37
Aluminium	4.56
Silicone	37.42
Potassium	0.96
Titanium	0.39
Iron	1.57

The changes made to the system resulted in the reactor setup C shown in Figure 5-7. It was decided that the induction coils and the graphite reactor would be returned to their original position and the ceramic feed tube replaced by this new tube material that is less conductive than the graphite reactor thus ensuring that the feed inlet would be hot and at a lower

temperature than the reaction zone. The introduction of the less conductive material along the feed path meant that the feed gases would never be below their respective boiling points and hence no condensation would occur. This ensured that the feed mixture was in the gas phase when entering the reaction zone.

The feed zone tube was separated from the graphite tube by a 2cm ceramic disc. The ceramic disc prevents the tube from heating up through conduction. The ceramic was effective in isolating the tube however the tube does heat up but at a considerably slower rate. From Figure 5-8 we can see that the tube's heating profile is perfect for this type of application.
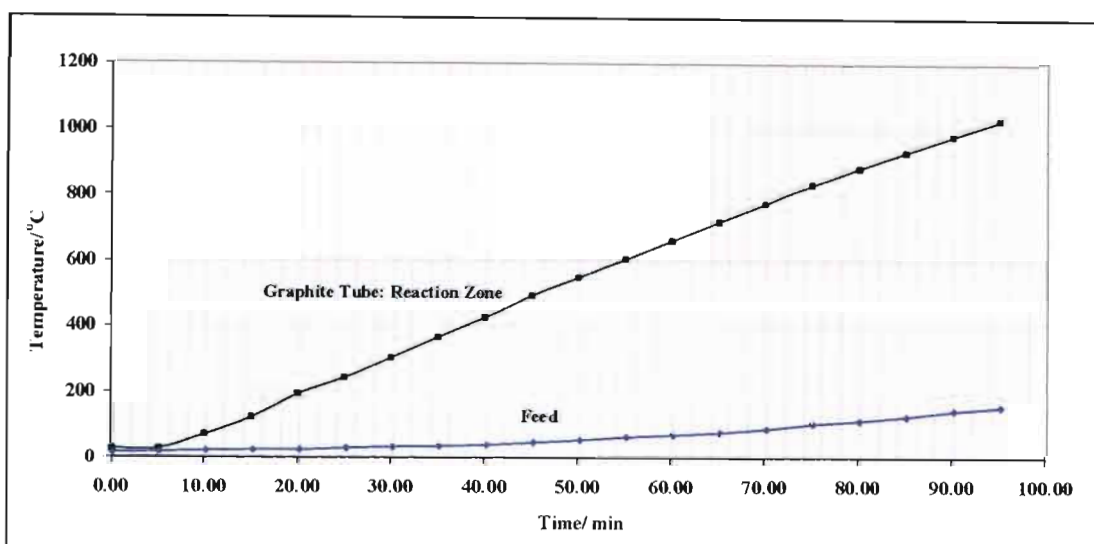
Figure 5-8: Temperature profile of the graphite reactor and the feed zone for an induction power input of 20kW.

The model compound, namely dichloromethane, was used for the initial test on the new system. After the run was completed the top of the reactor was opened and the system inspected. From visual observation no apparent signs of condensation were evident. Following the positive results from the preliminary test the next compound tested was trichlorobenzene. The experiments using trichlorobenzene also showed no signs of condensation in the feed zone. These tests were decisive in determining the effectiveness of the system to handle a range of boiling points.

It is important to note that the temperature of the feed zone can be controlled to a certain degree. If the reactor is heated from room temperature to approximately 1000°C then the feed zone will be at a temperature of ~160°C. However if a higher feed zone temperature is desired then the experiment was not started until the desired feed temperature was reached.

By allowing the system to standby the feed tube would slowly heat up through conduction from the hot graphite tube.

5.2.3 Collection System

The collection system is responsible for the trapping of the major products namely: solid carbon black and gaseous hydrogen chloride and the minor by-products formed. The aim was to design a collection system that was effective in stripping all the products (solids and gases) from the effluent stream before discharging the argon carrier gas to atmosphere. The effectiveness of the collection system would be largely decided by the closure of the mass balance.

5.2.3.1 Carbon Collection

5.2.3.1 (a) Previous System
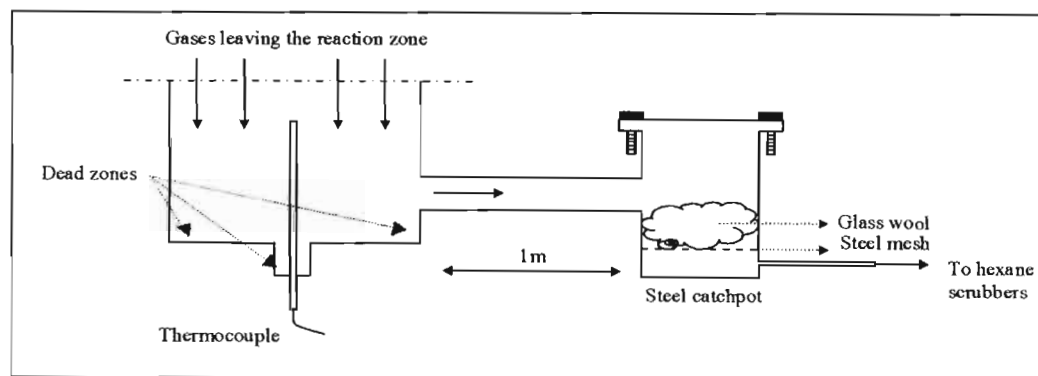
Figure 5-9: Showing the previous carbon collection system

The primary reason behind the design shown in Figure 5-9 lies in the fact that when the reactor was built, it was postulated that the exit gases would be at a similar temperature to the actual reaction zone (~1000°C). Therefore the product gases were allowed to cool in the 1 metre long pipe before trapping the carbon in the catchpot.

During experiments it was obvious that the design was very inefficient in trapping the carbon product in the glass wool, were it could later be quantified. In Figure 5-9 we can immediately see that there are a number of dead zones were the carbon could be trapped before actually reaching the catchpot. In most instances the majority of the carbon was found at the reactor bottom whilst the catchpot was practically carbon free.
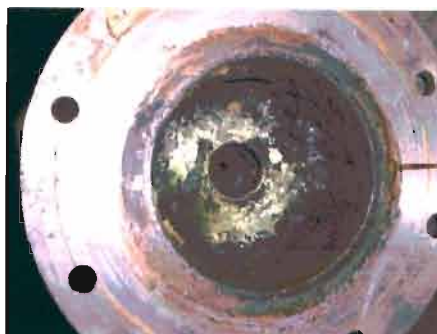
Figure 5-10: Picture showing the severity of the carbon deposition at the bottom of the reactor

The dead zones comprise not only of the reactor exit corners but also the 1m long steel pipe of 50mm internal diameter.

In the experiments where higher velocities and vacuums were used, a greater amount of carbon was trapped in the glass wool contained within the catchpot. However glass wool is a fairly dense material and thus quickly saturated with the carbon causing a pressure build-up in the reactor. In addition, glass wool caused a significant amount of contamination of the carbon, thus causing incorrect mass measurements and making analysis of the carbon through SEM difficult.

5.2.3.1 (b) Modified System
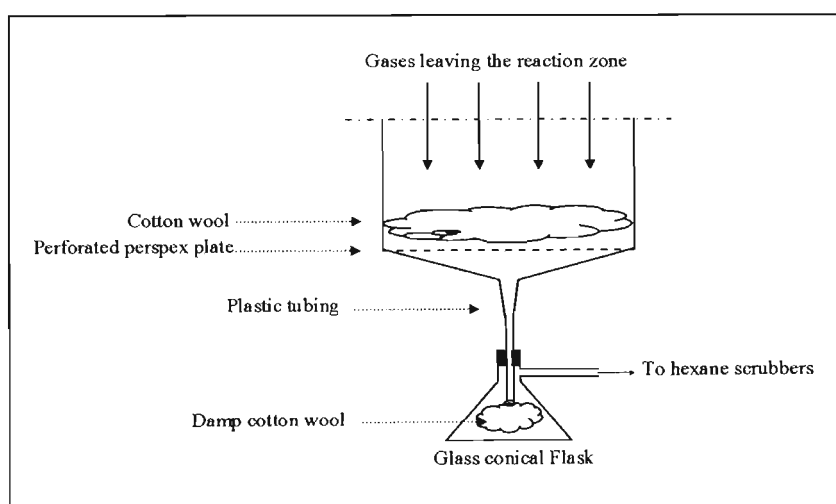
Figure 5-11: Showing the modified carbon collection system

The primary aim of the modified system was to:

- Remove all dead zones.
- Find a suitable replacement for glass wool.
- Trap the carbon formed in one location.

The new design was basic in its approach, and simply trapped the carbon at the reactor bottom. Cotton wool was found to be a suitable replacement for glass wool as it allowed for easy removal of the carbon with minimal contamination. Cotton wool was less dense than glass wool but still effective in trapping the carbon.

In addition to this system there was a back-up system that prevented any carbon from reaching the hexane scrubbers in the event that it escapes from the cotton wool at the reactor exit. The carbon particles could escape if the cotton wool becomes completely saturated with carbon. Under normal operating circumstances for a specific reactant only small amounts of feed are reacted, thus forming small quantities of carbon. However, if larger amounts of feed were used then the cotton wool would become easily overload with carbon. It must stated that the amount of carbon formed is also dependant on the nature of the reactant. Carbon not trapped can cause severe problems in the system. It would clog the sintered glass ends in the hexane scrubbers, thus preventing flow to the sodium hydroxide scrubbers. Since the sodium hydroxide scrubbers are operated under vacuum they would collapse due to the blockage. A pressure build-up in the reactor would also occur.

The buffer vessel was a 2lt glass conical flask that was half filled with cotton wool. The cotton wool was slightly dampened with hexane. The cotton wool was dampened due to the fact that the carbon particles are extremely light and small which means that they could easily escape from dry cotton wool in the buffer vessel, given its design.

Since the buffer vessel was glass, once carbon was seen in the vessel the reaction would immediately be stopped. This also prevented the sintered ends of the dreschel bottles from becoming clogged with the carbon particles.

This design was found to be accurate for the quantification of the amount of carbon found, thus allowing for a more complete mass balance.

4.2.3.2 Hydrogen Chloride Collection
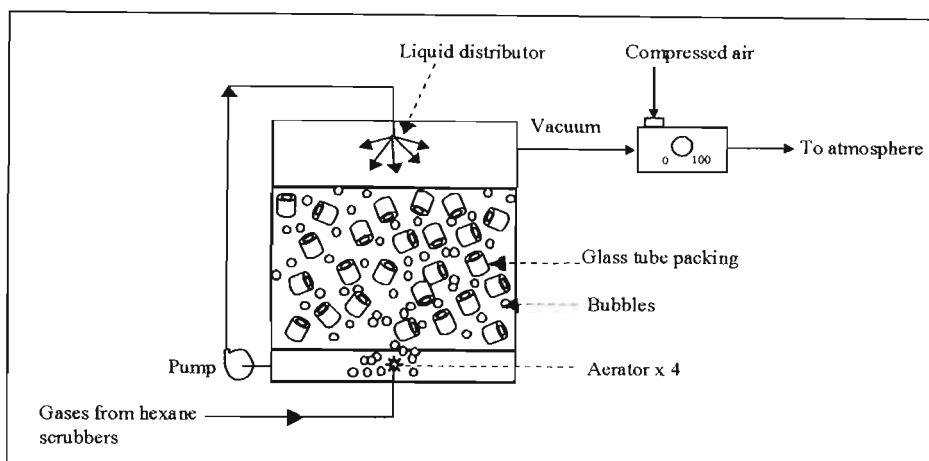
Figure 5-12: Schematic of the sodium hydroxide scrubbers used for trapping hydrogen chloride

The scrubber shown in Figure 5-12 was a packed bed scrubber with an internal recycle. This design ensured that maximum mass transfer occurred between the gaseous hydrogen chloride and the liquid sodium hydroxide. Submersible pumps were implemented in each of the two sodium hydroxide scrubbers. Their purpose is to circulate the solution in the scrubbers and thus produce a stripping effect. During experiments it was noticed that with a single aerator in the scrubbers the bubbles followed a specific path due to the low flowrates. In order to try to increase the amount of bubbles formed, and hence the amount of mass transfer, the exit line from the hexane scrubbers was split into 4 lines, each fitted with an aerator and then fed to the scrubbers. Having 4 inlet lines meant a higher vacuum was needed thus a compressed air vacuum apparatus was used. The efficiency of the system was tested by vaporising a known quantity of hydrochloric acid, using the experimental setup shown in Figure 5-13.

A small amount of water was placed in the glass beaker in order to prevent fracture of the beaker from the heat. The vaporised hydrogen chloride was mixed with argon before passing it into the sodium hydroxide scrubber. The hydrogen chloride that was formed was extremely hot and hence could not be passed directly through the scrubbers since the associated piping was plastic. The hot hydrogen chloride was first mixed with argon and then passed through the scrubbers.

Results from these efficiency tests have shown that the scrubber design in Figure 5-12 works exceptionally well since 100% efficiency was obtained.
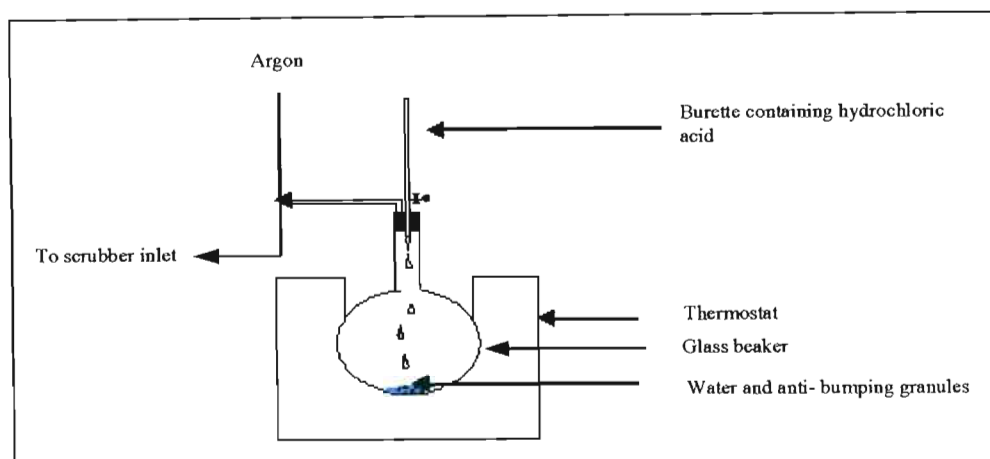
Figure 5-13: Experimental setup used to test scrubber efficiency

4.2.4 Final Design

Process Flow

A variable speed-dosing pump sends the liquid feed into a vaporiser. Depending on the compound the desired vaporisation temperature is set on the vaporiser temperature controller. The vaporised liquid feed exits the vaporiser and mixes with the argon feed stream before entering the reactor. In order to prevent condensation the exit line from the vaporiser to the reactor inlet is heated using electrical elements.

The internal feed zone is heated to a suitable temperature by induction, thus preventing condensation within the reactor. The gaseous mixture, made up of argon and the respective reactant, enters the hot reaction zone were it is bombarded by thermal radiation emitted from the graphite tube. The major reaction products formed, namely solid carbon black and gaseous hydrogen chloride, then exit the reaction zone and pass through the collection system.

The carbon black is trapped at the reactor exit by cotton wool before exiting the reactor. Extremely fine particles escaping the reactor are trapped by hexane damped cotton wool in a glass beaker. Gaseous products formed during the reaction are stripped from the effluent steam by a pair of chilled dreschel bottles containing hexane. The bottles are housed in an ice bath to ensure trapping of all volatiles. The hydrogen chloride gases exiting the hexane scrubbers are neutralised by sodium hydroxide contained in a pair of packed bed scrubbers. The collection system is run under a small vacuum to allow for the easy passage of the product gases through the system, with argon finally been discharged to atmosphere.
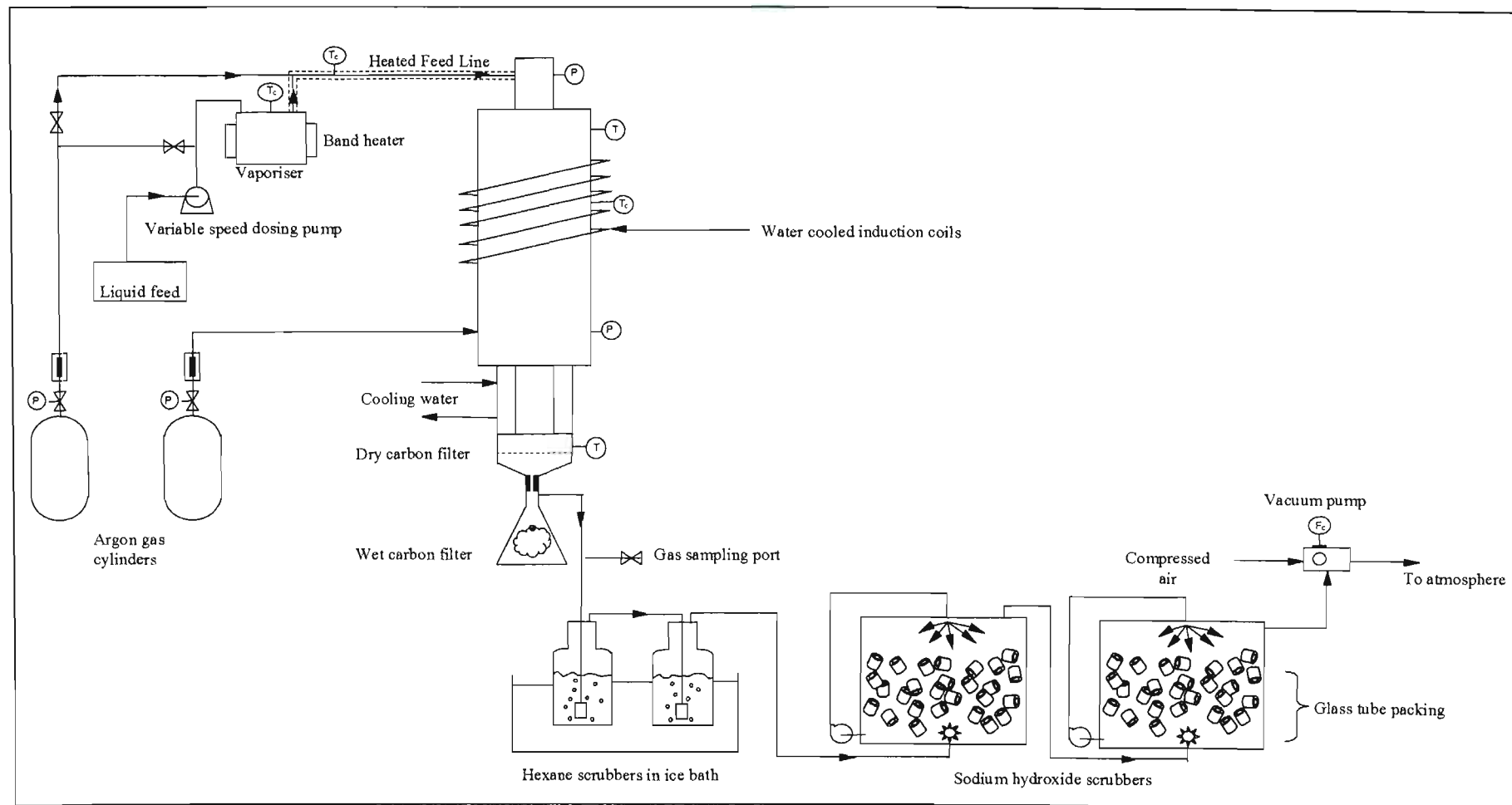
Figure 5-14: Schematic of the final experimental setup
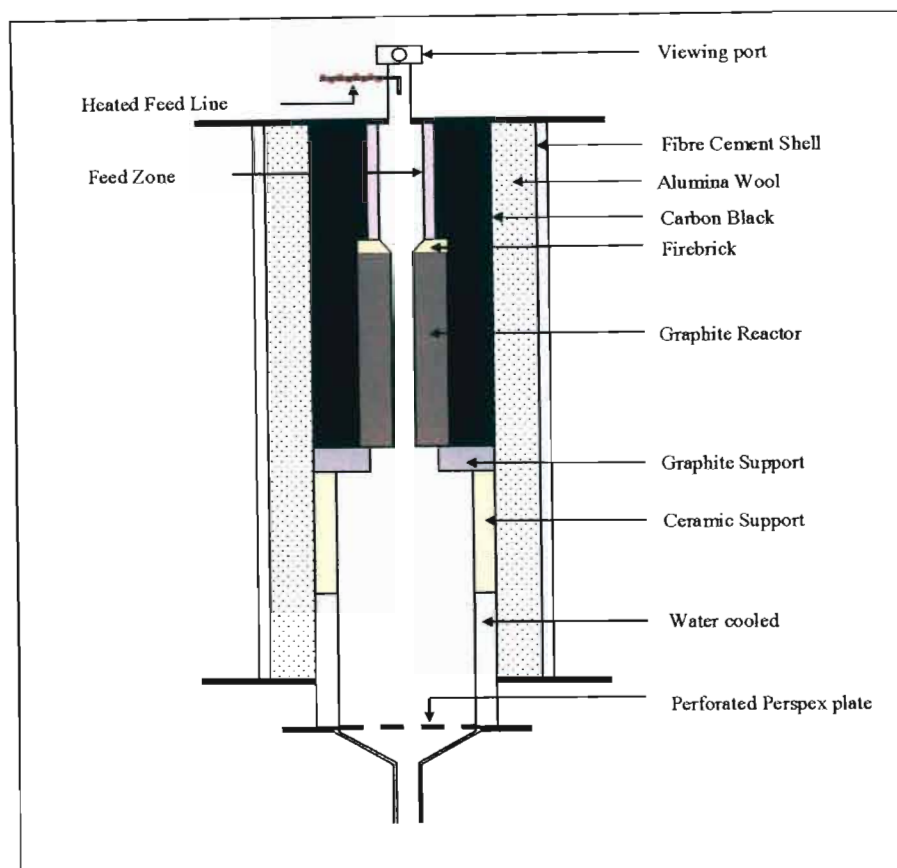
Figure 5-15: Simplified schematic of the final internal design of the pyrolysis reactor

5.3 System capabilities and limitations

5.3.1 Vaporiser

The vaporiser is capable of a maximum temperature of $650°c$ at a power input of 1.1kw. The vaporiser temperatures are accurately controlled by a Eurotherm temperature controller. This means that any liquid with a boiling point less $650°$ can be efficiently vaporised in this system. However the feed system is not only limited to liquid feedstock, but is also capable of handling solids as well.

In order to vaporise solid feedstock a small modification to the boiler must be made, namely removal of the dosing pump. The solid feed can be placed directly in the boiler pot and vaporised. By increasing the negative pressure inside the reactor from the collection side, the vapour can be sucked into the reactor on the feed side. Alternatively argon can be passed through the vaporiser, thus drawing the vaporised feed into the reaction zone. However, with

this system it is not possible to maintain accurate control over the feed composition entering the reactor, due to unsteady state boiling.

5.3.2 Reactor

The graphite reactor is able to withstand a maximum temperature of 2800°c, before melting. However the surrounding material, insulation and supports, are limited to a temperature of 1250°c. Therefore compounds can be tested to a maximum reactor temperature of 1200°C, in order to ensure safety.

Because the reaction zone is constructed of graphite a limitation is imposed on the type of reactants that can be tested. The presence of any oxygen at the high temperatures could react with the carbon reactor or in the worst case ignite the reactor. As a result of these possible dangers the feedstock was limited to oxygen free reactants.

5.3.3 Temperature measurements

In an ideal case one would consider the temperature of the gas in the reaction zone however in this situation we are limited to only measuring the temperature of the reactor wall, since it is practically impossible to measure the temperature in the reaction zone due to the following factors.

In the equipment design a slightly positive pressure is maintained in the shell which means that if a thermocouple is placed in the reaction zone the argon shell gas would escape into the main reactor. In addition a thermocouple placed in the reaction zone would experience the full effect of the electromagnetic radiation since it is concentrated in this region. This would result in major fluctuations in the temperature readings, even with a radiation shielded thermocouple.

Typically optical pyrometers are used to overcome complicated designed equipment where thermocouples cannot be used. However optical pyrometers rely on detecting the radiation emitted from the hot region. In the pyrolysis reaction fine carbon black particles are been formed. This poses a serious problem since the intervention of gases, smoke or vapours between the radiating body and the pyrometer will reduce the quantity of radiation received by the instrument and thus register false temperature measurements.

6. Experimental Procedure

In this chapter a detailed description of the procedures used during the experimental runs are given. Particular attention is paid to safety issues due to the inherent nature of the chemicals and the high temperatures at which the system is operated.

6.1 Start-up

6.1.1) Prior to a run been carried out the following safety checks were performed:

- The filter on the cooling water supply line to the induction unit was checked for any dirt. If the filter is dirty this can cause blockages, which means that the induction unit will not operate due to low water pressure safety cut off.

- All electrical connections were thoroughly inspected for any loose or raw wiring. The most important connection to check is on the boiler since the wires are exposed to the high boiler temperatures and degrade quickly.

- Argon was allowed to flow through the system to ensure that no gas leaks are present.

- The sodium hydroxide scrubbers were filled with water and operated under vacuum to ensure no leaks and a consistent vacuum.

6.1.2) Contamination of both the reactants and the products were avoided by taking the following precautions:

- Any dirt or chemicals present on the inside of the boiler vessel removed, and the surface cleaned with acetone.

- The sodium hydroxide scrubbers flushed out with water to remove all traces of chemicals from previous experiments.

- The hexane scrubbers thoroughly washed with acetone.

- Sintered tips of the hexane scrubber tubes inspected for any carbon particles. If any particles are present they are burnt off by placing these tips in a furnace at 600^0C for 3 hours.

- Some of the reactant is run through the feed pump since small quantities of previous reactants remain in the pump. To prevent contamination, when the pump was flushed, it was connected to a glass beaker instead of the boiler.

- The bottom section where the carbon collects was thoroughly cleaned with acetone. The reactor walls together with the lower section inspected for any residual carbon not removed.

6.2 Operation

6.2.1 Sequence of events to operate the Pillar Induction Furnace

Most induction units operate in the audible frequency range, and emanate a very piercing high pitched sound which meant that ear plugs were worn at all times when the unit was on. These units operate at high voltages (440 volts) thus these units are highly dangerous, consequently they must be operated correctly. The following are a sequence of steps that are used to ensure the correct and safe operation of the unit.

a) Before switching the induction unit on, the cooling water pump and cooling tower must be turned on.

a) When the main power to the induction unit is switched on the following lights will light up on the induction unit:

> - Voltage control on
> - Power control on
> - Hi inverter voltage

b) If all the lights in (a) are on, then the high frequency power start button can be pressed. When this button is pressed the H.F lights comes on.

c) At this point there should be four lights on in the induction unit. Before progressing further it is important to check that the power dial is on zero.

d) The green button can now be pressed. The firing of the induction unit is initiated with a loud screeching noise; in addition the inverter and power control lights come on.

e) Now that the unit is running, the power dial can be adjusted to a suitable level that does not exceed the maximum output the unit (67kW).

f) The induction unit is equipped with four safety trips:

➢ Low water pressure
➢ High water temperature
➢ High inverter trip
➢ Open door on induction unit

6.2.2 Operation

- When the reactor was at 100°C the argon feed gas was introduced into the system to flush out all gases present in the system. In addition to the feed argon a small bleed of the argon was allowed to flow through the shell.

- The boiler band heater was then turned on and the desired temperature set using the temperature controller. The variac controlling the feed line temperature was set to an appropriate voltage.

- Whilst the reactor heated up the sodium hydroxide and hexane scrubbers were filled with their respective chemicals.

- The vacuum for the sodium hydroxide scrubbers was set to a value such that only a very small vacuum existed at the exit. The scrubbers were run under a slight vacuum to ensure that no pressure build-up occurred in the reactor and also for easy removal of the products.

- When the reactor temperature was approximately 50°C away from the desired temperature the induction unit was switched off. This is done because a temperature rise occurs in the graphite reactor even after the power is switched off, which is characteristic of induction heating.

- Once the desired reactor temperature was reached, the speed controller and the pump were adjusted to their required settings and switched on.

- After the desired volume of reactants was fed into the system the pump and the speed controller are switched off.

- The system was allowed to stand for at least 30minutes to ensure that any remaining product gases are removed from the system.

- Argon was allowed to flow through the system during the cooling down stage to ensure that no air entered the reactor to form toxic by-products e.g. dioxins. When the reactor temperature reached 100°C the argon flow was stopped.

Note: During an experimental run a small beaker of ammonia was placed near the reactor. If any leaks were present the hydrogen chloride would react with the ammonia and form a white cloud (ammonia chloride).This allowed for the safe and easy detection of any gas leaks.

6.3 Shutdown

- When the reactor was sufficiently cool the cooling water pump and the cooling tower were switched off.

- The water that flows through the annulus in the lower section of the reactor was turned off when the reactor temperature reached 200°C.

- The vacuum on the sodium hydroxide scrubbers were turned off as well as the argon flowing through the system. Both the hexane and sodium hydroxide scrubbers were removed from the system.

- The bottom flange of the reactor was opened and removed. The carbon present in the respective sections in the reactor were removed. The flange and the reactor internals up to the graphite reactor were wiped with acetone and filled with a new layer of cotton wool.

- Between the flange and the reactor is a gasket, it is important to inspect this gasket as continuous removal of the flange can cause damage to the gasket and hence allow gas leaks in the system.

- Before the flange was bolted onto the reactor the bottom of the reactor was inspected for any carbon black on the walls. If any solid products are present they must be removed using a large extended paintbrush. The walls are then cleaned with acetone and the flange bolted on.

- It is important that the reactor is not open too long as the graphite tube easily traps the moisture present in the air. Thus to prevent trapping of moisture; whenever the reactor was opened a very small bleed of argon was allowed to flow through the system.

6.4 Sample Collection

- The samples taken from the hexane scrubbers were collected in two air tight glass vials. The first bottle was used for the GC/MS analysis whilst the second was refrigerated. This was necessary since in the event a sample needed to be rerun through the GC/MS the

initial sample could not be used since the sample septum had been pierced and thus there was a very real possibility of the volatiles escaping.

- The contents from the sodium hydroxide scrubbers were mixed together and a 500ml sample was taken for titrations. A large volume was necessary since all titrations were performed in duplicate and in some instances in triplicate.

- The carbon formed from the reaction was found in three different places:

    - Reactor walls
    - On the walls of section below the reactor i.e. ceramic and water cooled flange
    - In the catchpot

- The carbon from the respective locations was collected in separate containers in order to determine the percentages in the respective locations.

- The cotton wool in the catchpot containing the carbon was removed, weighed and sealed in a plastic bag. Carbon present on walls of the catchpot were dusted off using a paint brush and added to total catchpot carbon mass.

- The carbon on the other two locations were extremely fine and clinged to the walls, thus the reactor and the flange were carefully dusted with a 1.2m spherical paintbrush. The carbon was dusted on to a plastic sheet placed at the reactor bottom. Once all the carbon had been removed the carbon was transferred to glass beakers for weighing.

Chapter 7: Analytical Techniques

It is important to quantify all the products formed during the reaction in order to achieve a complete mass balance. In addition qualitative analysis is equally important to determine the optimal operating conditions. During this chapter each element involved in the analysis of the respective products will be discussed.
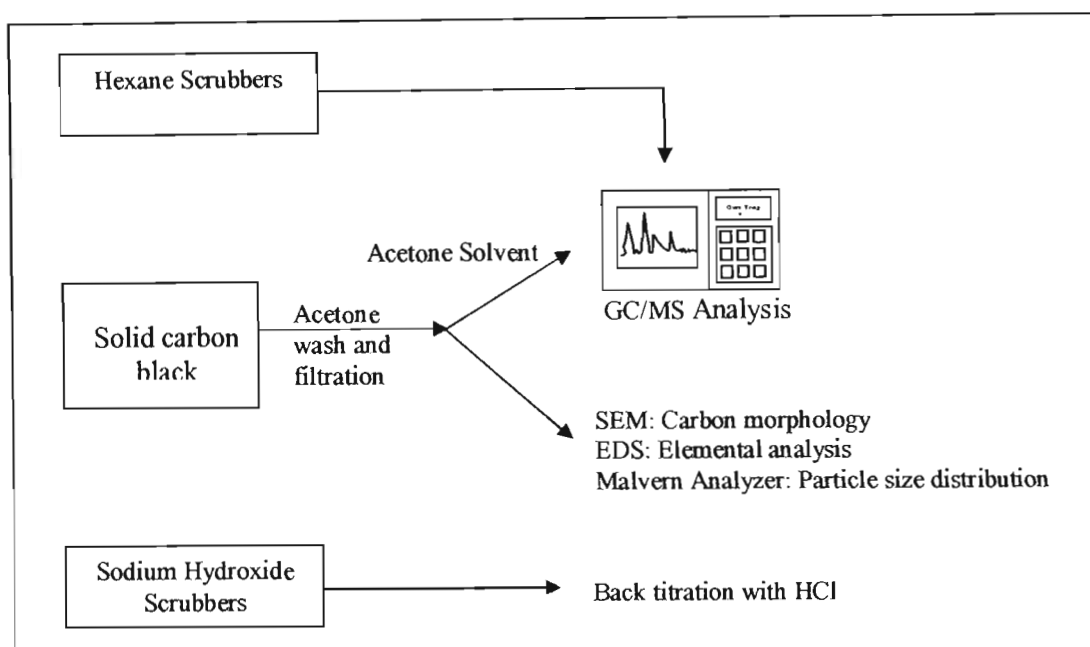
Figure 7-1: Overview of the analysis used for the respective products obtained from the pyrolysis system.

7.1 Analysis of Hexane Scrubbers

In order to determine the extent to which destruction of the respective chlorinated compound was achieved, analysis had to be performed on the hexane from the scrubbers for undestroyed reactants and chlorinated by-products. Chromatography is the most rapid and efficient technique for the separation of the components from a given system.

Initially a gas chromatograph (GC) equipped with a thermal conductivity detector was used to analyse the product stream. However the sensitivity and the corresponding detection limits of this analyser was extremely poor. The products trapped in the hexane scrubbers were finally quantified by using a gas chromatograph equipped with a mass selective (MS)

detector. Gas chromatography- mass spectrometry (GC/MS) combines the separating power of the GC with the powerful detection capabilities of the MS. The GC was a Perkin Elmer 900 Autosystem XL, with a Perkin Elmer electron impact detector. The column used was an Elite capillary column HP- 95% dimethyl, 5% diphenyl column, with a methylpolysiloxane stationary phase. The column dimensions are column length of 30m, diameter of 250µm and thickness of 0.25µm.

Every GC determination involves injection, separation and detection. For the capillary column the following two options are available for the injection method:

(1) *Split Ratio Injection:* only a portion of the injected volume enters the column
(2) *Splitless Injection:* the total injected enters the column

Initially splitless injection was used since this allowed for detection of trace amounts of compounds. However the resolution of the peaks were extremely poor and overloading of the solvent occurred in most of the analyses. The combination of these two factors meant that the MS could not correctly identify the compounds. The method was then changed to split ratio injection. In order to setup this method samples were injected using the splitless method and then the split ratio method. This allowed for comparison of the compounds detected by the two methods. This was a trial and error procedure to achieve the correct split ratio, with the aim of detecting the trace products whilst still achieving sharp distinct peaks. A final split ratio of 300:1 adequately satisfied the above mentioned requirements.

The additional variables shown in Table 7-1 were also manipulated in order to achieve satisfactory separation of the different components in the mixture. This analytical technique was optimised to ensure that all chlorinated species could be detected including low molecular weight species.

Table 7-1: GC/MS parameters and their corresponding values

Variable	Value
Injection Port Temperature/ °C	40
Hold Time/ min	3
Ramp Rate/ (°C/min)	10
Temperature/ °C	240
Hold Time/ min	1
Final Temperature/ °C	240
Scan Duration/ min	24
MS Interscan Time/ s	0.1
Injection Volume/ (µL)	1

During the separation of the components in the GC/MS mass spectral fragmentation patterns are recorded for each of the analytes. They are stored in the data system for subsequent qualitative and quantitative evaluation. These fingerprints are compared with those stored in the mass spectral database to assist in determining the identity of the unknown compounds. Although searching the mass spectral library was useful and timesaving considerable care was exercised in interpreting the results of such comparisons, as sometimes they were misleading.

A large variety of products were formed from the reactions involving the respective chlorinated compounds. The GC/MS allowed for detection of all chlorinated and non-chlorinated species in the mass range of 34 to 600 m/e. Most of the products were in trace quantities, indicated by extremely small peaks on the chromatographs. Quantification of these compounds would require calibration of the GC/MS, which would be very time-consuming as well expensive. Thus it was decided that the GC/MS would be calibrated only for the feed reactant and any other major components that were prominent in the chromatographs.

Van der Westhuisen (1994) made approximations for the concentration by roughly correlating the areas of the relevant peaks to the areas produced by known concentrations of chlorinated compounds that were calibrated for. A similar approach was followed in determining the mass percentages of the uncalibrated compounds. Thus these inferred mass percentages can at best be considered as indications of the order of magnitude of the real values.

7.2 Analysis of Carbon Black

The adsorbance properties of activated carbon is well known thus it is reasonable to assume that the very fine carbon particles formed from the pyrolysis process could behave in the same manner and trap volatile organic components from the effluent stream passing over it. However since the nature of the process conditions affect the structure as well as the purity of the carbon formed, qualitative analysis was also important.

The mass of the cotton wool was measured before and after a run, thus allowing for easy calculation of the amount of carbon black formed through difference in mass. It is important not to directly weigh the carbon mass by removing it from the cotton wool, since the carbon particles are extremely small. Thus most of the finer carbon particles cannot be removed from the cotton wool. In addition the cotton wool is fluffy and this could contaminate the carbon samples thus leading to misleading results.

It is essential to understand that the carbon collected is formed from a number from polymerisation reactions, which involve a number of different species (Section 2.3). In order

to identify these species the carbon was washed with acetone and the residue analysed using the GC/MS described in section 7.1.

The acetone does not strip the carbon of all the additional compounds contained within it, thus the carbon was subjected to energy-dispersive X-ray spectrometer (EDS) analysis in order to determine the elemental percentages. The EDS is much less accurate than the method of dissolving the carbon in acetone and then analysing the acetone.

For qualitative analysis a scanning electron microscope (SEM) was used to reveal the surface structure and the shape of the carbon particles. The average particle size and size distribution are determined by using the Malvern Analyser.

7.3 Analysis of Sodium Hydroxide Scrubbers

Reaction (7-1) is a well established reaction between an acid and a base. This reaction forms the basis for the sodium hydroxide scrubbers.

$$NaOH + HCl \rightarrow NaCl + H_2O \quad ......(7-1)$$
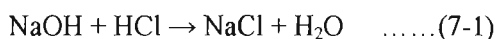
For each run an excess of sodium chloride was filled in the scrubbers. The hydrogen chloride formed during the reaction bubbled through the sodium chloride and reacted according to reaction (7-1). When the experiment was complete the scrubbers still contained some unreacted sodium hydroxide. A sample was removed from the scrubbers and back titrated with hydrochloric acid to its phenolphthalein end point. Performing a back titration allowed for the determination of how much unreacted sodium hydroxide was present in the scrubbers. Since the initial concentration of the sodium hydroxide was known, the amount of sodium hydroxide that reacted and hence the amount of hydrogen chloride formed during the experiment was easily determined.

7.4 Analytical Equipment

It is important to understand how some of these analytical equipment work in order to recognize their limitations and inaccuracies.

7.4.1 Scanning Electron Microscope (SEM) with Energy Dispersive Spectroscopy (EDS)

The sample is normally secured to a double sided graphite stub and is grounded to prevent the build up of static high voltage charges when the beam electrons strike the sample.

For EDS analysis the samples were not coated. Where images of the samples were required, the samples were sputter coated with a 10nm layer of gold in a Polaron E5100 SEM Coating Unit. The samples were viewed and analyzed in a LEO 1450 SEM which was fitted with a Link ISIS energy dispersive X-ray analysis system.

The SEM has a pair of lenses called the condenser and objective lenses. These lenses are used to generate a demagnified, focused spot of electrons that is scanned over the surface of an electrically conductive sample. As these impinging electrons strike the sample they give rise to a number of energy signals. A secondary electron detector is used to collect the electrons and to generate a signal that is processed by electronic equipment and ultimately displayed on monitors. The stored signal is than a detailed map of the sample surface. Since the electron beam also generates the emission of x-rays characteristic of the elements present, energy dispersive analysis of the x-rays provides a means of elemental identification.

The process is operated under a vacuum in order to remove air molecules that might impede the passage of the high energy electrons down the column, as well as to permit the low energy secondary electrons to travel to the detector.

One of the limitations of this unit is that it cannot detect hydrogen. There is a thin beryllium window in front of the detector crystal and it absorbs the lighter element x-rays (hydrogen to boron), which means that carbon is the first element to be detected.

7.4.2 Malvern Analyser

For different samples a standard operating procedure has to be defined. This allows one to set various parameters for both accurate and reproducible results. These parameters include:

- Number of measurements per sample
- Pump speed
- Stirrer speed
- Ultrasonic duration and intensity
- Feed rate
- Calculation Type

By using high efficiency ultrasonication the unit provides maximum dispersion efficiency. This together with the impeller and pump stirrer helps to keep all the particles in suspension. This ensures that sample conditioning is consistent from sample to sample.

The Malvern Analyser model Hydro 2000MU is ideal for the purpose of generating a particle size distribution for carbon. This unit uses a 1000ml beaker as the sample container in which water is used as the liquid medium for dispersion of the samples. A "dip-in pump" and stir head continuously agitates the samples and automatically circulates it through the measuring system. This creates a suspension of particles in water optimised using ultrasonics and surfactants were necessary. The ultrasonics breaks up any agglomerates and removes air bubbles. Whilst surfactants assist in breaking up agglomerates its primary purpose is to create a uniform suspension. For the carbon samples a simple dish washing liquid was used as the surfactant.

The diagram below shows a simplified schematic of a laser diffraction particle size analyzer. This comprises of a collimated helium neon laser beam, which is brought to focus by a reverse Fourier lens to a point at the centre of a focal plane detector array. This array consists of a large number of photosensitive elements radiating from a central point and increasing in area as they do so. At the centre of the array is a pinhole through which the laser beam passes and falls on a second detector known as an obscuration detector. If no particles are present in the laser beam, the entire laser light will fall on this second detector. However, as soon as particles enter the laser beam, they block and scatter light away from this detector and onto the other elements of the detector array.

The angle at which the light is scattered by a particle is inversely proportional to the size of the particle so that small particles will give rise to large angles of scatter and large particles will give rise to smaller angles of scatter. The reverse Fourier lens has the property of collecting the scattered light from an ensemble of particles and overlaying common angles of scatter onto the same portions of the detector array.

Figure 7-2: Schematic of the principle detection method of the Malvern Analyser

Chapter 8: Results and Discussion

The first part of this chapter is dedicated to the pyrolysis of a simple chlorinated aliphatic hydrocarbon namely dichloromethane. The discussion will focus on all of the major aspects involved in the process and chemistry specifically: product distributions, reaction schemes and the effect of process variables. Following the initial discussion on the pyrolysis of dichloromethane the more toxic chemical chlorobenzene will be discussed under the same subject matter as for dichloromethane.

8.1 Pyrolysis of dichloromethane

8.1.2 Effect of process variables on destruction efficiencies and yields

The work performed by Pillay (2001) demonstrated that at a temperature of 1000°C for gas phase residence times greater than 2.0s, dichloromethane was destroyed to a minimum destruction efficiency of 99.9999% (six nines) or 1 ppm. However there was a need to perform an intensive and systematic investigation to determine the relationship between the main process variables namely reactor wall temperature and mean gas phase residence time with destruction efficiencies, product yields and the properties of the carbon formed.

8.1.2.1 Effect of reactor wall temperature

In an ideal case one would consider the temperature of the gas in the reaction zone however in this situation we are limited to only measuring the temperature of the reactor wall, since it is practically impossible to measure the temperature in the reaction zone (Section 5.3.3).

8.1.2.1 (a) Experiments

Due to the large amount of work involved in setting up and performing the experiments each batch of experiments were designed such that a minimum amount of experimental work yielded maximum information with sufficient confidence in the validity of the results. For this purpose the book by Montgomery (2002) was used to structure the experimental plan.

The experiments were designed to test the effect of temperature over a temperature range from 327°C to 1000°C. During these experiments the residence time and the feed concentration were kept constant. The mole fraction of dichloromethane in the feed stream was maintained at a value of 27.6% together with a gas phase residence time of 2.57s. The

residence time was selected as 2.57s based on Pillay's (2001) data, which showed that mean residence times greater than 2.0s were needed for the complete destruction of dichloromethane (at 1000°C). In addition the high residence times would allow for a good range of destruction efficiencies versus temperature, which would be useful in modelling the system.

The temperatures for which the tests were performed are shown in Table 8-1. Experiments 2 and 4 were chosen arbitrarily to be repeated in order to validate the reproducibility of the results. It is clear from the results that the experiments show good reproducibility, both at low and high temperatures.

8.1.2.1 (b) Destruction Efficiencies

Table 8-1: Effect of reactor wall temperature on the destruction efficiency of dichloromethane.

Run Number	Reactor Temperature/ °C	% Destruction Efficiency
1	327	68.64
2a	540	73.94
2b	540	74.12
3	742	97.9870
4a	1000	100
4b	1000	100

The results in Table 8-1 illustrate that at temperatures less than 1000°C the reaction does not proceed fast enough thus resulting in low destruction efficiencies (<99.9999%). However at a temperature of 1000°C sufficient energy is supplied such that the reaction results in the complete destruction of dichloromethane. It is recognized that a destruction efficiency of 100% depends largely on the sensitivity of the equipment used for detection, in this case a gas chromatograph equipped with a mass selective detector (Chapter 7).

In order to determine the detection limits of the GC/MS, samples were made up and analyzed. The detection limit of the GC/MS was found to be of the order of 1ppb for dichloromethane in a hexane solvent. This was sufficiently accurate for the purpose of this study as it was well below the 1ppm limit set by the EPA. Thus 100% destruction efficiency is indicative of a minimum detection concentration of 1ppb of dichloromethane in hexane.

8.1.2.1 (c) Product Distribution

Due to the high temperatures at which pyrolysis reactions are conducted a large number of highly reactive species are formed, which leads a wide variety of products. Thus in the

present pyrolysis system a wide distribution of products were observed. The complete product distribution can be seen in Appendix C.

Depending on the temperature at which the reaction occurred, the major yields shifted from chlorinated derivatives to carbon black and hydrogen chloride. At temperatures less than 500°C the destruction of dichloromethane was low (less than 80%) hence a large number of chlorinated derivatives were observed in the product stream. Whilst at temperatures greater than 620°C where the destruction was greater than 90%, carbon and hydrogen chloride were the major observed products.

The minor products that were formed from the reaction were interesting. At the lower temperatures carbon black and hydrogen chloride became the minor products together with some chlorinated derivatives. Whilst at the high temperatures alkanes, alkenes and chlorinated derivatives of lower or equal chlorination were formed.
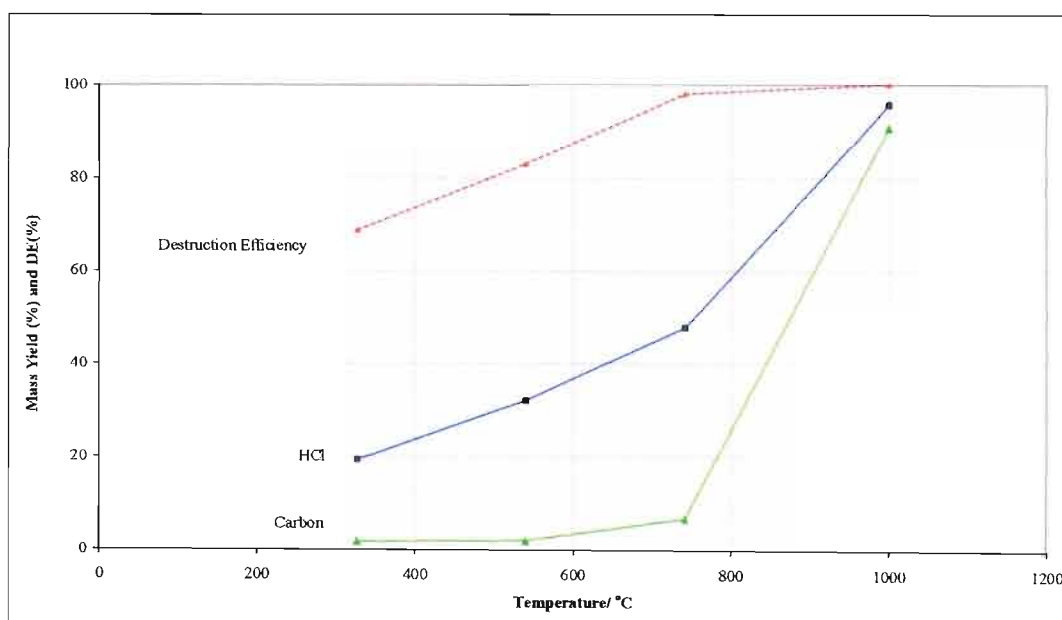
Figure 8-1: Effect of temperature on the yields of hydrogen chloride and carbon for the pyrolysis of dichloromethane. Data collected for a constant residence time of 2.57s and reactant concentration of 27.6%.

The major products that are formed from the pyrolysis of dichloromethane at destruction efficiencies greater than 90% are hydrogen chloride and carbon irrespective of the reaction atmosphere (oxygen or inert gas) (Taylor, 1991). From the data shown in Figure 8-1 it was reasonable to assume that once a destruction of 99% is reached in the pyrolysis system the mass yields for hydrogen chloride and carbon will remain constant up to 100% destruction at

1000°C. This trend was tested and proved by observing no discernable effect in the carbon and hydrogen chloride yields at DEs greater than 99%.

Above the temperature of 1000°C it is uncertain what will happen to these yields in the pyrolysis system.

8.1.2.2 Effect of mean residence time

The volume of the pyrolysis graphite reactor is fixed therefore according to the equation shown below the mean residence time can be changed by varying the total flowrate.

Residence Time = Reactor Volume ÷ Total flowrate

Variations in the total flowrate can be achieved by either changing the argon flowrate or the reactant flowrate. The respective flowrates were adjusted appropriately in order to maintain a consistent feed mixture concentration. It should be noted that since the residence time is dependant on the temperature in the reaction zone, which is an irresolute variable (Section 8.1.2.1), a certain amount of inaccuracy is involved.
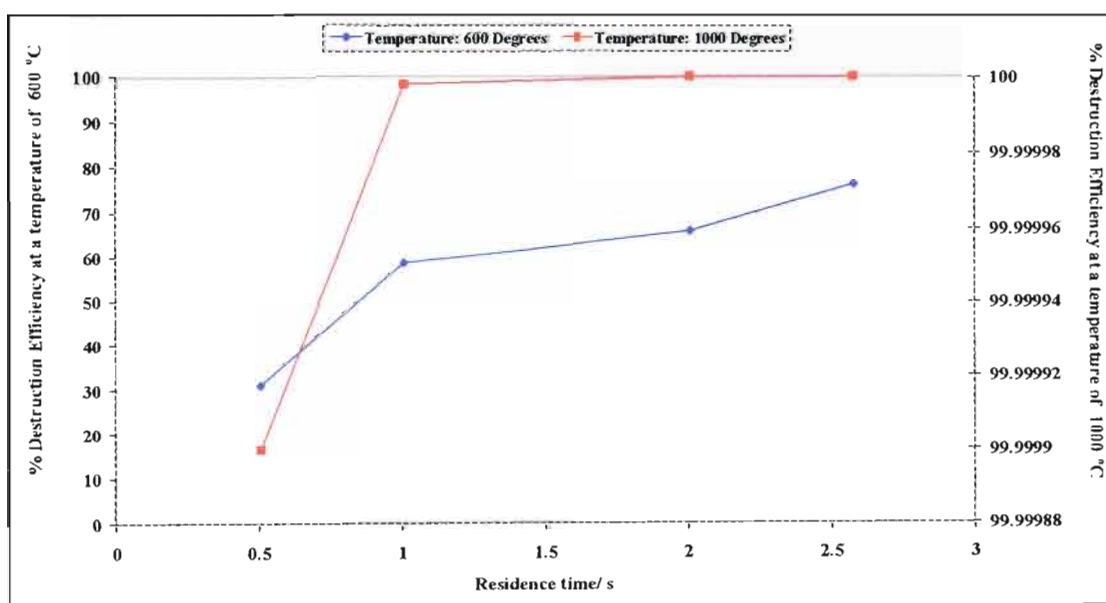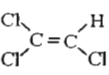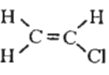
Figure 8-2: Effect of mean residence time on the destruction efficiency of dichloromethane at two different temperatures. Data collected for a constant reactant concentration of 27.6%.

At a temperature of 600°C the residence time has a major affect on the destruction efficiency of dichloromethane. Figure 8-2 shows that increasing the residence time from 0.5 to 2.57 caused a corresponding increase in the destruction efficiency from 31% to 76%. At these low temperatures the product distributions consisted primarily of chlorinated derivatives, as shown in Table 8-2. Increasing the residence time caused an increase in the degree of chlorination and the quantity of these derivatives. Dichlorobenzene and trichlorobenzene have isomers but are not shown due to the inability of the GC/MS to accurately distinguish between the isomers.

It is postulated that the longer residence times at low destruction efficiencies allows more time for the chlorinated products formed, and also the highly reactive chlorine radicals, to undergo a number of recombination and substitution reactions. (Discussed later in Section 8.1.3.1)

Table 8-2: Showing some of the more toxic products observed from the pyrolysis reactions at 600°C.

Compound	Molecular Formula	Structure
Chlorobenzene	C_6H_5Cl	
1,2- Dichlorobenzene	$C_6H_4Cl_2$	
1,2,3-Trichlorobenzene	$C_6H_3Cl_3$	
Chloroform	$CHCl_3$	
Trichloroethylene	C_2HCl_3	
Chloroethene	C_2H_3Cl	
Benzene	C_6H_6	

In contrast to the pronounced effect the residence time has on both the destruction efficiency and the product distribution at 600°C, is the fine effect at a temperature of 1000°C. The residence time has a very subtle effect on these two variables at the high temperature limit. It serves merely to improve the destruction greater than six nines. Equally the observed product distribution was practically unchanged with variations in the residence time at a 1000°C.

8.1.3 Reaction Mechanisms

From the product distribution shown in Appendix C acceleration and inhibition effects are apparent. Therefore it is important to develop quantitative insights into the pyrolysis mechanism in order to better understand and ultimately optimize these reaction processes. The purpose of the following discussion is to systematically develop a reaction mechanism that accounts for the observed reaction products. The mechanism will be developed by using relevant reaction pathways constructed by past researchers that have investigated the destruction of chlorinated compounds.

The reaction mechanism can be divided into two parts namely one that accounts for the observed gas phase products and secondly the formation of solid carbon black. It must be recognized that these mechanisms are not independent of each other and are interlinked. In Chapter 2 a detailed discussion was presented on the possible mechanisms for the formation of carbon black, thus this section will focus on the reaction pathways leading to the observed gas phase products and carbon black precursors.

8.1.3.1 Gas Phase Products

8.1.3.1 (a) Basic mechanism

Rice and Herzfeld (1934) formulated an approach to pyrolytic chains, which has since become the foundation for the analysis of product distributions by many researchers. It is based on the premise that the fastest mode of reaction is the abstraction of a hydrogen atom from a hydrogen containing molecule by a radical. If this is followed by a unimolecular decomposition of the product radical into an unsaturated olefin and a radical then a pyrolytic chain exists. What makes such a rapid sequence feasible is the fact that the unimolecular decomposition step has a low activation energy since the normally endothermic bond breaking is compensated by multiple bond formation. This approach works particularly well for chlorinated systems and thus will also be followed.

All the products formed during the pyrolysis reaction gives us an idea of what reaction pathways are been followed. It is vital not only to look at the major products but also the products formed in trace quantities since these compounds are instrumental in forming a complete picture of the reaction pathway.

The pyrolysis of dichloromethane is initiated by cleavage of the C-Cl bond due to its low bond energy compared to the C-H and C-C bond. The most important reaction following C-Cl bond cleavage is the abstraction of hydrogen by chlorine to form the corresponding hydrocarbon radical and hydrogen chloride.

$$CH_2Cl_2 \qquad = \cdot CH_2Cl + \cdot Cl \qquad (8\text{-}1)$$
$$CH_2Cl_2 + \cdot Cl \quad = \cdot CHCl_2 + HCl \qquad (8\text{-}2)$$
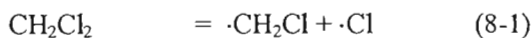
This is consistent with the Rice and Herzfeld (1934) concept. Ho *et al.* (1992) reported these abstraction reactions, (8-1) and (8-2), by chlorine to be fast with Arrhenius factors greater than E+13 and low activation energies. The result is a rapid production of hydrocarbon and chlorocarbon radicals early in the reaction. Weissman and Benson (1984) predicted that the fastest step in the dichloromethane system is reaction (8-2). Thus on this basis there are more $CHCl_2$ radicals formed in reaction (8-2) than CH_2Cl, produced primarily in the C-Cl bond cleavage reaction (8-1). However in Chapter 2 it was stated that HCl elimination is also one of the reaction paths that are available. Thus HCl elimination is also a possible initiation path that can be considered.

$$CH_2Cl_2 = :CHCl + HCl \qquad (8\text{-}3)$$

Taking the main features of the chloromethane mechanism by Weissman (1984) as a guideline, a basic dichloromethane pyrolysis mechanism was inferred by Frenklach (1986) for dichloromethane.

$$\cdot CH_2Cl + CH_2Cl_2 = CH_3Cl + \cdot CHCl_2 \qquad (8\text{-}4)$$

$$\cdot CHCl_2 + \cdot CHCl_2 = 1,1,2,2\text{-}C_2H_2Cl_4 \qquad (8\text{-}5)$$

$$\cdot CH_2Cl + \cdot CH_2Cl = 1,2\text{-} C_2H_4Cl_2 \qquad (8\text{-}6)$$

$$\cdot CHCl_2 + \cdot CH_2Cl = 1,1,2\text{-} C_2H_3Cl_3 \qquad (8\text{-}7)$$

$$1,1,2,2\text{-} C_2H_2Cl_4 = C_2HCl_3 + HCl \qquad (8\text{-}8)$$

$$1,2\text{-} C_2H_4Cl_2 = C_2H_3Cl + HCl \qquad (8\text{-}9)$$

$$1,1,2\text{-} C_2H_3Cl_3 = C_2H_2Cl_2 + HCl \qquad (8\text{-}10)$$

$$C_2H_3Cl = C_2H_2 + HCl \qquad (8\text{-}11)$$
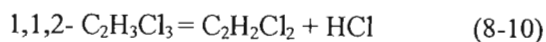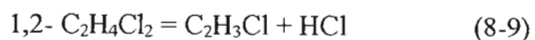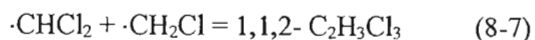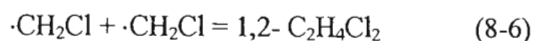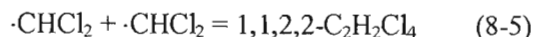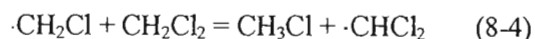
The recombination of radicals from reactions (8-5) to (8-7) results in the production of chlorinated ethanes, which in turn rapidly decompose to HCl and chlorinated ethylenes through reactions (8-8) to (8-10). On the basis that $CHCl_2$ is more abundant than CH_2Cl, Frenklach (1986) expected the product distribution to be: $[C_2HCl_3] > [C_2H_2Cl_2] > [C_2H_3Cl]$.

However he observed $C_2H_2Cl_2$ to be in the highest concentration and thus proposed that $CHCl_2$ recombination is very much faster than the other recombination reactions. This fast forward rate results in a rapid increase in the rate of the reverse direction thus bringing this reaction to a state of partial equilibrium early in the pyrolysis. As a result the net rate of reaction (8-5) becomes smaller than the net rates of reactions (8-6) and (8-7).

It is apparent from Frenklach's (1986) mechanism that the major product formed through hydrogen abstraction is hydrogen chloride, which is consistent with the results obtained. However chlorinated ethylenes have not been observed which could imply that these products are unstable intermediates which quickly breakdown to form precursors that lead to carbon formation.

Ho *et al.* (1992) found that the recombination reactions (8-5) and (8-6) proceed through the formation of stable energized intermediate complexes called adducts. For example the recombination of the CH_2Cl radical proceeds through the following sequence of steps:

$$\cdot CH_2Cl + \cdot CH_2Cl \leftrightarrow [\, CH_2ClCH_2Cl \,]^{\#} \text{ (adduct)} \qquad (8\text{-}12)$$

$$\rightarrow \cdot Cl + \cdot CH_2ClCH_2 \qquad (8\text{-}13)$$

$$\rightarrow HCl + C_2H_3Cl \qquad (8\text{-}14)$$

$$\rightarrow CH_2ClCH_2Cl \qquad (8\text{-}15)$$

Reaction channels available to these adducts include stabilization, four center elimination, Cl_2 elimination, Cl elimination and H elimination. However because of the relatively weak C-Cl bond the CH_2ClCH_2 radical rapidly decomposes by beta scission to form Cl and C_2H_4. These pathways can be considered as important to the formation of carbon precursors, especially to those described by the polyyne model (Section 2.3.4). The chlorine produced rapidly reacts, preferably through hydrogen abstraction, with other species present to produce HCl and a radical thus continuing the chain.

Franklin (1969) used group additivity estimates to determine the activation energies for the available reaction paths. He found that the pathways excluding HCl elimination have activation energies greater than 293kJ/mol. HCl elimination activation energies were less than 251kJ/mol. Kim (1974) confirmed that HCl elimination was the lowest energy channel for both $CH_2ClCHCl_2$ and CH_2ClCH_2Cl by reporting activation energies of 246 kJ/mol and 224 kJ/mol. On the basis of the above discussion it is safe to make the assumption that the only feasible decomposition route for the adducts is by HCl elimination.

Bozzelli (1992) found that atomic chlorine is formed at early reaction times and that it reacts rapidly with other hydrocarbon species. In the above mechanism, and discussion, the most
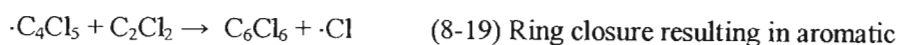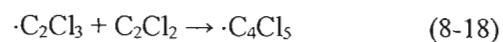
important reaction path at the investigated temperatures ($\geq$ 1000K) are predominately abstraction of hydrogen by chlorine to form the corresponding hydrocarbon radical and hydrogen chloride. He also confirmed that the production of hydrogen chloride has favorable thermodynamics and have high concentrations very early in the reaction. Therefore it is reasonable to assume that at longer residence times and lower temperatures there is a significant recycle of HCl to form chlorine; which is then available for molecular growth reactions.

8.1.3.1 (b) Mechanism for observed high molecular weight species

The above reaction pathways rationalize the formation of the observed chlorinated and non-chlorinated aliphatic species. The primary mechanism will now be built on to account for aromatic production from aliphatics.

Chlorinated benzenes appear to be stable reaction intermediates from the pyrolysis of highly chlorinated alkanes and alkenes. Taylor (1988) demonstrated that chlorinated aromatic species readily form from the pyrolysis of simple chlorinated precursors. He postulated that although not all of the higher molecular weight products are common to each parent compound, they may be formed by some common mechanism.

Trichloroethylene can either form through reaction (8-8) or through recombination of CH_2Cl and $CHCl_2$ radicals with subsequent HCl elimination.

$$C_2HCl_3 \quad \rightarrow C_2Cl_2 + HCl \qquad \text{(8-16) Low energy unimolecular decomposition}$$

$$C_2HCl_3 + \cdot Cl \rightarrow \cdot C_2Cl_3 + HCl \qquad \text{(8-17) Chain propagation through H abstraction}$$

$$\cdot C_2Cl_3 + C_2Cl_2 \rightarrow \cdot C_4Cl_5 \qquad \text{(8-18)}$$

$$\cdot C_4Cl_5 + C_2Cl_2 \rightarrow C_6Cl_6 + \cdot Cl \qquad \text{(8-19) Ring closure resulting in aromatic}$$
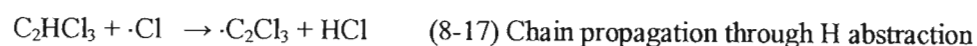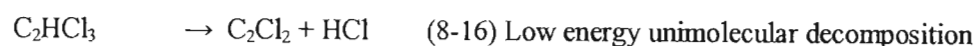
The key to this mechanism lies in the species C_2Cl_2 since following its formation, rapid molecular growth of aromatics and higher molecular weight compounds was found by Taylor (1988). Furthermore C_2Cl_2 is the species that predominates at temperatures of 500°C-600°C, which is significant since at these lower temperature aromatics were common in the pyrolysis experiments.

The above mechanism shows the pathway for the formation of hexachlorobenzene. The radicals/molecules C_xCl_y can undergo similar type of reactions to yield other chlorinated aromatics and higher molecular weight species. Reactions (8-20) and (8-22) are typical

growth reaction steps that are possible through the formation of the high energy adducts C_4Cl_5 and C_4Cl_7.

$$\cdot C_2Cl_3 + C_2Cl_2 \leftrightarrow C_4Cl_5^{\#} \rightarrow C_4Cl_4 + \cdot Cl \qquad (8\text{-}20)$$

$$\cdot C_2Cl_3 + C_2Cl_4 \leftrightarrow C_4Cl_7^{\#} \rightarrow C_4Cl_6 + \cdot Cl \qquad (8\text{-}22)$$
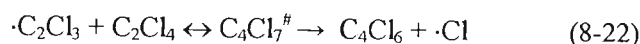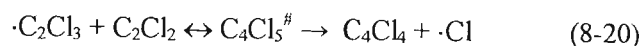
It is recognized that in principal there are many reactions that can result in the formation of stable higher molecular weight molecules. However at a destruction efficiency of greater than 90% these higher molecular weight species (including aromatics) were observed only in trace quantities which suggest two possibilities:

(1) The reactions required to form the initiating species were too slow to be significant against the major competing reaction pathways.

(2) A destruction efficiency of greater than 90% is observed only at high temperatures. At these temperatures the more complex species become unstable and fragmentation reactions occur. These reactions ultimately result in the observed simpler final products.

8.1.3.1 (c) High tendency of dichloromethane to form carbon black

From experiments with other chlorinated aliphatic hydrocarbons, namely chloroform and carbon tetrachloride, it was observed that dichloromethane produces more carbon black than these chlorinated counterparts. Dichloromethane had a similar propensity for carbon black formation to that of trichloroethylene.

Between dichloromethane, chloroform and carbon tetrachloride, it was expected that chloroform would be the highest carbon black former. Since its higher chlorine content would result in a higher concentration of chlorine atoms which would result in a higher rate of chlorine catalyzed production of C_2H_2, C_2H and C_2H_3, which are known precursors for carbon formation. Trichloroethylene should according to theory yield the maximum amount of carbon, in contrast to other saturated chlorinated compounds discussed above, because they are intermediates of the route to soot formation and thus have a much faster path.

Frenklach (1983) postulated that dichloromethane undergoes another route that allows for more carbon formation. Carbon black yields from allenes are comparable to aromatics than to other aliphatics. Radical C_3H_3 formed in reaction (8-23) was suggested to be the cause of the high propensity to carbon formation from dichloromethane.

$$:CHCl + C_2H_2 = \cdot C_3H_3 + \cdot Cl \qquad\qquad (8\text{-}23)$$
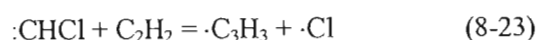
Thus the rapid formation of C_3H_3 in (8-23) initiates an efficient pathway to soot, characteristic to the allene system, which explains the outstanding sooting propensity of dichloromethane.

8.1.4 Analysis of carbon black samples

The carbon formed from the reaction was deposited in three locations. The amount of carbon deposited at the different locations was approximately distributed as shown in Table 8-3.

Table 8-3: Showing the approximate percent distribution of carbon deposition at different locations within the reactor system; at destruction efficiencies greater than 90%.

Location	Percent Carbon
Reactor Zone walls	5
Ceramic Walls	15
Catchpot	70

The majority of the carbon was found in the catchpot, as this was the intended collection point. It was interesting to find carbon present on the reactor walls. When the feed entered the hot reaction zone the carbon formation was instantaneous and almost violent; thus carbon would have been deposited on the reactor walls. It was expected that this carbon would have been swept along to the catchpot region or reacted with other species in the high temperature reaction environment (>900°C) to yield further gas phase products.

8.1.4.1 GC/MS Results

In Section 7.2 it was stated that the solid carbon black formed from a pyrolysis reaction was able to trap other gas phase products as they passed over them. The basis for this statement is the fact that when a porous solid comes into contact with a gas the solid begins to absorb the gas onto its surface and then into its pores (Cal, 1995). Activated carbon is a type of carbon that has well recognized absorbance properties. It is widely used to remove synthetic organic contaminants (e.g. trichloroethylene). Bansal et al. (1988) stated that the effectiveness of activated carbon as an absorbent is accredited to qualities such as:

- large surface area
- high degree of surface reactivity
- universal adsorption effect
- favorable pore size distribution

Although carbon black may not be as efficient as activated carbon in trapping organic compounds it still absorbs a small percentage of compounds from overflowing gases. Analysis of the acetone solvent used to wash the carbon revealed this statement to be true.

GC/MS results of the acetone solvent showed a similar product distribution to that observed from the reaction. Although proper quantification of the products was not undertaken it can be inferred from the very small areas on the chromatograph that they were in trace quantities. In addition to these products was the strong presence of higher molecular weight alkanes and alkenes.

Table 8-4: Higher molecular weight compounds that were prominent on carbon black from the pyrolysis of dichloromethane.

Compound	Molecular Formula
Nonane	C_9H_{20}
Decane	$C_{10}H_{22}$
Decene	$C_{10}H_{20}$
Tridecane	$C_{13}H_{28}$
Tetradecene	$C_{14}H_{28}$
Hexadecane	$C_{16}H_{34}$
Hexdecene	$C_{16}H_{32}$

The presence of both high and low molecular weight alkanes is consistent with the carbon model discussed in Section 2.3.4. A number of oxygenated compounds were also identified from the chromatographs. The most commonly observed were: 1-propen-2-ol, acetate, hexanal, 1-butanol, 2-ethyl, 1-octene, 3-ethyl and pentanal, 2-methyl. Their existence will be explained in the subsequent discussion.

8.1.4.2 Carbon Morphology

By means of the scanning electron microscope the surface structure of the carbon black was analysed.

<div align="center">Catchpot   Ceramic / Reactor</div>
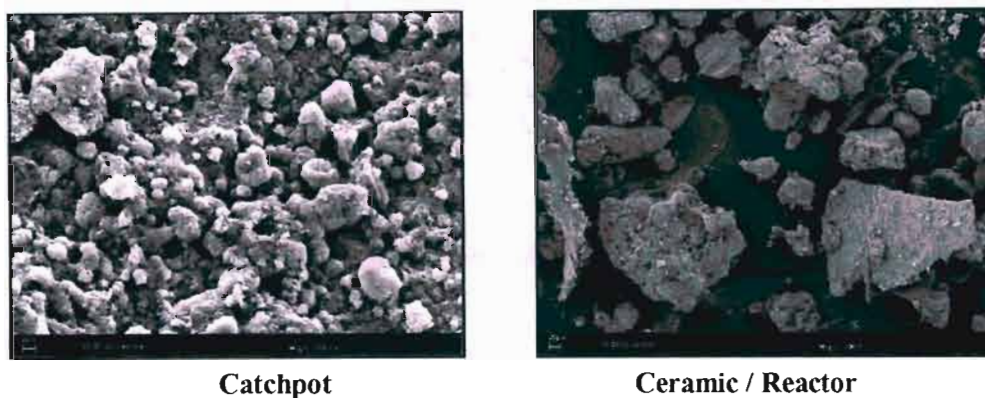
Figure 8-3: Micrograph showing the morphology of the different carbon formed from the pyrolysis of dichloromethane at a temperature 1000°C and a residence time of 0.5s

In the present pyrolysis system carbon was found in two distinct forms. The first type was found on the walls of the reactor and on the ceramic tube supporting the reactor. The second type was trapped in the cotton wool catchpot located at the bottom of the reactor. As observed from Figure 8-3, the catchpot sample exhibits clusters of spherical particles whilst the reactor sample displays flat flaky agglomerates.

During the comparison of the surface structures of the respective carbons a distinctive feature was noticed on the reactor carbon surface. A close examination of the reactor carbon surface structure revealed a very porous surface. This was observed for almost all the reactor carbon samples. These pores are possibly the result of the hot reaction gases passing through them.
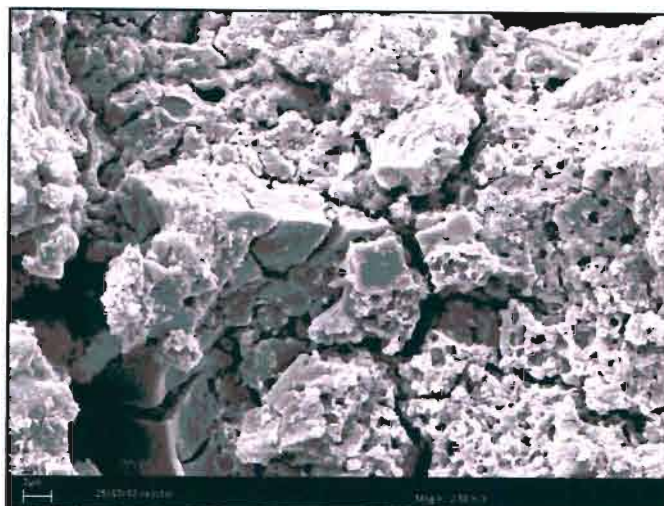
Figure 8-4: Micrograph showing the porous surface of the reactor carbon from dichloromethane pyrolysis

8.14.3 Composition of the carbon

The electron dispersive spectroscopy (EDS) analysis of the catchpot carbon revealed that they mainly contained C, O and Cl in the ratio of approximately 94:5:1 (wt). The absence of hydrogen from the composition is due to the inability of the EDS to detect hydrogen (Section 7.4.1). The presence of oxygen can be explained by post reactions of the highly reactive carbon with the ambient atmosphere. This means that when the carbon is exposed to the atmosphere it reacts with the air to form surface complexes. This post reactive behavior has been well documented in literature for activated carbon.

There is a significant difference between the elemental composition of the two kinds of carbon. The reactor carbon contained C, O, and Cl in the ratio of 82:12:6 (wt). The catchpot carbon contained much more carbon and less chlorine than the reactor carbon, indicating different molecular constitutions and physical properties.

Although the tendency to form carbon and the extent of carbon formation depend markedly on the experimental conditions the structure and intrinsic properties of the carbon particles formed appear to be only weakly dependant upon the conditions under which they are produced.

Over the temperature range 540°C–1000°C no changes in the catchpot carbon content were observed. The ratio of C:Cl also remained constant. However the reactor sample showed a decrease in the carbon content and an increase in the chlorine content for higher temperatures. These changes were less than 2% and hence not significant. Decreasing the residence time caused an increase in the carbon content by 6% and decreased the chlorine

content by 4%. Both the reactor and catchpot carbon samples showed similar percentage changes.

Decreasing the concentration of argon in the feed mixture resulted in a 14% decrease in the carbon content for both carbons. The chlorine content showed only a minor increase of approximately of 3%.

It is clear from the results that the concentration of argon in the feed stream is the major factor affecting the purity of the carbon sample and hence the production of byproducts. This dependence on the feed stream concentration seems to be logical if one looks at the global carbon formation process. The primary particles hardly exist in an isolated form but fuse together into aggregates. These aggregates develop when individual particles adhere to others and become fused by the deposition of further carbon from the gas stream. Therefore an increase in the concentration of carbon forming species contributes to this scheme.

These results also show that the carbon formed on and below the reactor contained a significant quantity of oxygen. This observation implies that the reactor carbon is much more reactive than the carbon trapped in the catchpot. This observation can be explained in terms of the "collection temperature". In the preceding chapters it was stated that the system was well insulated and because of this the reactor cooled down very slowly. Typically a single experiment would be performed each day. At the time when the carbon samples were removed from the system the core reaction zone and parts close to this zone were still hot, observed temperatures were around 200°C, whilst the catchpot samples were at ambient temperature. The presence of oxygen on the any of the carbon samples were attributed to the reactions of the carbon with the atmosphere, since no oxygen was present within the reactor. Therefore the carbon collected closer to the hot reaction zone would also be hot and hence more reactive with the atmosphere.

8.1.4.4 Effect of process variables on particle size distribution

The size distribution remained relatively constant as the process conditions were changed. In Figure 8-5 a typical particle size distribution for the two different types of carbon formed.
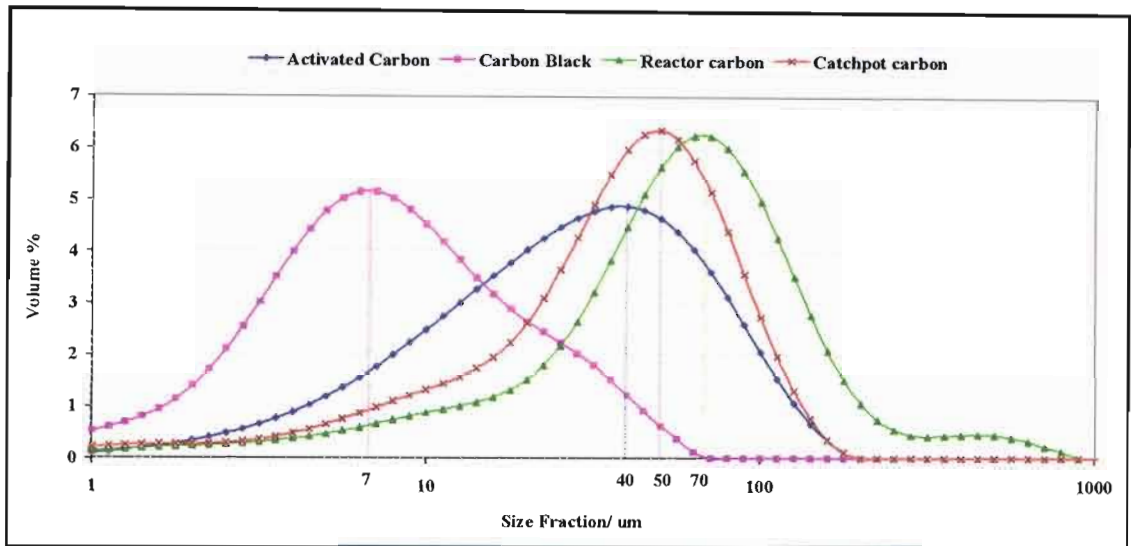
Figure 8-5: Comparison of the particle size distribution, obtained from the Malvern analyzer, for the pyrolysis carbon produced from dichloromethane against two commercial carbons.

Figure 8-5 illustrates that the reactor carbon has more particles in the higher size fraction than the catchpot carbon. Comparison of the size distribution of the carbon obtained from the pyrolysis of dichloromethane with activated carbon and a commercial carbon black sample is also shown in Figure 8-5. The catchpot carbon seems to have a closer distribution to the activated carbon. The relative closeness of the size distributions indicated that the catchpot carbon could possibly be activated. However a SEM of the two samples surface reveals completely different surface structures.

Activated Carbon   **Catchpot Carbon**
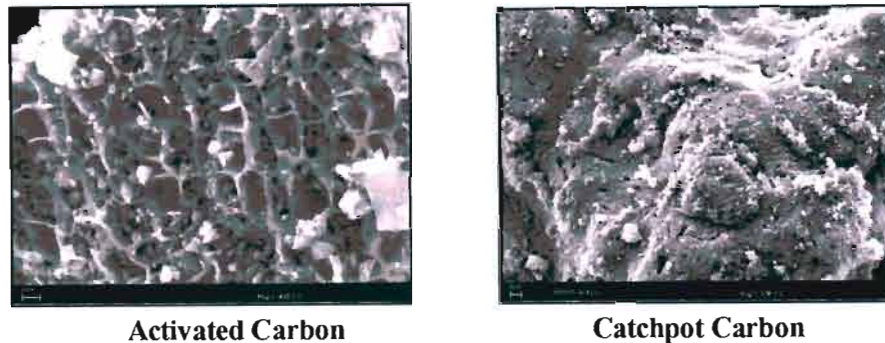
Figure 8-6: Micrographs comparing the surface of the catchpot carbon, from dichloromethane pyrolysis, and activated carbon

8.1.4.5 Effect of process variables on the specific surface area and average diameter

In section 8.14.4 it was stated that the temperature and mean residence time have a subtle effect on the composition of the carbon and the particle size distribution. In contrast to this observation is the pronounced effect of these experimental conditions on the particle diameter and surface area.

The temperature and the residence time did not affect the reactor carbon diameter and surface area. The fact that residence time did not have an effect on the particle diameter is perplexing since the temperature was higher at the location where they form which meant that they should have been more reactive, hence capable of absorbing more species to allow for mass growth. It is possible that the species were more reactive and did absorb a larger amount of molecules at the higher residence times and temperatures. However the high temperatures at where the reactor carbon formed caused them to essentially burn off the absorbed species and thus maintain their original size.

Contrasting the negligible effect of the temperature and residence time on the reactor carbon is the prominent effect on the carbon trapped in the catchpot. Therefore the focus of the following discussion is on the catchpot carbon.

8.1.4.5 (a) Effect of temperature

It is clear from Figure 8-7 that the reaction temperature has a distinct affect on the particle size. An increase in the reaction temperature resulted in larger diameter particles. However the trend is unclear with respect to the surface area.
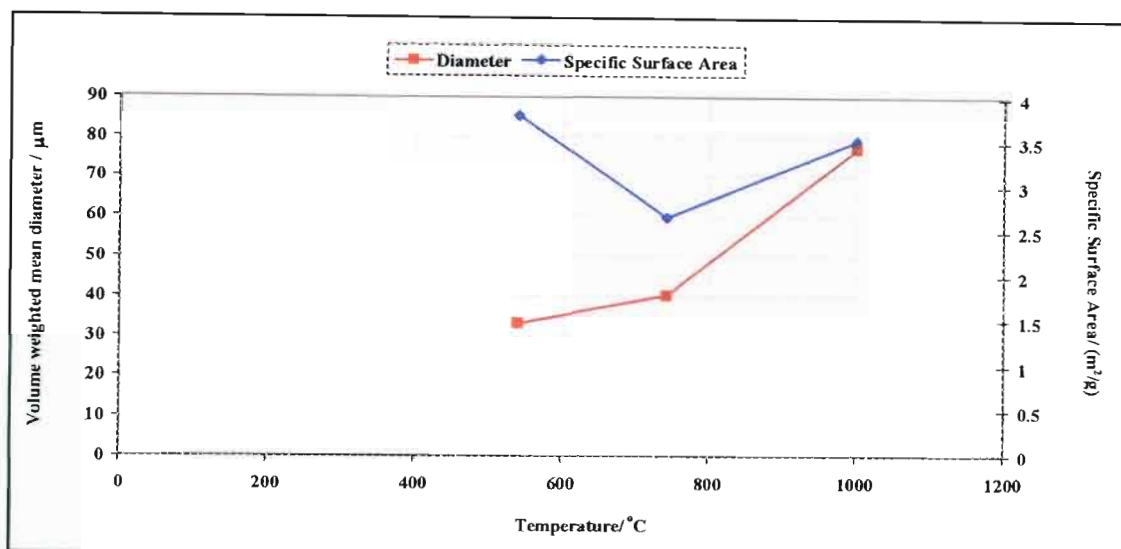
Figure 8-7: Effect of temperature on the particle diameter and surface area of the catchpot carbon obtained from dichloromethane pyrolysis.

It should be mentioned that the first point in Figure 8-7 was at a temperature of 326°C however it was omitted. The data at this point was not very accurate in view of the fact that a very small amount of carbon was formed at this low temperature and the Malvern analyzer requires that enough carbon sample be used in the analysis such that sufficient laser obscuration occurs (Section 7.4.2). Unfortunately due to the lack of carbon, the laser obscuration was poor hence causing major inaccuracies in the low temperature results.

8.1.4.5 (b) Effect of mean residence time

Figure 8-8 indicates that the mean residence time at a reactor temperature of 1000°C is important to the particle diameter and surface area. Doubling the residence time to 1s produced a sharp increase in the surface area of the carbon particles. After this rapid increase to $76m^2/g$ the surface area tends to level out with residence time.

The residence time also produces a steady increase in the particle diameter. The increase in particle diameter is consistent with the fact that the carbon particles grow by absorbing reactive species in the product stream. This statement coupled with the observation that increasing the residence time produced much more species both chlorinated and unchlorinated, adequately accounts for the observed increase in particle diameter at a reactor temperature of 1000°C.
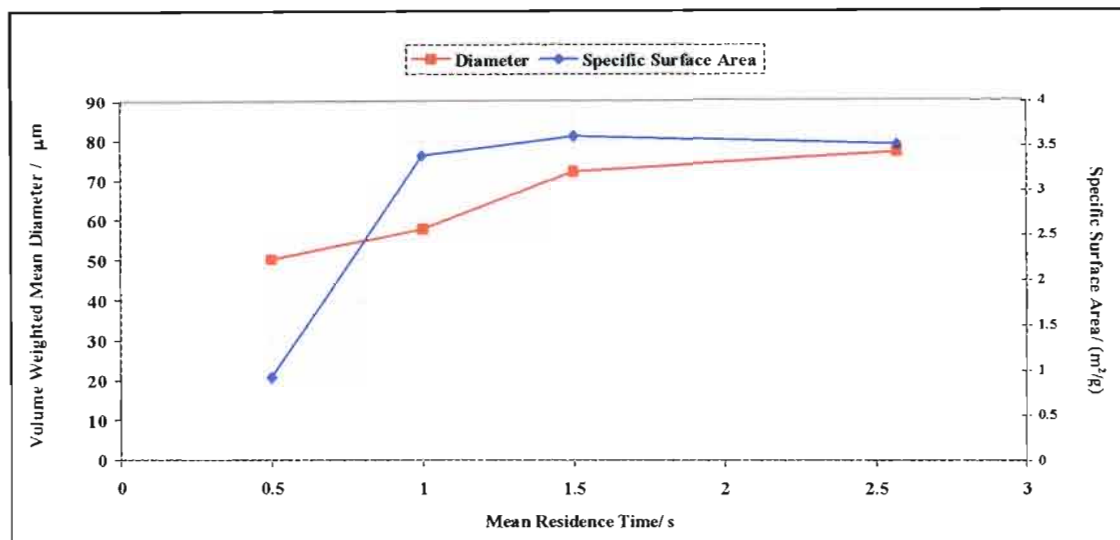
Figure 8-8: Effect of mean residence time on the particle diameter and surface area of the catchpot carbon obtained from the pyrolysis dichloromethane at 1000°C.

Better deductions and conclusions with respect to the observations for the carbon properties can only be made if the concentration profiles of the reactive species in the reaction are continuously monitored.

8.1.5 Comparison of different reaction atmospheres

Tirey *et al.* (1990) investigated the decomposition of dichloromethane in an oxygen-rich atmosphere. At a temperature of 755°C and a residence time of 2.0s, they observed a destruction efficiency of 99%. Whilst Wen-Pin *et al.* (1992) reported a destruction efficiency of 99% at a temperature of 820°C also for a residence time of 2.0s. Wen-pin maintained an atmosphere consisting of 1% hydrogen and 1% oxygen on a molar basis. By interpolation of the data given in Table 8-1 the temperature required for 99% destruction of dichloromethane in the pyrolysis system was calculated to be 871°C. It is clear from these results that the significant destruction of dichloromethane starts at a lower temperature in systems that contain oxygen.

It is interesting to note from Figure 8-9 that at temperatures less than 600°C approximately no destruction occurs in an environment containing oxygen whilst in a purely pyrolytic environment significant destruction occurs.
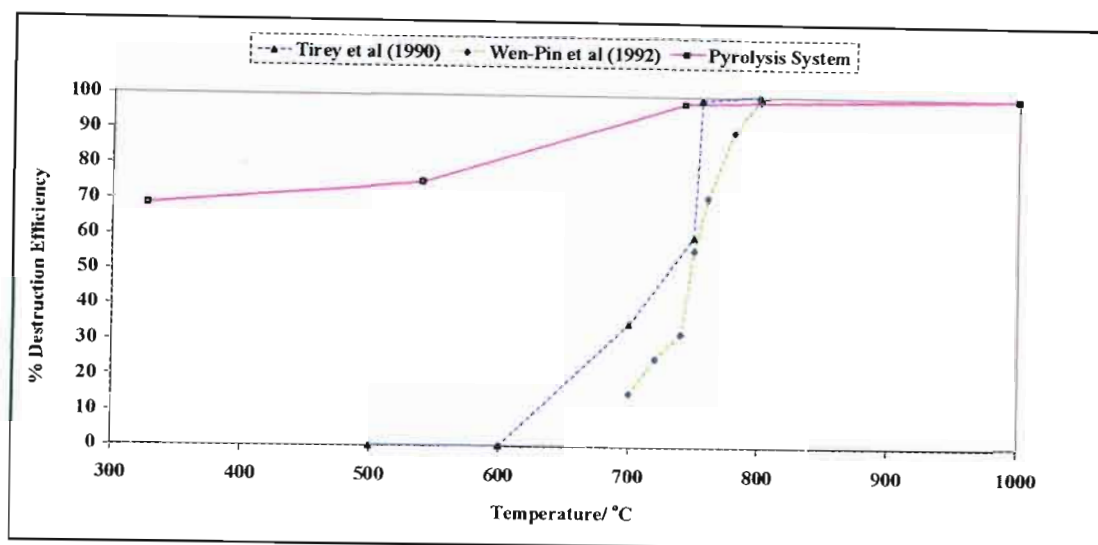
Figure 8-9: Comparison of the effect of temperature on the destruction efficiency of dichloromethane in different atmospheres. Data collected for pyrolysis system at a constant residence time of 2.57s and reactant concentration of 27.6%.

It is acknowledged that the data for the pyrolysis system is at a residence time of 2.57s whilst the other systems data are given for a residence time of 2.0s. Although this may be a possible reason for the higher destruction efficiencies it is unlikely that the increased residence time would allow for significant degradation at lower temperatures in an oxygen atmosphere. The principle reason for this statement is the different pathways for initiation of the reaction sequence.

Whilst degradation starts at higher temperatures in an oxygen atmosphere the increase in destruction is rapid once a temperature of 600°C is reached. It is clear that if the data of Wen- Pin (1992) and Tirey (1990) is extrapolated that a destruction efficiency of 100% will be achieved at a temperature in the region of 900°C.

The apparent lower stability of dichloromethane in oxygen rich environments as compared to pyrolytic environments is due to the different reactive species. Taylor (1991) reported that under oxygen rich conditions chlorine atoms, ClO radicals and OH radicals are the reactive species in the highest concentrations. The major reaction channel for the initial degradation occurs through OH abstraction of a hydrogen atom. Thus the presence of OH radicals and their high reactivity with chloromethanes explains the lower stability of dichloromethane in oxygen environments. Conversely in a pyrolytic environment chlorine atoms are the reactive species in the highest concentration. It is logical that the highest reactivity of the chlorine atom is with hydrogen in hydrogen containing chloromethanes since chlorine abstraction by chlorine atoms is a highly endothermic process (Tsang, 1990).

Comparison of the product distribution obtained by other researchers in an oxidative atmosphere shows some interesting results. Wen-Pin *et al.* (1992) found that over a temperature range of 700°C-800°C and a residence time of 1s the compounds shown in Table 8-5 were present.

Table 8-5: Observed products by Wen-Pin (1992) for the pyrolysis of dichloromethane in an oxygen atmosphere. Temperature range of 700°C-800°C and mean residence time 1 s.

Major Products		Minor Products	
Name	Formula	Name	Formula
Chloromethane	CH_3Cl	Ethene	C_2H_4
Methane	CH_4	Ethylene	C_2H_2
Carbon monoxide	CO	Chloroethene	C_2H_3Cl
Carbon dioxide	CO_2	1,1 Dichloroethene	$1,1\text{-}C_2H_2Cl_2$
Hydrogen chloride	HCl	1,2 Dichloroethene	$1,2\text{-}C_2H_2Cl_2$
		Trichloroethene	C_2HCl_3

For the given temperature range in Table 8-5 the destruction efficiencies exceeded 99%. Similar product distributions were also reported by Tirey *et al.* (1990) and Taylor *et al.* (1991) for the oxidative pyrolysis of dichloromethane. These results share a similarity with the product distribution for the pyrolysis system been investigated, since at destruction efficiencies greater than 90% HCl is a major product and also carbon (present as CO and CO_2 in oxygen rich atmospheres). Unfortunately past researchers have not mentioned reaction products formed at lower destruction efficiencies specifically at the lower temperatures.

It is interesting to note that Frenklach (1986) only observed formation of carbon black at a temperature of 1500K in an oxidative atmosphere. It possible that the difference lies in the fact that Frenklach (1986) defines soot as being a lumped property meaning species that is detected by means of a helium-neon laser beam at a wavelength of 632.8.

Wen-Pin (1992) reported a relatively negligible effect of residence time on the destruction efficiency at a temperature of 600°C in an oxygen rich atmosphere (98 mol %). Thus it is apparent that increasing the residence time does not significantly improve the destruction efficiency for low temperatures in an oxygen abundant atmosphere.
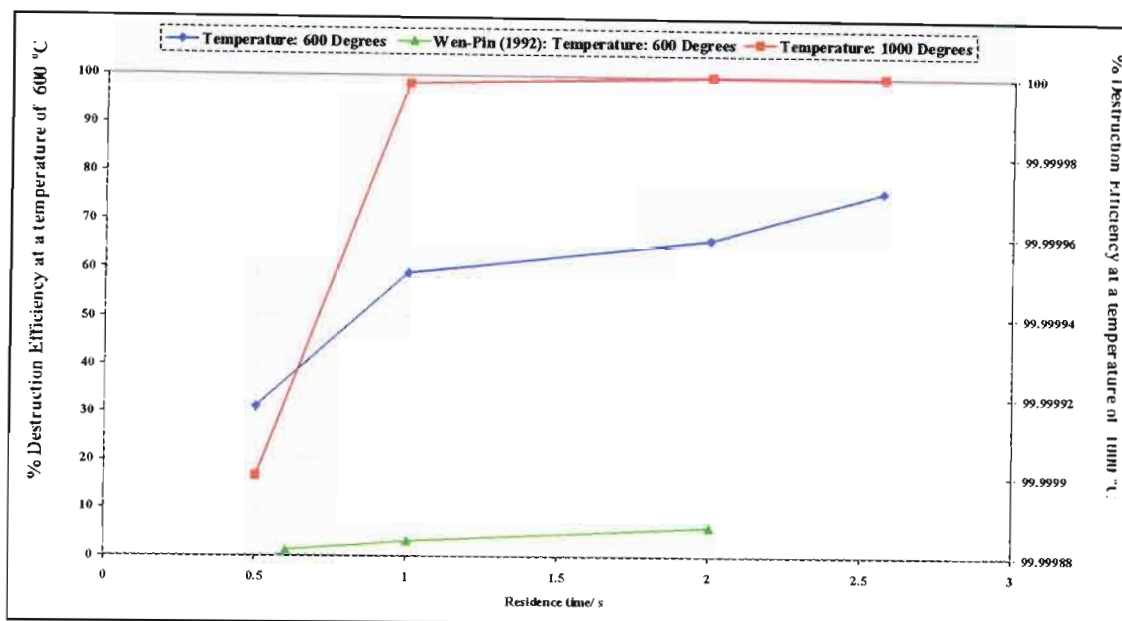
Figure 8-10: Effect of mean residence time on the destruction efficiency of dichloromethane at two different temperatures. Data collected for a constant reactant concentration of 27.6%.

This result is in contrast with the pyrolysis system where the residence times significantly affect the destruction. The improvement is much more apparent at the lower temperatures were destruction is low, whilst at the higher temperatures, where the destruction is significant; the effect of residence time is very subdued.

8.2 Pyrolysis of chlorobenzene

The transition from chlorinated aliphatics to aromatics is complicated thus it was approached with caution. Typically for aliphatics with a low chlorine to hydrogen ratio the general statement that they do not produce higher chlorinated derivatives can be made. However in aromatic systems this statement is not necessarily true, since most toxic chlorinated compounds come from reactions involving chlorinated aromatics. It seems that aromatics are more susceptible to recombination reactions than aliphatics.

8.2.2 Effect of process variables on destruction efficiencies and yields

In Section 8.1.2 an extensive general discussion was given on the main process variables namely reactor temperature and mean residence time. Therefore the introduction to these variables will not be considered in the subsequent discussion.

8.2.2.1 Initial experiments

The first experiment that was performed was at a temperature of 1000°C, 1.5s mean residence time and a feed chlorobenzene concentration of 26.4% (molar basis). A major cause for concern was the fact that as the run progressed; liquid droplets could be seen exiting the feed pipe in the reactor. The poor vaporization meant that liquid chlorobenzene was passing through the reaction zone; this was reflected in a poor destruction efficiency of 59%. It was uncertain what caused the poor vaporization since the external and internal feed lines were maintained at a temperature of 200°C, which was 70°C higher than the boiling point of chlorobenzene. Two actions were taken to solve this problem namely:

- Increase the respective feed line temperatures to 300°C.
- Decrease the feed stream concentration of chlorobenzene to 15% (molar basis).

The second experiment was performed using the new values stated above. Throughout the experiment no liquid could be seen leaving the internal feed pipe. This observation was encouraging as this meant that the feed mixture was homogenous when entering the reaction zone and could degrade as intended. The destruction efficiency for this run was calculated to be 98.24%. For the purpose of completeness the top of the reactor was stripped and inspected for liquids, none were observed.

From these two experiments it was clear that proper vaporization of the feed and hence maintaining a homogenous feed stream was critical in achieving high destruction efficiencies. For future experiments an upper limit of 15% for the feed concentration, and feed line temperatures of not less than 300°C were set as boundary conditions.

To study the effect of feed concentration at values lower than 15% would mean having to change the feed pump, since the present pump did not work well at low flowrates, thus it was decided to abandon investigating the effect of concentration. Rouzet (2001) evaluated the degradation of chlorobenzene at two different initial molar concentrations namely 0.1% and 0.59% for varying reactor temperature. The experiments at the different initial concentrations were conducted by Rouzet (2001) from 727°C to 1177°C. The data showed good similarity between the two destruction profiles. Unfortunately other researchers have not investigated the effect of higher reactant concentration. Therefore on the basis of Rouzet's (2001) results and the lack of information on the effects of initial feed concentration these effects on the destruction efficiency and product formation are assumed to be negligible for low initial concentrations.

8.2.2.2 Reactor Temperature

8.2.2.2 (a) Destruction Efficiencies

The effect of temperature on the chlorobenzene system was studied over a temperature range from 500°C to 1000°C. For the purpose of only investigating the effects of temperature the feed concentration and residence time were fixed at 15% and 2.0s respectively.

Table 8-6: Effect of temperature on the destruction efficiency of chlorobenzene. Data collected at a constant feed concentration of 0.15 and residence time 2.0s

Experiment	Temperature/ °C	% Destruction Efficiency
8.2a	500	10.56
*8.2a	500	11.97
8.2b	650	58.289
8.2c	800	94.959
*8.2c	800	93.561
7.2d	1000	99.992
7.2e	1100	100

* Indicates duplicate run

Experiments 8.2a and 8.2c were chosen arbitrarily to determine the reproducibility of the results. As seen in Table 8-6 the results obtained from these experiments showed good consistency. The detection limits of the GC/MS for chlorobenzene in hexane was calculated to be 1ppb. The data showed that chlorobenzene requires a reaction temperature of 1100°C and a residence time of 2.0s for it to be undetectable in the exit stream.
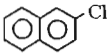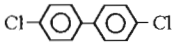
Chlorobenzene is a much more stable compound than dichloromethane, since it only initiates destruction at a temperature of 500°C. This result was expected since most aromatics show greater stability than aliphatics due to their compact structure, complex nature and most importantly their higher bond strengths.

8.2.2.2 (b) Product Yields

At the lower destruction efficiencies a number of toxic compounds were observed. The most commonly observed products are shown in Table 8-7. A number of chlorinated derivatives were also formed; this was due largely to the easy generation of the phenyl radical. At low temperatures hydrogen abstraction by the chlorine radical is poor thus making the chlorine

radical available for reactions with the highly reactive phenyl radical. This is the fastest pathway that leads to the formation of the observed chlorinated aromatics.

Table 8-7: Higher molecular weight compounds formed at low destruction efficiencies from chlorobenzene pyrolysis

Compound	Molecular Formula	Structure
Chlorobenzene	C_6H_5Cl	
1,2- Dichlorobenzene	$C_6H_4Cl_2$	
1,2,3-Trichlorobenzene	$C_6H_3Cl_3$	
Napthalene	$C_{10}H_8$	
Chloronapthalene	$C_{10}H_7Cl$	
Biphenyl	$C_{12}H_{10}$	
Dichlorobiphenyl	$C_{12}H_8Cl_2$	
Styrene	CH	

The major products observed at high destruction efficiencies were benzene, hydrogen chloride and solid carbon. The non-chlorinated minor products consisted of a number of alkanes and alkenes. One alkane that was consistently observed throughout the experiments was octane. The only chlorinated compound present, at these high destruction efficiencies, was dichlorobenzene. The lack of chlorinated products is expected since the ratio of hydrogen to chlorine is 5 on an atomic basis, which makes chlorine abstraction by hydrogen feasible. The presence of dichlorobenzene validated our initial statement that in aromatic systems a high H:Cl ratio does not necessarily guarantee the absence of higher chlorinated derivatives from the reaction.

It is evident that temperature plays an important role in determining the destruction efficiencies which in turn affects the major products observed. From Figure 8-11 it is apparent that carbon formation is not important below 800°C but rises up to 50% at 1100°C. The formation of carbon and the respective yields are consistent with the results stated by Ritter (1990) since he reported a yield of 30% at 1010°C in the absence of a hydrogen donor.
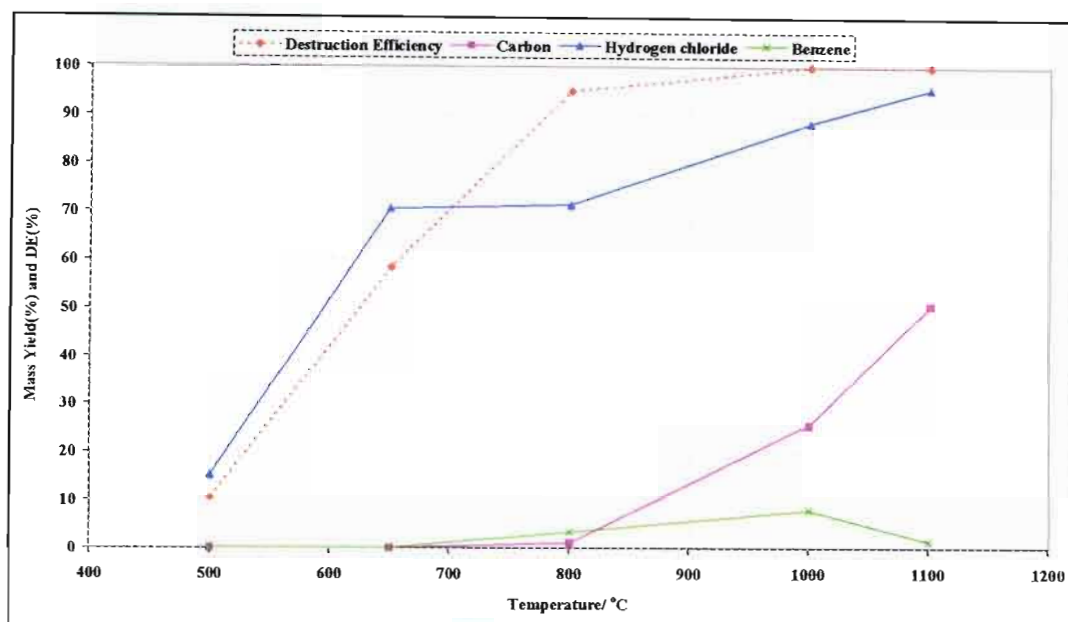
Figure 8-11: Effect of temperature on the major products formed from the destruction of chlorobenzene at a mean residence time of 2.0s.

The conversion of chlorine to hydrogen chloride varies significantly with temperature but it peaks at a value of 95% at 1100°C and thereafter levels out. Most researchers have reported hydrogen chloride yields between 80 to 99%. It is interesting to note that the formation of benzene reached a maximum at 1000°C. Beyond this point benzene yields decreased and solid carbon yields started to increase.

The product distribution observed at high destruction efficiencies is similar to that of Rouzet *et al.* (2001). However two major products that were not observed in the pyrolysis system were molecular hydrogen and methane. The lack of detection of these compounds can be attributed to the method used to trap reaction products, since it does not work particularly well for volatile compounds.

Cullis (1958), Graham (1986), Ritter (1990) and Rouzet (2001) have reported trace quantities of a number of polychlorobiphenyls (e.g $C_{12}H_9Cl$, $C_{12}H_8Cl_2$) throughout their

respective experiments. In the pyrolysis system these compounds were not present at high destruction efficiencies only at the lower destruction efficiencies.

8.2.2.3 Effect of residence time

8.2.2.3 (a) Destruction Efficiencies
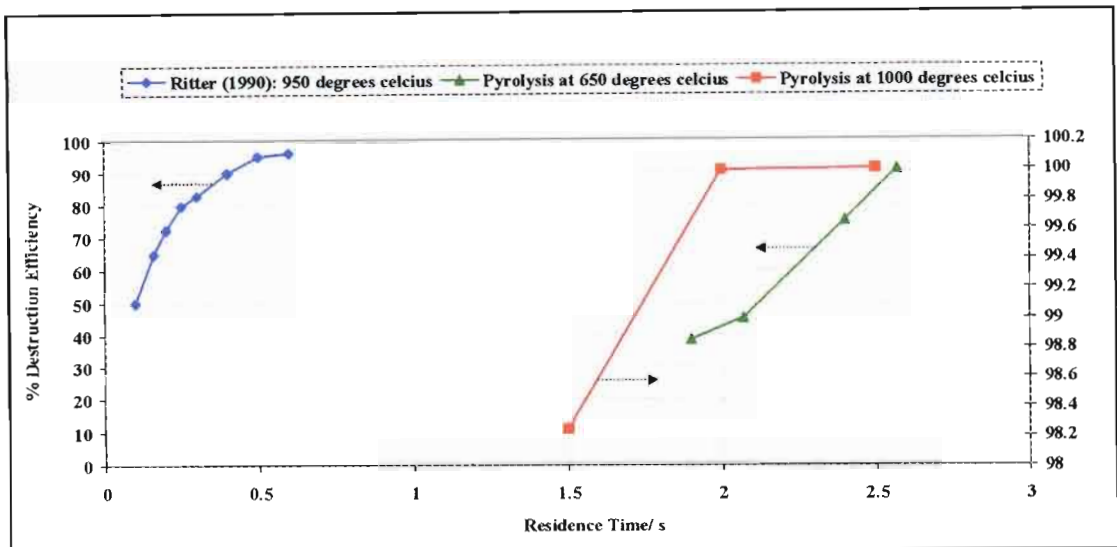
Figure 8-12: Effect of mean residence time on destruction efficiency of chlorobenzene.

Figure 8-12 illustrates the effect of residence time at two temperatures namely 650°C and 1000°C. At a temperature of 650°C the residence time clearly has a significant influence over the destruction of chlorobenzene. Increasing the residence time by a factor of 1.7 showed a corresponding increase in the destruction efficiency by 50%. At a temperature of 1000°C the six nines destruction criteria of chlorobenzene was not met, only 99.99% achieved, however by increasing the residence from 2.0s to 2.57s a subsequent increase in the destruction efficiency to 100% was observed.

Although there are a great number of papers on the degradation of chlorobenzene, there is a lack of data on the effects of residence time. To our knowledge only Ritter (1990) has studied the effect of mean residence time on destruction efficiencies. Ritter's (1990) data shown in Figure 8-12 is for an initial chlorobenzene concentration of 0.37% (molar), whilst the remainder of the feed was made-up of hydrogen. Even at these low concentrations residence time has a distinctive effect on the degradation of chlorobenzene.

8.2.2.3 (b) Product Yields
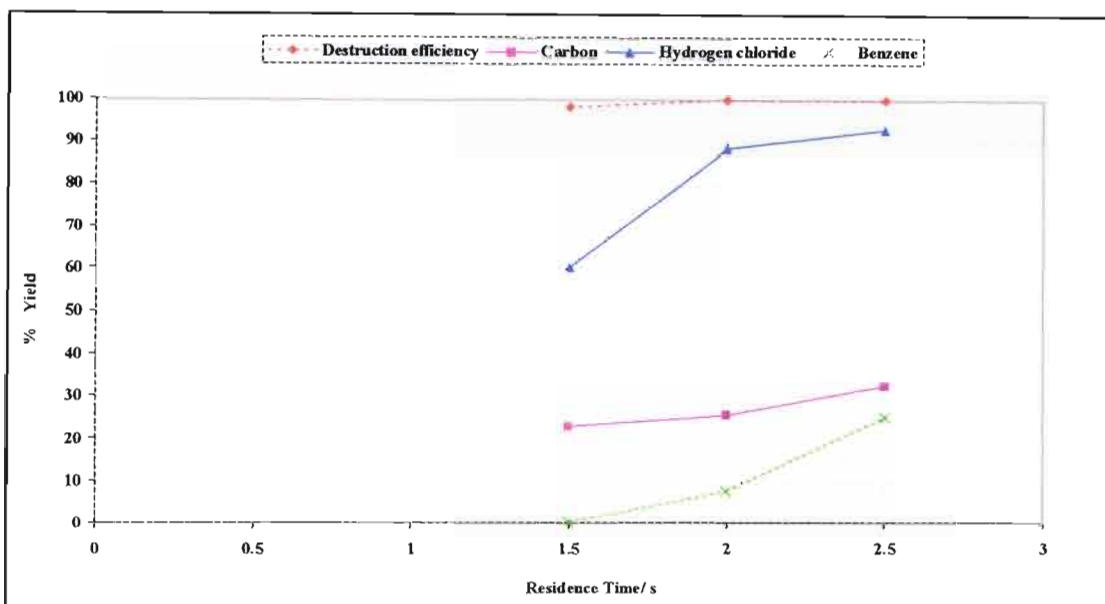
Figure 8-13: Effect of mean residence time on the major products obtained from the destruction of chlorobenzene at a temperature of 1000°C.

At 1000°C the mean residence time affects the benzene and hydrogen chloride yields considerably. Increasing the residence time produces a corresponding increase in the hydrogen chloride and benzene yields. However the carbon yields remains practically constant with only a 9% increase over the time range studied.

Of particular interest is the 17% increase in benzene yields that was observed when the residence time was increased from 2.0s to 2.5s.

8.2.3 Reaction mechanism

8.2.3.1 Basic mechanism

Due to the importance of chlorobenzene extensive research has been done by the research community into determining possible reaction mechanisms. These mechanisms are specific to the reaction conditions and hence the observed product distribution. Therefore although they have been well documented the correct reaction pathways had to be identified for the pyrolysis system.

The general consensus is that chlorobenzene degradation initiates through reactions (8-24) to (8-28) (Rouzet, 2001; Kiefer, 1985; and Cullis, 1958). The first step of the mechanism is the cleavage of C-Cl bond to yield phenyl. The C-Cl bond has a bond energy of 397kJl/mol whilst the C-H bond is 477 kJ/mol (Kerr, 1983) thus making this first step feasible. The displacement of chlorine by hydrogen atoms provides a very simple means of dechlorination.

$$C_6H_5Cl \qquad\qquad = \quad C_6H_5\cdot \quad + \quad Cl\cdot \qquad (8\text{-}24)$$

$$C_6H_5Cl \qquad\qquad = \quad C_6H_4Cl\cdot \quad + \quad H\cdot \qquad (8\text{-}25)$$

$$C_6H_5Cl \quad + \quad H\cdot \quad = \quad C_6H_5\cdot \quad + \quad HCl \qquad (8\text{-}26)$$

$$C_6H_5Cl \quad + \quad H\cdot \quad = \quad C_6H_4Cl\cdot \quad + \quad H_2 \qquad (8\text{-}27)$$

$$C_6H_5Cl \quad + \quad H\cdot \quad = \quad C_6H_6 \quad + \quad Cl\cdot \qquad (8\text{-}28)$$
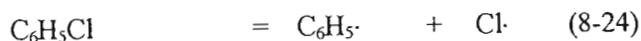
The feasibility of reaction (8-28) was demonstrated by Ritter (1990) by calculating the potential energies involved (Figure 8-14).
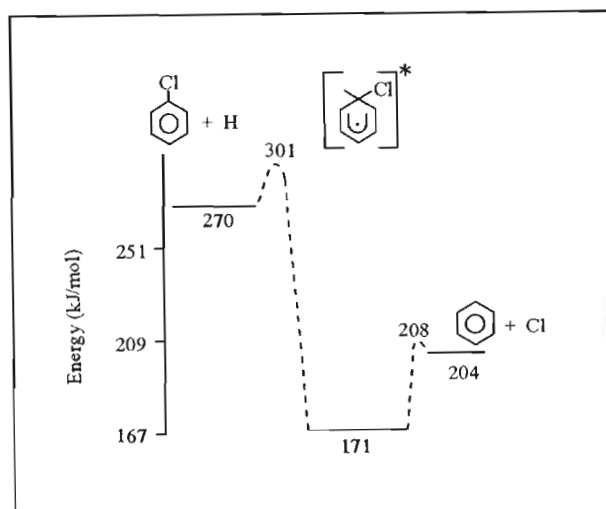
Figure 8-14: Potential energy diagram for addition of hydrogen to chlorobenzene (Ritter, 1990)

In Figure 8-14 the addition of the hydrogen atom to the chlorine carbon in chlorobenzene forms an energized complex and results in a rapid dissociation of the adduct to benzene plus chlorine. This scheme represents the lowest energy exit channel. Reactions (8-26) and (8-28) are believed to be a major pathway for the hydrodechlorination of chlorobenzene to form benzene and hydrogen chloride at high destruction efficiencies.

As mentioned earlier reactions (8-24) through (8-28) are widely accepted as the norm for the initial steps in the chlorobenzene destruction, following which a number of different pathways can be followed. Ritter (1990) suggested that the formation of benzene can either occur through reaction (8-28) or via reaction (8-29). The latter reaction seems to be more

feasible since there are a large number of highly reactive phenyl radicals present during the degradation.

$$C_6H_5\cdot + H\cdot = C_6H_6 \qquad\qquad (8\text{-}29)$$

The presence of trace quantities of dichlorobenzene at high temperatures can explained through reaction (8-30). This reaction is a recombination reaction between two highly reactive radicals namely chorine and chlorophenyl.

$$C_6H_4Cl\cdot + Cl\cdot = C_6H_4Cl_2 \qquad\qquad (8\text{-}30)$$
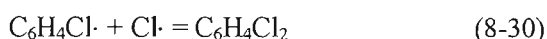
Earlier it was mentioned that the benzene yields reached a maximum at 1000°C and then began to decrease whilst a corresponding increase in the carbon and acetylene yields was observed. This means that there was either cleavage of the phenyl ring to give rise to these two species instead of benzene or dehydrogenation of an unstable benzene molecule (at these temperatures) to form a phenyl radical with subsequent ring opening.

$$C_6H_5\cdot = C_4H_3\cdot + C_2H_2 \qquad\qquad (8\text{-}31)$$
$$C_6H_5\cdot = C_4H_2 + C_2H_3\cdot \qquad\qquad (8\text{-}32)$$
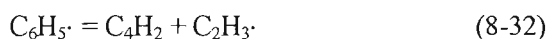
The final steps for the above sequence have been extracted from Kiefer's (1985) mechanism. These are a dehydrogenation reaction to yield solid carbon.

$$C_4H_3\cdot + M = C_4H_2 + H\cdot + M \qquad\qquad (8\text{-}33)$$
$$C_4H_2 \quad = C_4H\cdot + H\cdot \qquad\qquad (8\text{-}34)$$
$$C_4H\cdot \quad = C_4 + H\cdot \qquad\qquad (8\text{-}35)$$
$$C_4 \quad = C\ (\text{solid}) \qquad\qquad (8\text{-}36)$$
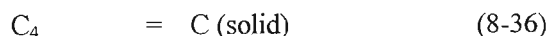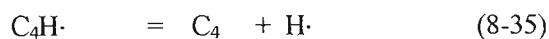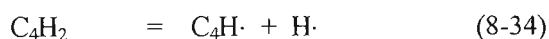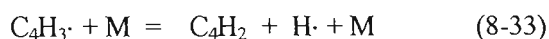
8.2.3.2 Formation of higher aromatics at low temperatures

The pathway to the aromatic products can occur through a number of different routes. Fields *et al.* (1966) stated that chloronaphthalene can be formed through the following set of reactions.

$$C_6H_5Cl \qquad = C_6H_4 + HCl \qquad\qquad (8\text{-}37)\ \ \text{HCl elimination}$$
$$C_6H_4 + C_6H_5Cl = C_{12}H_9Cl \qquad\qquad (8\text{-}38)\ \ \text{Chlorobenzene addition}$$
$$C_{12}H_9Cl \qquad = C_{10}H_7Cl + C_2H_2 \qquad\qquad (8\text{-}39)\ \ \text{Acetylene elimination}$$
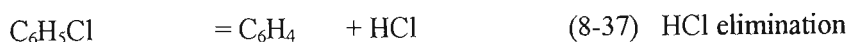
If this mechanism was in operation then acetylene would be observed or increased carbon formation, since the acetylene carbon theory states that carbon particles are formed from acetylene by simultaneous polymerization and dehydrogenation (Section 2.3.4). However the

However certain modifications had to be made to the equation contained in Femlab to allow for variations in the physical properties with temperature and pressure. For example in the momentum balance expression, the shear rate is included inside of the divergence, which is necessary to treat variations in viscosity. However the continuity equation does not account for variations in density. Therefore the variation in density was introduced in the F term. It should be noted that in the energy balance, radiation was ignored and only convection and conduction were used as the modes of heat transfer. Radiation was ignored since we are working on the basis that radiation would not affect argon.

Since Femlab is a computation fluid package it needs a schematic of the path that the gas follows through the reactor. Thus the first step was to construct the flow path of the gas through the reactor system (See Figure 4-2). The system was simplified by taking advantage of the symmetry of the reactor. Suitable boundary conditions were applied to each section of the reactor.
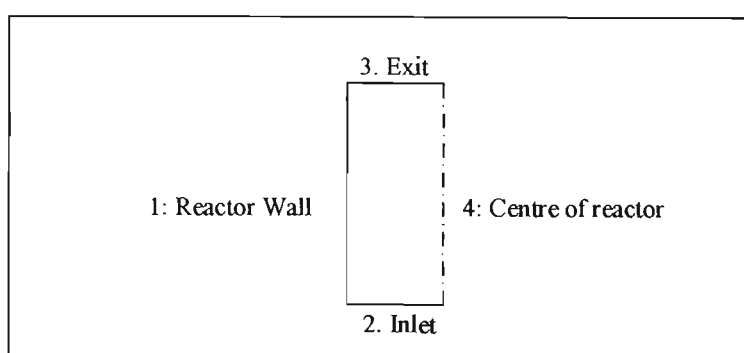
Figure A-1: Showing a simplified schematic of the reactor diagram used in Femlab simulations

Table A-1: Showing the boundary conditions used in the Femlab model of the pyrolysis reactor

Balance	Boundary Conditions			
	Boundary 1	Boundary 2	Boundary 3	Boundary 4
Momentum	$(u,v)=0$	$u=o,\ v=vo$	$p=po$	$n.(u,v)=0$
Mass	$Ni.n=0$	$c=co$	$Ni.n=$convective flux	$Ni.n=0$
Energy	$T=Twall$	$T=To$	$q.n=$convective flux	$q.n=0$

Appendix A: Femlab Modelling

A1) Introduction

Femlab is a powerful interactive environment that is used for modelling and solving scientific as well as engineering problems which are described by partial differential equations (PDEs). It contains a comprehensive graphical user interface, which covers all aspects of the modelling process: computer aided drawing, specification of material data, boundary conditions, assembly and solution of the resulting finite element model and finally post processing and visualization of the solution.

The PDE describing the problem is approximated with a problem containing a finite number of unknown parameters, the so-called discretization of the original problem. This involves introducing finite elements, or shape functions that describe the possible forms of the approximate solution. The starting point for the finite element method is a mesh, which is a partition of the geometry into small units of a simple shape. For two dimensional problems the subdomains are partitioned into triangles, or mesh elements.

A2) Assembly of the problem in Femlab

The basis of modelling the transport reaction process in the pyrolysis reactor rests upon 3 fundamental balances namely mass, heat and momentum balances. These balances, in combination with the initial and boundary conditions, define the mathematical models that describe the system of interest.

Momentum Balance: $\rho \dfrac{\partial u}{\partial t} - \nabla.\eta \left(\nabla u + \left(\nabla u \right)^{T} \right) + \rho \left(u.\nabla \right) u + \nabla p = F$ ......(A-1)

Energy Balance: $\rho C_{p} \dfrac{\partial T}{\partial t} + \nabla.\left(-k\nabla T + \rho C_{p} T u \right) = Q$ ......(A-2)

Mass Balance: $\dfrac{\partial c_{i}}{\partial t} + \nabla.\left(-D_{i}\nabla c_{i} + c_{i}u \right) = R_{i}$ ......(A-3)

These three balances were selected in Femlab as:
- Navier Stokes equation to describe the momentum balance
- Convection and conduction for the energy balance
- Convection and diffusion for the mass balance

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- Reactor sleeve / catalyst basket
- Graphite Reactor
- Catalyst
- Perforated end
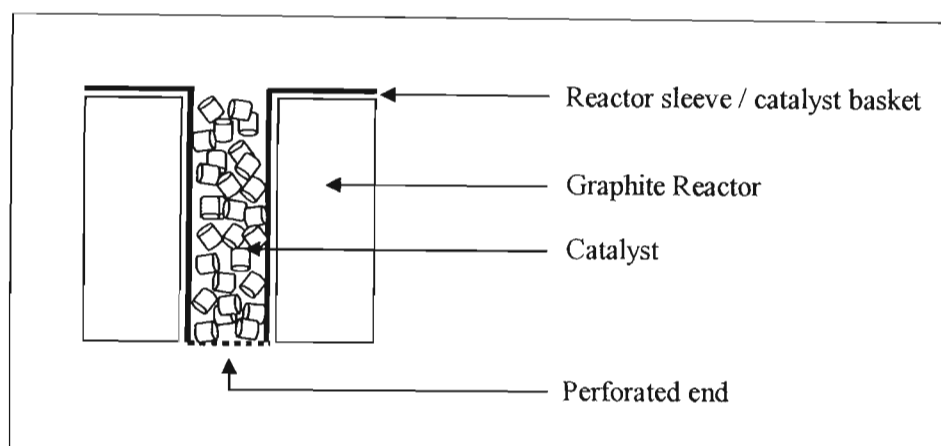
Figure 12-1: Design modification for the addition of a catalyst basket to the pyrolysis reactor

12.6 Future Work

➢ The results from this project have given a strong indication that the project is ready for the next phase namely construction of a larger more sophisticated pilot scale plant. The plant should be capable of destroying chlorinated wastes with a minimum operating capacity of 1.0kg/hr continuously. This would bring the project on par with the regulations stipulated by the UNEP.

➢ Typically destruction technologies are not restricted to only one type of waste. This implies that they are capable of destroying a range of wastes but are setup and optimized depending on the composition of the feed stream. With this in mind it is clear that the pyrolysis of other waste systems e.g. sulphur or fluorinated wastes should be investigated.

➢ During this project only pure components have been pyrolysed. There is evidence from Graham (1986) and Taylor (1988) that the destruction of a mixture of chlorinated wastes could possibly be more feasible in terms of higher destruction efficiencies at lower reactor temperatures. Therefore the pyrolysis of a mixture of chlorinated hydrocarbons should be investigated however a hydrogen to chlorine ratio, preferentially, greater than one should be maintained.

➢ The synthesis capabilities of the equipment have only been touched on during this project. With the implementation of a more sophisticated sampling system and possibly a catalyst basket a number of synthesis reactions can be explored.

12.4 Implementation of a better sampling system

In both the destruction experiments and particularly the synthesis experiments the condensable gases, which consisted of C_1-C_4 hydrocarbons and also hydrogen, were undetectable due to the limitations imposed by the solvent extraction method used. In order to allow for a comprehensive assessment of all the reaction products formed it is recommended that analysis of the product stream be performed online, preferably by means of a GC/MS. In addition to allowing for a complete analysis of the product stream online measurements permit for detailed kinetic studies.

It is recognized that online GC/MS analysis is expensive. However preliminary inquiries has revealed that a GC equipped with three columns namely Duropak, Poropak Q and Carbosphere will perform the same function at a fraction of the cost. The Duropak column detects the C_1-C_4 hydrocarbons whilst isomers are separated and detected in the Poropak Q column. The Carbosphere column allows for the detection of methane and also any oxygenated species e.g. carbon dioxide.

12.5 Implementation of a catalyst basket

The design of the reactor is compact and versatile. It is this versatility that allows for a number of systems to be pyrolysed. In order to extend the range of possible reactions, a catalyst basket should be implemented, since there has been an enormous amount of interest in catalytic reactions this could possibly open a vast amount of opportunities to be explored.

The equipment can be easily modified for the insertion of a catalyst basket in the reaction tube. A possible design modification has been suggested in Figure 11-1. Due to the reaction zone been tubular a sleeve can easily be inserted, which can then be filled with a catalyst.

When choosing the reactor sleeve material the following factors must be kept in mind:

➤ the material must be able to withstand high temperatures
➤ good heat transfer between the walls and the sleeve to the reaction zone
➤ similar heating profile to the graphite reactor

However it is unclear what the effect of induction heating will have on the catalyst itself.

Chapter 12: Recommendations

The following recommendations should allow for an increased fundamental understanding of core concepts and reaction chemistry as well enhance the commercial viability of the technology.

12.1 Thermal transparency

The calculations concerning the thermal transparency of argon are relatively crude. Therefore in order to determine the true radiation properties of argon further experimental work needs to be performed. The basic experimental technique used in measuring gas radiation properties is sighting with a radiometer through a length of gas into a cavity or other reference target. Detailed reviews of experimental radiation measurements are given by Hottel (1967).

12.2 Design of a carbon removal system

Depending on the operating conditions large amounts of carbon black were formed during the destruction. Although the current carbon trapping system has proven to be effective the inability of the system to handle large amounts of carbon has hampered long runs. A suitable design is required that is capable of trapping and removing fine carbon particles as they are formed. An added advantage of solving this carbon removal problem is the operation of the plant on a continuous basis.

12.3 Temperature measurements

Temperature measurements were limited only to the reactor wall thus leaving uncertainty in the temperature of the bulk gas. These limitations are a consequence of the reactor design and also the fact that radiation is concentrated in the core reaction zone which causes severe disturbances to electrical equipment located in the vicinity. Therefore in order to provide confidence in the temperature measurements the following areas should be investigated:

- ➢ new reactor design
- ➢ better thermocouple shielding
- ➢ more advanced equipment for temperature measurement

Dichloromethane and chlorobenzene were chosen as model compounds due to a number of reasons outlined in Chapter 1. Much of the previous work was performed in mixtures or under oxidative atmospheres. Thus this study has presented a comprehensive assessment of the pyrolysis of representative aliphatic and aromatic compounds in a purely pyrolytic environment. The pyrolysis of these two model chlorinated hydrocarbons has been studied under varying temperature and residence time. The purpose of these experiments was to construct the mechanism of the pyrolytic reactions and to determine suitable operating conditions for the production of desirable products whilst maintaining a minimum destruction efficiency of 99.9999%.

It was observed that dichloromethane was undetectable in the product gases at a temperature of 1000°C and residence time of 2.0s. Chlorobenzene shows much higher stability and required a reactor temperature of 1100°C and a residence time of 2.57s to be completely undetectable. The common major products observed at high destruction efficiencies consisted of solid carbon and hydrogen chloride. In addition to these compounds chlorobenzene destruction yielded benzene and some incondensable gases. It has been proven that although it is important to maintain a hydrogen to chlorine ratio of one if the destruction is low then the product stream will be dominated by toxic byproducts.

To our knowledge no other study to date has provided such a complete analysis of the carbon formed from the destruction of chlorinated wastes. The analysis of these carbon samples has provided valuable information on the types of reactions taking place and in addition the effect of temperature and mean residence time on the carbon morphology and composition.

Attempts have been made at determining the potential applicability of the pyrolysis technology as a means of synthesizing valuable low molecular weight olefins. These experiments involving hexane were inconclusive due to the lack of detection of the reaction products. Therefore the question whether this technology can be used for synthesis remains unanswered. The research into synthesis warrants further investigation purely on the basis that the process might provide a commercial route to products that are valuable to industry.

Chapter 11: Conclusions

A pyrolysis system that incorporates induction as a means of heating has been designed and demonstrated for the purpose of destroying chlorinated wastes. Coupled with the demonstration of the pilot plant was the understanding of the principles behind the technology.

The fundamental task of proving that argon is a thermally transparent medium was undertaken. It has been successfully shown through calculations that energy of the photons at a temperature of 1000°C does not meet the minimum energy required by argon to be affected. The two calculations are only approximate methods to determine the energy of the photons however there is sufficient confidence in the results.

Another aspect linked with the thermal transparency of argon was the supposed observation that argon was at a temperature less than 50°C after leaving a reaction zone at 1000°C. Earlier studies (Pillay, 2001) have claimed that since argon is thermally transparent it shows only moderate heating. A computational fluid dynamic model of the flow of argon through the system combined with extensive experimental work has lead to contradictory conclusions. In the model radiation was not included as means of heat transfer but convection and conduction were taken into account. The results from the model clearly demonstrated that argon heated up in the reactor within a centimeter of entering the reaction zone at a 1000°C and then rapidly cooled down within a centimeter after leaving. This provided the basis for additional experiments which confirmed that argon was heating up within the reaction zone.

This study has provided a comprehensive investigation into the pyrolysis of dichloromethane and chlorobenzene with the aims of:

> ➤ demonstrating the effectiveness and competitiveness of the system in destroying chlorinated wastes
> ➤ provide a more elementary understanding of chlorinated pyrolysis systems.

The secondary objective of this work was to establish an experimental technique which provided reliable data on the respective pyrolysis reactions. In addition this has lead to increased confidence in the accuracy of the fundamental kinetic parameters. Thus the feasibility of obtaining accurate data for the pyrolysis of chlorinated hydrocarbons under well-defined and consistent experimental conditions has been adequately demonstrated.

typical dissociation energies between 381-427 kJ/mol for the primary, secondary and tertiary positions (Layokun, 1979).

$n\text{-}C_6H_{14} \rightleftharpoons \quad \cdot C_2H_5 + \cdot C_4H_9$ (10-1) Cleavage at the primary carbon

$n\text{-}C_6H_{14} \rightleftharpoons \quad \cdot CH_3 \ + \cdot C_5H_{11}$ (10-2) Cleavage at the secondary carbon

$n\text{-}C_6H_{14} \rightleftharpoons \quad \cdot 2C_3H_7$ (10-3) Cleavage at the tertiary carbon

$n\text{-}C_6H_{14} \rightleftharpoons \quad \cdot C_6H_{13} + \cdot H$

$\cdot C_4H_9 \quad \rightleftharpoons \quad C_2H_4 + \cdot C_2H_5$ (10-4)

$\cdot C_5H_{11} \quad \rightleftharpoons \quad C_2H_4 + \cdot C_3H_7$ (10-5)

$\cdot C_3H_7 \quad \rightleftharpoons \quad C_2H_4 + \cdot CH_3$ (10-6)
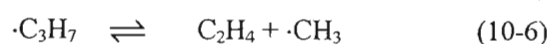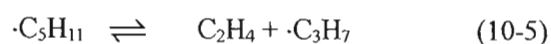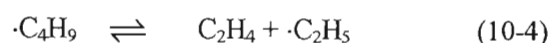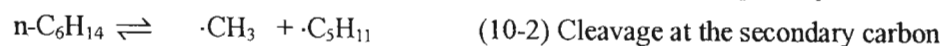
The second stage encompasses reactions which allow the products from reactions (10-3) to (10-6) to undergo the following possible pathways:

- reactions involving further pyrolysis of the olefins
- hydrogenation and dehydrogenation reactions where paraffins, diolefins and acetylenes are produced
- condensation reactions wherein smaller fragment combine to produce large stable structures such as heptane, octane or aromatics.

These pathways can allow for a number of reaction products to form. Due to the uncertainty in the products obtained the mechanism will not developed further but it is clear that the species formed from these initial steps allow for products from the following reactions:

- cracking
- polymerisation
- isomerisation
- ring formation

10.4 Hexene pyrolysis

Due to the poor trapping of reaction products from the pyrolysis of hexane it was decided to abandon future experiments using hexene, since most authors have reported similar lower molecular weight product distributions between alkanes and alkenes with lower than 10 carbons.

However the carbon found on the reactor walls showed a completely different surface structure. As seen in Figure 10-1 the surface is flat and flaky with spherical globules on top.

The structure of the carbon formed at 1000°C in the catchpot section was relatively unchanged from the carbon formed at 600°C. It is interesting that the reactor and ceramic carbon formed at 1000°C showed no resemblance to their counterparts at 600°C however showed a striking similarity to the carbon formed from the chlorobenzene runs.
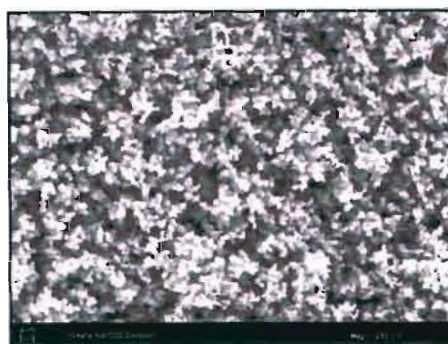
Figure 10-2: Micrograph of the reactor carbon formed from the pyrolysis of hexane at 1000°C.

The carbon surface illustrated in Figure 10-2 is made up of small polymeric globules sticking together in a complex network. One might postulate that the different structure may be indicative of another route to carbon formation other than cracking reactions to form elemental carbon. It is likely that the carbon shown in Figure 10-2 was formed through a gas phase mechanism involving species like C_2H and C_3H_2.

10.3.3. Reaction Mechanism

Due to the lack of information on the major and minor products produced from the pyrolysis of hexane, formulation of a concise reaction mechanism was impossible. Therefore in this section an attempt only to ascertain the most logical and probable pathways for the observed products has been made.

In general most researchers consider the pyrolysis of hydrocarbons occurring in two stages. The first stage is designated as the primary reactions wherein the reactants are decomposed through the free radical chain mechanisms into the principal primary products. Initiation may occur by cleavage of either a C-C bond or a C-H bond. The strengths of C-C bonds for saturated hydrocarbons up to octane lie in the range 325-350 kJ/mol, whilst C-H bonds have

Earlier studies on hydrocarbon pyrolysis (Kershenbaum (1986), Pramanik (1985), Layokun (1979), Doue (1969)) have also reported observing lower molecular weight products for temperatures less than 650°C. The gaseous products that are consistently mentioned throughout literature are hydrogen, methane and propane. These products were not observed in this study due to the inability of the collection system to adequately trap these volatile compounds.

At 1000°C nearly the same products were observed but the areas were smaller. Since the residence time was kept constant for both temperatures it is clear that the decrease in the areas can be attributed to more severe cracking reactions to yield two primary gas phase products namely methane and hydrogen.

It is clear that the main products formed from the pyrolysis reaction are non-condensable gases, since other products observed in the scrubbers were only in trace amounts and could not account for the total product distribution.

10.3.2 Solid Products

The yield of carbon from the parent at 600°C was approximately 10% for both residence times of 2.0s and 3.0s. At a temperature of 1000°C the carbon yield increased to 50%. This trend was expected since the higher temperature would promote cracking reactions to yield elemental carbon. This viewpoint is substantiated by the results of Cozzani (1997), who found decreasing hydrogen content in the carbon formed, from the pyrolysis of polyethylene, as the temperature was increased from 500°C to 800°C.

98% of the solid carbon was trapped in the catchpot whilst the remaining 2% was distributed between the ceramic and the reactor walls. The catchpot and ceramic carbon formed at a temperature of 600°C showed little difference in the morphology.

| Ceramic | Reactor |
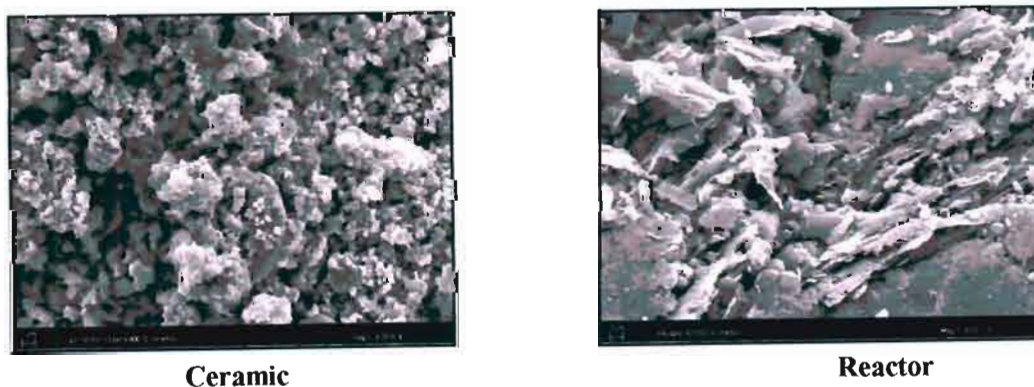
Figure 10-1: Micrograph of the respective carbons formed from the pyrolysis of hexane at 600°C.

10.2 Experiments

The feed was a homogenous gas phase with argon as the carrier gas with no supplementary additives. The experiments were performed at two temperatures and two residence times for each chemical pyrolysed. The reason for the lack of extensive testing over a wide range of experimental conditions was primarily due to time constraints. Hence the experiments were designed only to determine the applicability of the technology in terms of synthesised products. It should be duly noted that no calibrations were undertaken for the reaction products due to:

a) time constraints
b) large number of products
c) no outstanding major product observed in the chromatographs

It was decided to start testing the compounds with low temperatures and low residence times, and then moving on to high temperatures at low residence times and finally high temperature with high residence times. This sequence allowed for the gradual and safe acquisition of the characteristics of the system under varying process conditions.

For the previous destruction experiments hexane was used as the solvent to trap reaction products in the scrubbers. However for these synthesis experiments hexane was one of the compounds used and there was a possibility that hexane could be formed from hexene. Lower molecular weight products would readily be formed from these experiments thus the best option was to eliminate the scrubbers and take gas samples. However this procedure was not adopted since the GC/MS was continually been used by other researchers and secondly the argon peak overshadowed the smaller peaks thus making their detection impossible. After taking these points into consideration and consulting literature it was decided that cyclohexane would be used as the scrubber solvent.

10.3 Hexane Pyrolysis

10.3.1 Gaseous products

The products that were observed at a temperature of 600°C and a residence times of 2.0s and 3.0s were primarily lower molecular weight alkanes and alkenes namely pentane, pentene, hexene, heptane, octane and 2-methylpentane. All of the reaction products showed very small peak areas. The only aromatic that was observed was 1,3 cyclopentadiene. The influence of the respective residence times at these lower temperatures did not have a significant affect on the product distribution, as observed by the lack of change in the peak areas on the chromatographs.

Chapter 10: Hydrocarbon Pyrolysis

Any high temperature reactor has the potential for many possible reactions. To explore the possibility of using the pyrolysis reactor for reactions other than destruction namely synthesis reactions, was attractive. Such a reactor that can operate at both ends of the reaction spectrum is particularly valuable in terms of profitability and also marketability. This was sufficient motivation to add this synthesis element to the scope of the current destruction project.

During this chapter a discussion will be presented on the results that were used to explore the opportunity for using the designed system as a means of synthesizing valuable chemicals.

10.1 Feed stock used for experiments

In chapter 5 the physical limitations of the equipment as well as the capabilities of the equipment were described. These criteria were the decisive factors used to determine the chemical systems to be tested in the pyrolysis environment. In addition to these criteria was the important aspect of safety.

After consulting literature it was decided that simple chemicals like hexane and hexene would be reasonable starting materials. They were chosen since they conformed adequately to all the criteria stipulated:

- Have low boiling points
- Contain no oxygen
- Minimal possibility of forming dangerous aromatics
- Low explosive characteristics

In addition there is a growing interest in the dehydrogenation of light alkanes due to the increase in the demand for light alkenes for the production of polymers and gasoline additives.

9.4 Model results

The plot of the predicted and experimental data points are shown in Appendix E.

9.4.1 Dichloromethane

The model fitted the data very well for the dichloromethane system. The rate constant at the reference temperature of 600°C was $0.887s^{-1}$. The final regressed value of the activation energy was 29272 J/mol.

9.4.2 Chlorobenzene

The calculation of the rate constant at the reference temperature of 650°C was poor. The model predicted the conversion well at a mean residence of 2.0s and thereafter over predicted the conversion by approximately 5% at a mean residence time of 2.57s. However the prediction of the activation energy was in direct contrast and showed an exceptional fit to the experimental conversion. The final value of the reference rate constant was $0.5191s^{-1}$ at a temperature of 650°C whilst the activation energy was 82341 J/mol.

Input Experimental data: Temperatures, mean residence times, conversions
Initial Guess: k_o and E_a

Use the initial k_o at low experimental conversions with varying residence times, to calculate the conversion by solving equations (9-4) and (9-8).

Use k_o at T_o as reference values to calculate k at specific temperatures using equations (9-4) and (9-12). In equation (9-12) the initial value for Ea was used.

Substitute new values for k_o and E_a

Use the different k values determined from above to calculate the conversion for different temperatures using equations (9-4) and (9-8)

Use the least squares method to calculate the difference between the experimental and predicted conversions.

Check if the sum of the errors meets set tolerance

No

Yes

Output the respective rate constants and activation energy

Figure 9-3: Flow chart for determining the rate constants and activation energies by fitting the respective model to experimental data

(9-11) by k also defined by equation (9-11). Therefore by setting a common reference rate constant (k_o) at the corresponding reference temperature (T_o) in equation (9-12) we are able to determine other rate constants.

$$k = k_o \exp\left[\frac{E_a}{R}\left(\frac{1}{T_o} - \frac{1}{T}\right)\right]$$ (9-12)

The flow chart in Figure 9-3 clearly depicts the way in which the model was constructed and solved. The model was solved using Matlab. The complete Matlab code for the model is shown in Appendix D.

regime radial variations in the concentration also occur in addition to axial variations. In the pyrolysis reactor a continuous homogenous gas phase reaction occurs.

9.3.2 Selection of mixing model

It was decided that maximum mixedness model would be more appropriate as it allowed for interactions between the molecules which was consistent with the reactor description. However since a first order reaction was initially assumed for the system this was a special case.

Were the reaction order is one Zwietering (1959) has proven mathematically that the maximum mixedness model reduces to the segregation model. This occurs because the rate of change of conversion for a first order reaction does not depend on the concentration of the reacting species hence the independence of the type of mixing. This result was convenient as it meant that the simpler segregation model could be solved for the conversion.

9.3.3 Model construction and solving

The data obtained from the pyrolysis experiments were:

> ➤ conversions versus residence times at a fixed temperature where conversion was low
> ➤ conversion versus reactor temperature at a fixed residence time

Many researchers have successfully used a first order rate law to interpret their data, similarly a reaction order of one was chosen.

$$-r_a = k\ C_a \qquad (9\text{-}10)$$

It is a well known fact that raising the temperature increases the reaction rate. Quantitatively this relationship between the temperature and the rate at which a reaction proceeds is determined by equation (9-11). This equation is called the Arrhenius equation.

$$k = A\exp\left(\frac{-E_a}{RT}\right) \qquad (9\text{-}11) \qquad \text{where } R = 8.134 \text{ J/mol.K (gas constant)}$$
$$A = \text{Frequency factor}$$
$$T = \text{Absolute temperature in kelvin}$$

The Arrhenius equation was modified to allow for the calculation of the rate constant at different temperatures. Equation (9-12) is easily obtained by dividing k, defined by equation
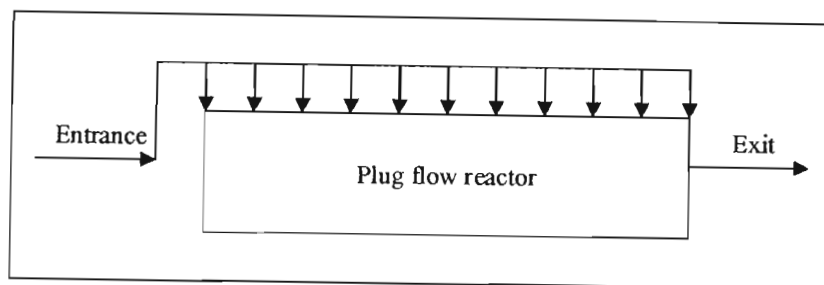
Figure 9-2: Pictorial representation of Zwietering's (1959) maximum mixedness model

In Figure 9-2 the feed streams enter through side entrances and instantaneously mixes radially with the main flow to satisfy the residence time distribution. Zwietering (1959) has provided a detailed derivation of the maximum mixedness model. The final mathematical form of the model is given by equation (9-9).

Maximum Mixedness Model: $\dfrac{dX}{dt} = \dfrac{r_A}{C_{Ao}} + \dfrac{E(t)}{1 - F(t)}(X)$ (9-9)

9.3 Modelling the system

The primary aim was to find a model to fit the data obtained from the pyrolysis experiments. By a fitting a suitable model that is representative of actual operating conditions the rate constant (k) and the activation energy (E_a) were determined for two systems namely dichloromethane and chlorobenzene.

9.3.1 System description

Before we proceed to the model used, to determine the reaction kinetics, let us characterize the system. The reactor is a tubular flow reactor that operates in the laminar flow regime. The flow regime was determined by calculating the Reynolds Number (R_e).

For all of the experimental conditions that the equipment was tested under namely varying temperatures and flowrates, the Reynolds number was always less than 2100 and hence operating under laminar flow.

In tubular reactors the reactants are continually destroyed as they flow down the length of the reactor hence an axial concentration profile exists. Since the reactor operates in the laminar

9.2.1 Segregation Model

The segregation model states that molecules of the same age remain in a group as they move through the reactor and do not interact with any other groups until they leave the reactor. Since these groups do not interact with each other they can be considered as batch reactors.

Levenspiel (1966) stated that the boundary of each group is chemically inert and only role is to preserve the individuality of each group. The molecules within each of these groups are able to interact with each other. If any of these groups collide with each other, the group still remains unchanged through the collision, thus there is no inter group interactions.

Thus solving the defining equation for a batch reactor we obtain equation 9-7 .This represents the conversion for a single group of molecules with the reactor.

Batch Reactor: $$\frac{dN_A}{dt} = -r_A V \qquad (9\text{-}6)$$

*Conversion for a batch reactor:* $X(t) = 1 - e^{-kt}$ $\qquad$ (9-7)

To calculate the average conversion of the exit stream we need to average the conversion of all the individual groups within the reactor.

Segregation Model: $$\overline{X} = \int_0^\infty X(t)E(t)dt \qquad (9\text{-}8)$$

9.2.2 Maximum Mixedness Model

The maximum mixedness model is the direct opposite of the segregation model and allows for mixing of all molecules irrespective of their age in the reactor. This implies that as soon a molecule enters the reactor it is mixed with other molecules.

An incoming fluid particle is dispersed on a molecular scale in a time much less than the mean residence time. Thus any molecule entering a maximum mixedness reactor immediately becomes associated with other molecules with which all of it eventually leaves the reactor, and thus the whole life of its lifetime is spent in the neighborhood of molecules of the same life expectation. Furthermore molecules of the same life expectation are completely mixed regardless of the age.
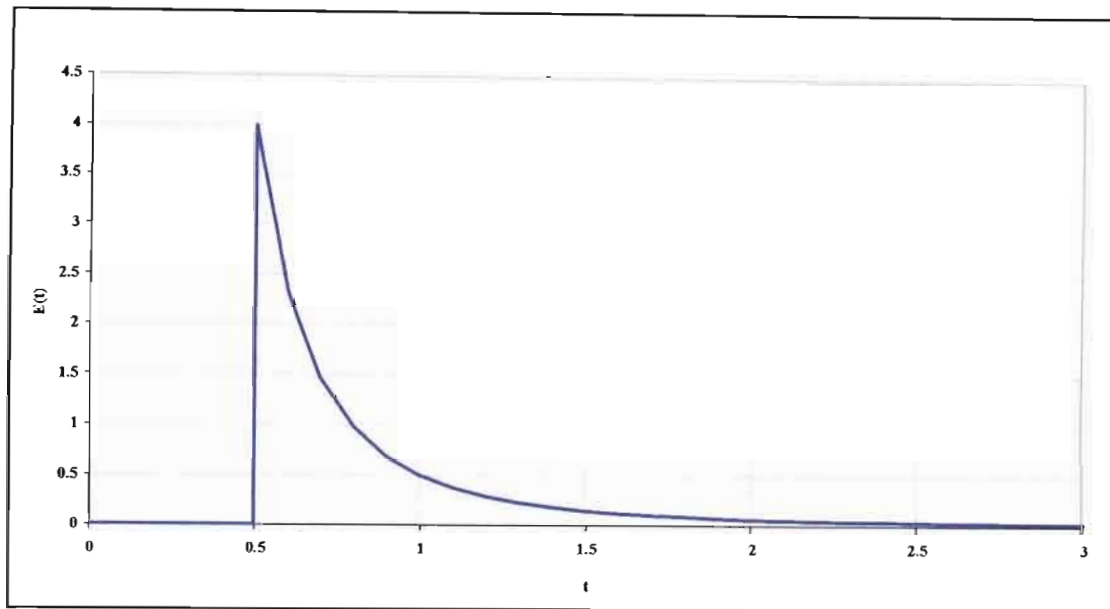
Figure 9-1: Simulation of the RTD curve for a laminar flow reactor. Mean residence time 1.0s

Danckwerts (1953) stated that its shape is independent of the length and diameter of the reactor and of the viscosity and velocity of the fluid provided that the flow is laminar.

9.2 Mixing Models

In order to correctly characterize a reactor the given RTD cannot be applied by itself but must be used in conjunction with a suitable model that describes the mixing in the system. The term mixing refers to the interaction between the molecules in the reactor. It must be recognized that mixing of the different reacting species is a major aspect in describing the behaviour of a chemical reactor. Thus it is critical that the model chosen to describe the mixing behaviour of a system is accurate in its description.

In section 9.1.1 it was stated that the RTD is characteristic of the mixing in a system, however more complex mixing models exist that can better describe these mixing effects in terms of molecular interactions. The segregation model and the maximum mixedness model were the two models that were considered to describe the mixing occurring during the pyrolysis reaction.

$$\theta = \frac{t}{t_m} \qquad\qquad (9\text{-}2)$$

The implementation of θ into E(θ) changes the form to:

$$E(\theta) = t_m E(t) \qquad\qquad (9\text{-}3)$$

9.1.2 RTD for laminar flow reactors

It is well recognized that laminar flow in tubular reactors has a parabolic velocity profile, where molecules near the center spend a shorter time in the reactor than those near the wall. Using this fact Danckwerts (1953) has shown that for laminar flow reactors the RTD function is described by the following expression:

$$E(t) = \begin{cases} 0 & t < \dfrac{t_m}{2} \\[2mm] \dfrac{t_m^{\,2}}{2t^3} & t \geq \dfrac{t_m}{2} \end{cases} \qquad\qquad (9\text{-}4)$$

In equation (9-4) t represents the overall age of a molecule at the exit by staying in the system for a length of time longer than the mean residence time namely the maximum in-system age. Therefore the overall age t is a sum of the initial age (at the mean residence time) and the maximum in-system age.

$$t = \theta_{tm} + \theta_{max} \qquad\qquad (9\text{-}5)$$

A plot of equation (9-4) is shown in Figure 9-1 for an arbitrary mean residence time of 1.0s. It is clear to see from Figure 9-1 that there is a period, defined as half the mean residence time, were no particles are seen exiting the laminar flow reactor. The shape of the curve is defined as such due to the parabolic velocity profile observed in laminar flow reactors. The bulk amount of particles in the center of reactor appear first whilst the others that are closer to the walls are affected by friction and take longer to pass through the reactor.

9. Modelling

Modelling in Chemical Engineering has become extremely important to new processes for their development and optimization. The combination of experimental work and theoretical analyses in computer models is aimed to both accelerate understanding and decrease development costs for new processes. The selection of a reactor design that operates safely in the most efficient manner is key to the economic success or failure of a chemical process. This chapter focuses on the determining the kinetics of the respective destruction reactions.

9.1 Residence Time Distribution (RTD) Theory

9.1.1 Introduction

The time that molecules spend in a reactor is called the residence time of the molecule in the reactor. Depending on the type of reactor, complex flow patterns may exist which results in different molecules have varying residence times hence the term residence time distribution (RTD).

The RTD of a reactor is a characteristic of the mixing that occurs in the chemical reactor. In any type of reactor the RTD can significantly affect its performance thus it is critical to correctly characterize the RTD for a given system.

The primary way of describing the RTD for a given system is by means of E(t) called the RTD function or the exit age distribution function. It is simply a function that describes in a quantitative manner how much time different fluid elements have spent in a reactor. Denbigh (1984) defined E(t) in a more formal manner by stating that E(t)dt is equal to the fraction of material in the outlet stream which has been in the system for times between t and t+dt. Consequently equation (9-1) follows from this statement, since the sum of all the fractions must be one.

$$\int_0^\infty E(t)\, dt = 1 \qquad (9\text{-}1)$$

A normalized RTD function is used by defining a function θ given by equation 9-2. This is done to allow for a direct comparison of the flow performance inside reactors of varying sizes. In equation (9-2) t_m represent the mean residence time. θ is often called the reduced time.

The compounds tested were pyrolysed at a temperature of 1000°C, mean residence time of 2.0s and a feed concentration of 15%. All compounds were successfully destroyed to below the detection limits of the GC/MS. Although the detection limits have not been determined through calibration for these compounds, it is reasonable to assume that since dichloromethane and chlorobenzene have detection limits of the order 1ppb these compounds should also follow this trend.

Obtaining high destruction efficiencies was promising however the production of a number of chlorinated aliphatic and aromatic compounds were also observed, similar to that shown in Tables 7-2 and 7-7. Thus reinforcing the general assumption that a H:Cl ratio of one or higher must be maintained to ensure the non-production of higher toxic byproducts than the initial reactant.

The second phase of testing involved the addition of methane to the feed gas stream. The presence of methane would serve as a hydrogen donor and thus eliminate the formation of higher chlorinated derivatives by maintaining a favorable hydrogen to chlorine ratio. Unfortunately only a single experiment was performed with methane and chloroform. Analysis of the product stream showed a significant decrease in the amount and number of chlorinated derivatives. The only chlorinated products formed were chloromethane and dichloromethane. The major observed products were carbon and hydrogen chloride. For this experiment only 20ml of chloroform was fed to the process due to the large amount of carbon formed from methane. The observed product distribution is consistent with our earlier statements.

Further experimentation was not possible since the bottom cooling section on the exit of the reactor had a small pit through which water was escaping into the reactor. Inspection of the cooling section showed a number of pits but only one was severe. The pit was located awkwardly within the reactor which meant that it could only be welded by completely stripping the reactor. A quick fix paste was tried to seal the pit but the high temperatures burnt it off.

Due to the late stage of the project and time constraints further experiments were not performed as it would take a considerable amount of time to strip the reactor. The fact that we achieved our goals of successfully destroying three higher chlorinated compounds and demonstrated that the addition of a hydrogen donor is necessary in such systems allowed for some confidence in the decision.

However a clear trend can be seen as the reaction atmosphere changes. If oxygen is present in the system then much lower temperatures are required for destruction. However in a completely oxygen free system temperatures in excess of 1000°C degrees are required for complete destruction of chlorobenzene. These observations were similar to that noticed for dichloromethane.

Looking at the general trends in Figure 8-10 it would have been expected that in a pyrolytic environment the destruction temperatures should be higher than that for a hydrogen rich atmosphere. A possible explanation for the observed trend could lie in the fact that significantly higher concentrations were used in the present pyrolysis experiments as compared to any of the other researchers. Although the assumption was that variations in low initial feed concentrations are negligible, higher concentrations could infact possibly be more advantageous by initiating degradation at lower temperatures.

8.3 Pyrolysis of additional chlorinated hydrocarbons

So far the pyrolysis of a chlorinated aliphatic and aromatic compound with hydrogen to chlorine ratios less than or equal to one was investigated. A survey of the literature indicates that authors, who have investigated destruction of chlorinated hydrocarbons, recognize the importance of the hydrogen to chlorine ratio. The consensus is that for a hydrogen to chlorine ratio of 1 or greater , the chlorine radical will preferentially abstract hydrogen. This reaction is important as it produces the simple non-toxic molecule hydrogen chloride whilst higher chlorinated derivatives are avoided.

In chlorine rich systems hydrogen is deficient and is only able to react with a small portion of the chlorine whilst the remainder of the chlorine participates in a mirad of reactions including polymerisation to eventually produce much more complex and toxic chlorinated molecules.

Although for most chlorinated systems the H:Cl ratio does not affect the destruction efficiency, in some instances it does because of the possible recombination reactions to form the parent. This simply means that even though the initial reactant is destroyed more of the parent is formed through recombination reactions. This effect is particularly dominant in aromatic systems since recombination reactions are common owing to the highly reactive phenyl radical.

An important motive for this research was to test this proposal and also to explore the applicability of the system in destroying other chlorinated compounds. Thus in the following discussion the effect of this ratio in the pyrolysis system has been investigated. To this effect trichloroethylene, chloroform and carbon tetrachloride were pyrolysed.
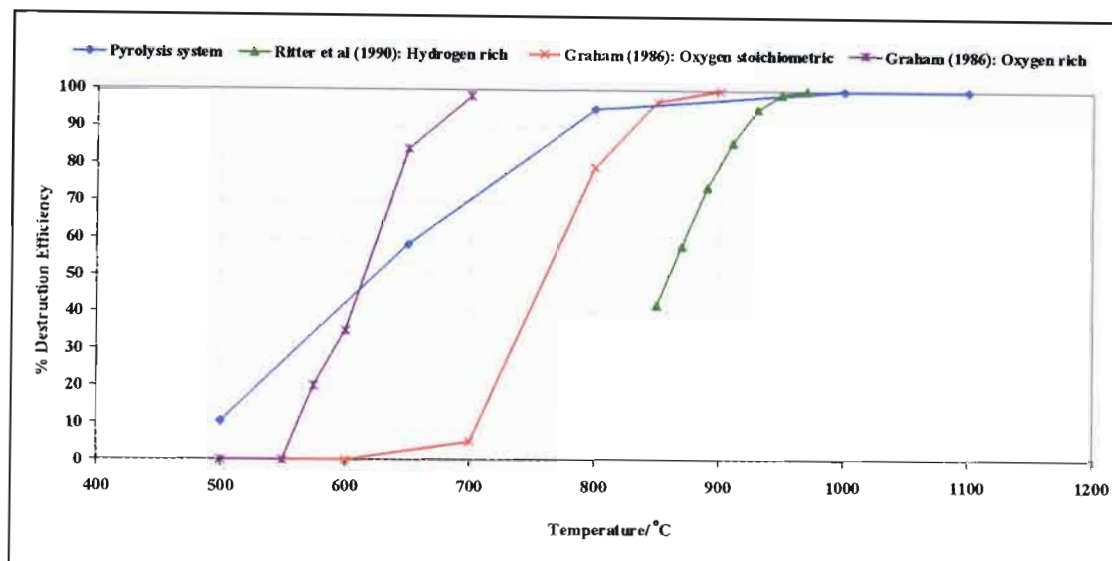
8.2.5 Comparison of different reaction atmospheres

Figure 8-20: Effect of reaction temperature on the destruction efficiency of chlorobenzene under different atmospheres.

In Figure 8-20 the effects of 4 different reaction atmospheres on the destruction of chlorobenzene is compared. We cannot make a direct comparison of the destruction efficiencies in Figure 8-20 because of the difference in residence times and to a lesser extent the initial feed concentration.

Table 8-9: Conditions for the data plotted in Figure 8-20

Researcher	Atmosphere	Residence Time/ s
Graham (1986)	O_2 in stoichiometric amount	2
	O_2 rich	2
Ritter *et al.* (1990)	0.37 mol% C_6H_5Cl in H_2	1
Current Researcher	15 mol% C_6H_5Cl in Argon	1.5

8.2.4.3 Particle size distribution and specific surface area
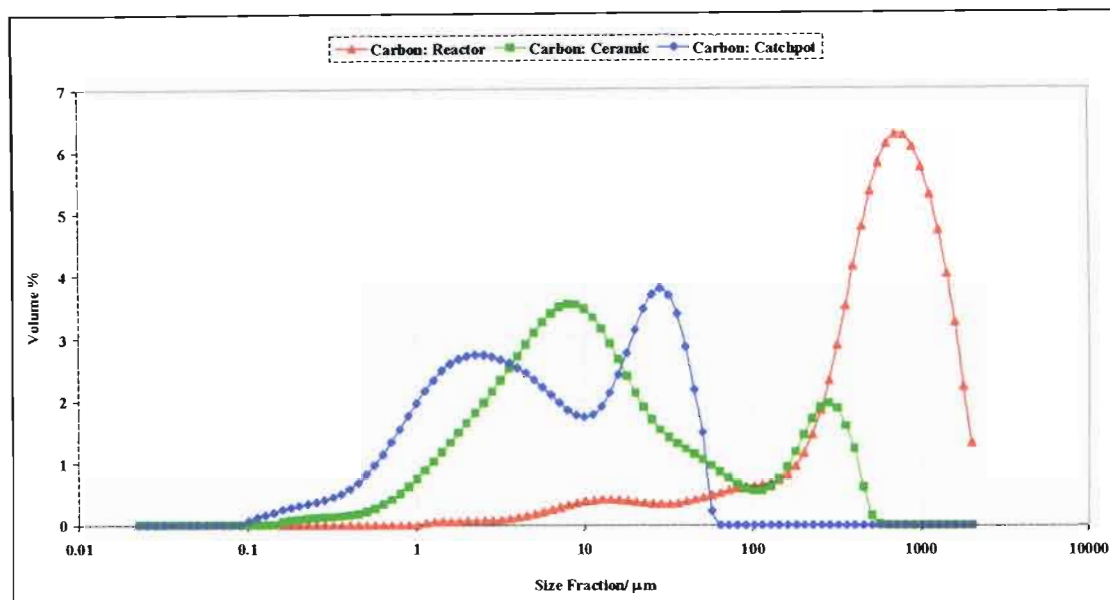
Figure 8-19: Particle size distribution of carbon formed from the pyrolysis of chlorobenzene at 1000°C and at a mean residence time of 2.5s.

Accurate information about the particle size distribution could not be obtained by using the Malvern Analyzer. Figure 8-19 shows the poor distribution that was obtained for the respective carbons. A good distribution should mirror a normal Gaussian curve similar to that observed in Figure 8-5 for carbon from dichloromethane. In order to get a better distribution a number of runs were repeated, surfactants were employed and also the time of the ultrasonic was increased to try to breakup the carbon agglomerates. The poor distribution is likely due to the complex nature of the carbon and the difficulty in breaking up the agglomerates that make the carbon to obtain the true particle size distribution.

Therefore owing to the inability of the Malvern analyzer to properly analyze the carbon samples no information about the particle size distribution and specific areas can be discussed.

The compositions of the respective carbon samples did not exhibit any particular trend with respect to the various process variables. The observed maxima and minima of the elements that were present on the carbon sample is given in Table 8-8. The data in Table 8-8 was obtained from different experimental runs, hence the sum of the respective elemental percentages do not sum to one.

Table 8-8: Elemental weight percent maxima and minima for the carbon black samples obtained from the pyrolysis of chlorobenzene.

| Element	Minimum Weight % Value	Maximum Weight % Value
Carbon	89	96
Oxygen	3	11
Chlorine	0.15	1.3

The amount of oxygen on the carbon samples was not insignificant. This indicates that the carbon surfaces were highly reactive with the atmosphere and were able to adsorb large quantities of oxygen. This result is not surprising since the surface structure of the carbon promotes adsorption or trapping of oxygen molecules through its complex arrangement (See Figure 8-16).

8.2.4.2 GC/MS analysis of acetone solvent

Mass spectral analysis of the acetone used to wash the carbon showed trace levels of high molecular weight compounds e.g. hexadecane. Amongst these compounds were also a number of aromatics. The aromatics that were consistently observed were methylcyclohexane, ethylcyclopentane and cycloheptane. The presence of these compounds is attributed to:

> ➤ phenyl polymerization reactions leading to carbon growth
> ➤ adsorption of reactive species from the product stream

In addition to these species were oxygenated compounds, these were formed through surface complexes.
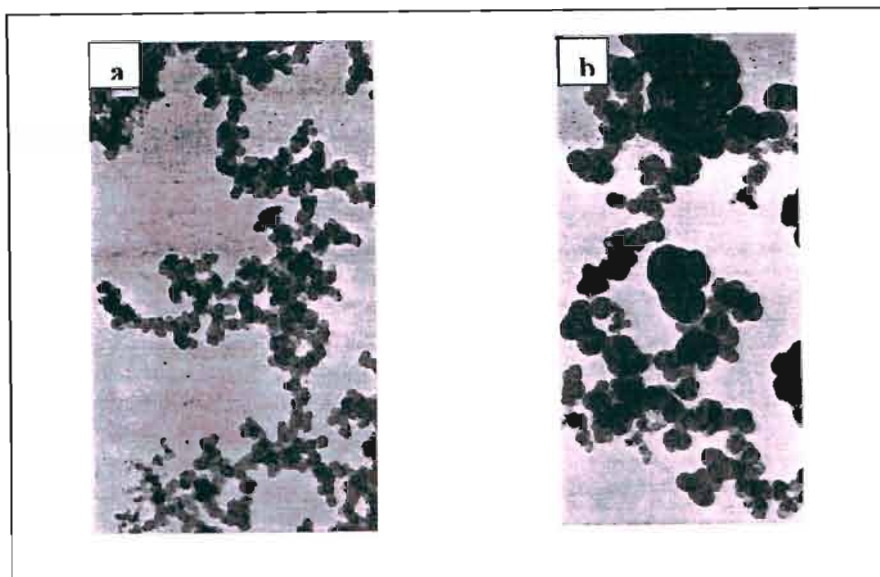
Figure 8-17: Micrographs of commercial carbon black samples. Micrograph a is for a carbon black obtained from oil furnace black whilst micrograph b is from gas furnace black. (Smith, 1964)

The distinction between the carbons is one of degree rather than kind, and is based on particle size, surface area and chemical composition of the surface. The only dissimilarity that could be noticed between the carbons was the presence of white spots on some of the carbon samples. It is unclear what these spots represent. The occurrence of these spots were random and was confined only to a particular location for any given run. A thorough analysis of their existence with variations in reaction conditions lead to no discernable trends.
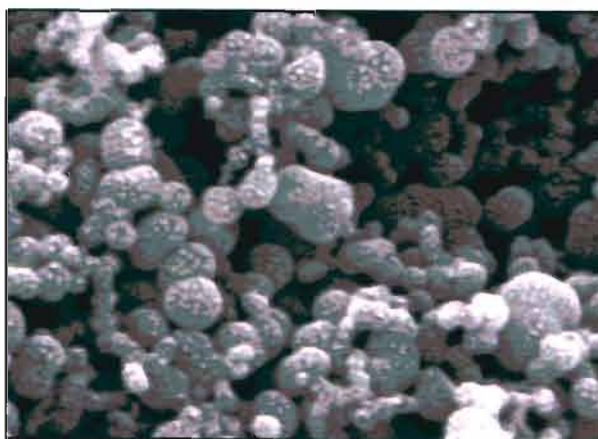
Figure 8-18: Micrograph of spots on the surface of a carbon sample obtained from the pyrolysis of chlorobenzene.

8.2.4.1 Carbon morphology and composition

The micrographs of all the carbon blacks revealed that, regardless of the process conditions under which they were formed, they possess essentially the same morphology. Likewise the carbon formed from the three locations were similar. Shown below in Figure 8-16 is a common image of the carbon morphology that was witnessed for all of the respective carbons.
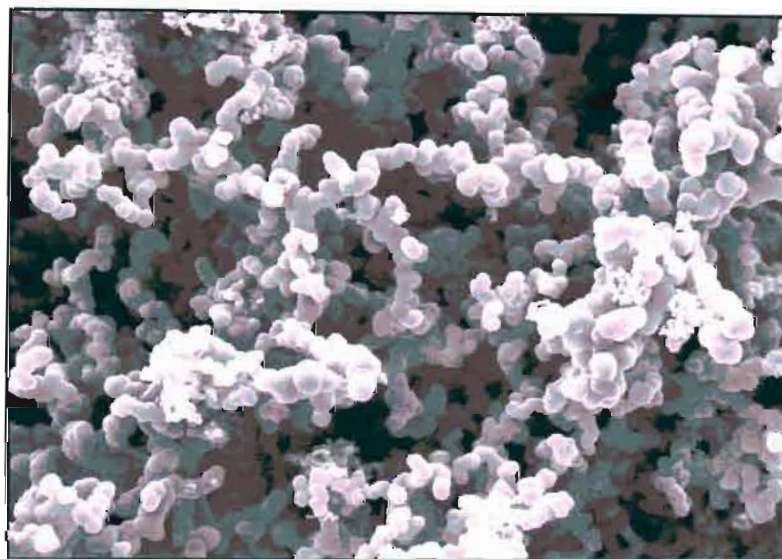
Figure 8-16: Micrograph of a reactor carbon sample obtained from the pyrolysis of chlorobenzene. Process conditions were 1000°C and a mean residence time of 2.5s

When viewed under the electron microscope all carbon blacks appeared as essentially spherical particles clinging together to form complex network like structures. The carbon morphology identified in these micrographs is analogous to commercial carbon blacks shown in Figure 8-17.
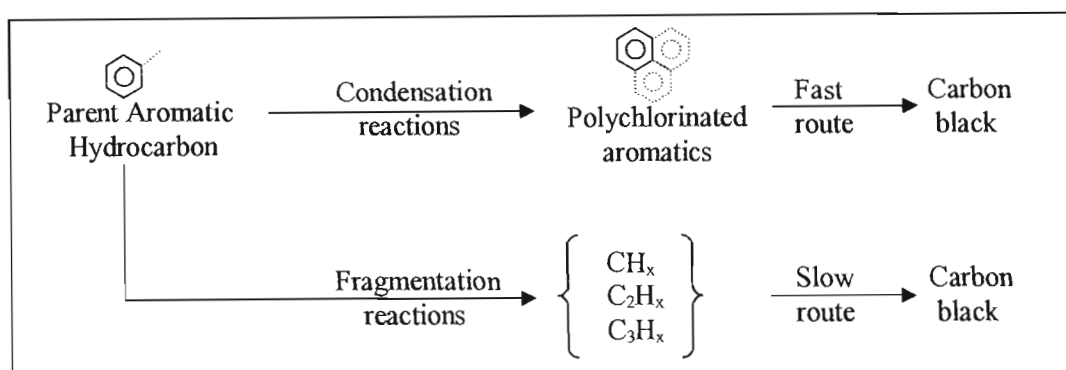
Figure 8-15: Competing routes suggested by **Graham *et al.* (1975)** for carbon formation from aromatics.

The decomposition of the ring is a unimolecular process and has a high activation energy. Frenklach (1983) stated that for this type of reactions activation energy is of the order of 400kJ/mol whilst for growth reactions it is only 150-200kJ/mol.

It is reasonable to assume that carbon formed by the pyrolysis of chlorobenzene occurs through a combination of the two routes outlined in Figure 8-15. The fast route is more likely to be the dominant pathway at low temperatures since not much ring cleavage occurs. This does not mean that it is not the dominate pathway for carbon formation at high temperatures since these condensation reactions are fast. At the higher temperature the fragmentation reactions become more competitive, due to the formation of a larger number of smaller radical species, and hence contribute to a greater extent to carbon formation than at the lower temperatures.
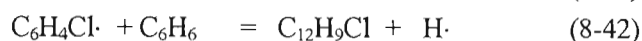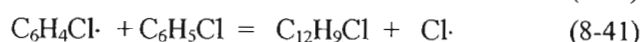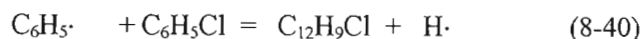
8.2.4 Analysis of carbon black samples

During the discussion for dichloromethane it was stated that carbon formed from the pyrolysis process was deposited in three locations namely:

> - reactor walls
> - ceramic tube wall below the reactor
> - cottonwool in the catchpot located at the system exit

The pyrolysis of chlorobenzene yielded similar observations.

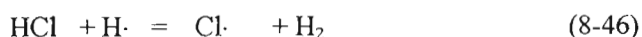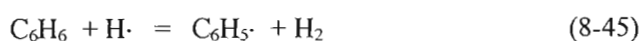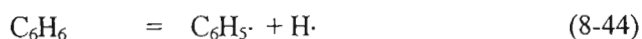lack of formation of acetylene or carbon at these low temperatures contradicts Fields (1966) mechanism.

A more direct pathway is through the recombination of the phenyl and chlorophenyl radicals which does not need any breakdown of the aromatic ring. An example of this type of reactions was illustrated by Ritter (1990) for the formation of dichlorobiphenyl.

$$C_6H_5 \cdot \quad + C_6H_5Cl = C_{12}H_9Cl + H \cdot \qquad (8\text{-}40)$$
$$C_6H_4Cl \cdot + C_6H_5Cl = C_{12}H_9Cl + Cl \cdot \qquad (8\text{-}41)$$
$$C_6H_4Cl \cdot + C_6H_6 \quad = C_{12}H_9Cl + H \cdot \qquad (8\text{-}42)$$
$$C_6H_4Cl \cdot + C_6H_5Cl = C_{12}H_8Cl_2 + H \cdot \qquad (8\text{-}43)$$

8.2.3.3 Pathway for the formation of hydrogen

Although hydrogen was not analysed for in our system it is indeed possible that it has been produced by the pyrolysis reaction, since sufficient evidence has been provided by other authors. Therefore to form a complete picture of the reaction mechanism it is worthwhile to account for the formation of hydrogen as it illustrates plausible pathways.

From the observed radicals produced the phenyl radical dominates the radical pool, whilst hydrogen chloride is the species that is produced very early in the reaction. Therefore it is feasible to assume that the mechanism involves phenyl and hydrogen chloride. The following reactions are the most likely pathway for hydrogen formation.

$$C_6H_6 \quad = \quad C_6H_5 \cdot + H \cdot \qquad (8\text{-}44)$$
$$C_6H_6 + H \cdot = C_6H_5 \cdot + H_2 \qquad (8\text{-}45)$$
$$HCl + H \cdot = Cl \cdot \quad + H_2 \qquad (8\text{-}46)$$

8.2.3.4 Pathway for the formation of carbon

Graham (1975) hypothesized for aromatic compounds there is competition between two parallel reaction pathways, condensation and fragmentation. The fast direct route is the addition of aromatics to form large clusters (condensation reactions) whilst the slow indirect route involves cleavage of the rings to yield the building blocks for carbon formation. An increase in fragmentation will decrease the amount of carbon formed via the fast direct route. The fragmentation process is controlled by unimolecular processes associated with the parent ring.

Table A-2: Explanation of the boundary conditions shown in Table A-1

Balance	Boundary Conditions			
	Boundary 1	Boundary 2	Boundary 3	Boundary 4
Momentum	Sets the axial and radial velocities to zero. This sets a no slip condition.	Sets the radial velocity to zero and the axial velocity to vo.	Sets a reference pressure of po at the exit.	Indicates the normal velocities are zero. This implies a symmetry condition.
Mass	Indicates that the normal components of $N_i = (-D_i \nabla c_i + c_i\mathbf{u})$ are zero. This implies an insulation or symmetry condition. In this case an insulation condition.	Set the concentration of the feed.	This implies that convection is greater than diffusion at the exit. i.e.$(c_i\mathbf{u}).n \gg (-D_i \nabla c_i).n$ which allows for the approximation that $(-D_i \nabla c_i).n = 0$ and $\mathbf{N}_i.n = (c_i.\mathbf{u}).n$	Similar to boundary 1 except this implies a symmetry condition.
Energy	Specifies the temperature.	Specifies the temperature.	This implies that convection is greater than conduction at the exit. i.e.$(\rho C_p T\mathbf{u}).n \gg (-k \nabla T).n$ which allows for the approximation that $(-k_i \nabla T).n = 0$ and $\mathbf{q}.n = (\rho C_p T\mathbf{u}).n$	Sets the normal component of $q = (-k \nabla T + \rho C_p T\mathbf{u})$ to zero. This implies symmetry.

Appendix B: Reactant feed pump curves
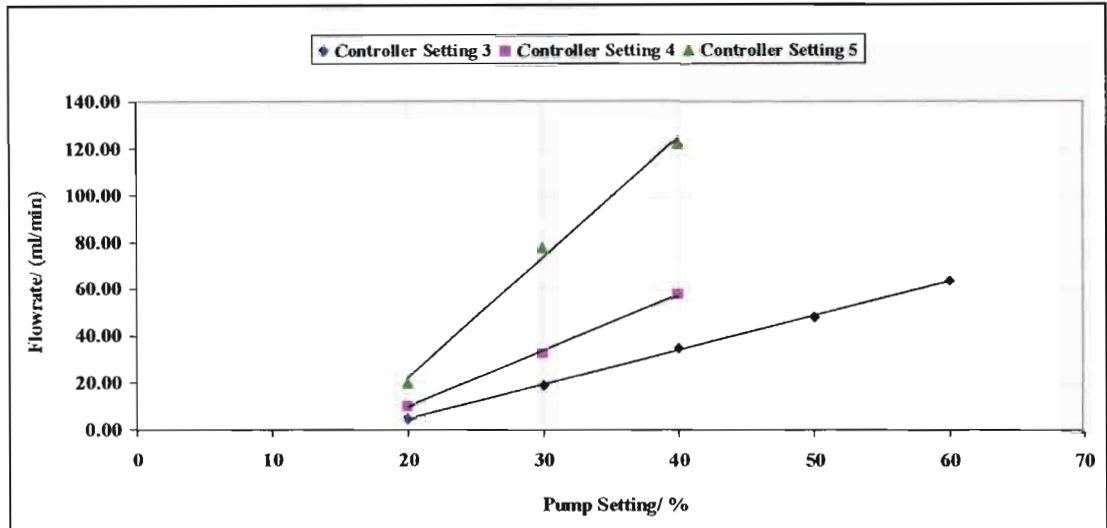
Figure B-1: Pump characteristic curves obtained for varying speed controller settings.
Pump Specifications: Alldos dosing pump, Primus Series, Type M,
Maximum Output 75 l/hr

Appendix C: Product Distribution for dichloromethane

Table C1: Minor product distribution obtained from the pyrolysis of methylene chloride. Reactor temperature 1000°C, mean residence time 1.5s and feed concentration 27.6%. Products shown have been identified by mass spectroscopy with a minimum of 80% certainty.

Compound Name	Molecular formula
Butane, 2-methyl	C_5H_{12}
Pentane, 2,4 –dimethyl	C_7H_{16}
Butane- 2,2dimethyl	C_6H_{14}
Hexane, 2,2,5,5- tetramethyl	$C_{10}H_{22}$
Pentane 2,3- dimethyl	C_7H_{16}
Hexane 2,4- dimethyl	C_8H_{18}
Hexane 2,3,4- trimethyl	C_9H_{20}
Hexane 3- methyl	C_7H_{16}
Heptane 3,4- dimethyl	C_9H_{20}
Heptane	C_7H_{16}
1-Heptene, 5-methyl	C_8H_{16}
Heptane	C_6H_{16}
1-Hexen-4-methyl	C_7H_{14}
2-Butyl-1-decene	$C_{14}H_{28}$
Octane 2,4,6- trimethyl	$C_{11}H_{24}$
Decane 2,5,6- trimethyl	$C_{13}H_{28}$
Pentane 2,2,4,4- tetramethyl	C_9H_{20}
Heptane, 3-methyl	C_8H_{18}
Hexane, 2, 4-dimethyl	C_8H_{18}
Hexane, 3-methyl, 2-ethyl	C_9H_{20}
Benzene 1,2-dimethyl	C_8H_{10}
P-xylene	C_8H_{10}
Nonane	C_9H_{20}
Undecane, 5,7-dimethyl	$C_{13}H_{28}$
Eicosane	$C_{20}H_{42}$
Decane	$C_{10}H_{20}$
Tridecane	$C_{13}H_{28}$
Dodecane	$C_{12}H_{26}$

Undecane	$C_{11}H_{24}$
Eicosane	$C_{20}H_{42}$
Hexadecane	$C_{16}H_{34}$
Tetradecane	$C_{14}H_{30}$
Nonadecane	$C_{19}H_{40}$
Eicosane	$C_{20}H_{42}$

Appendix D: GC/MS Calibration Curves
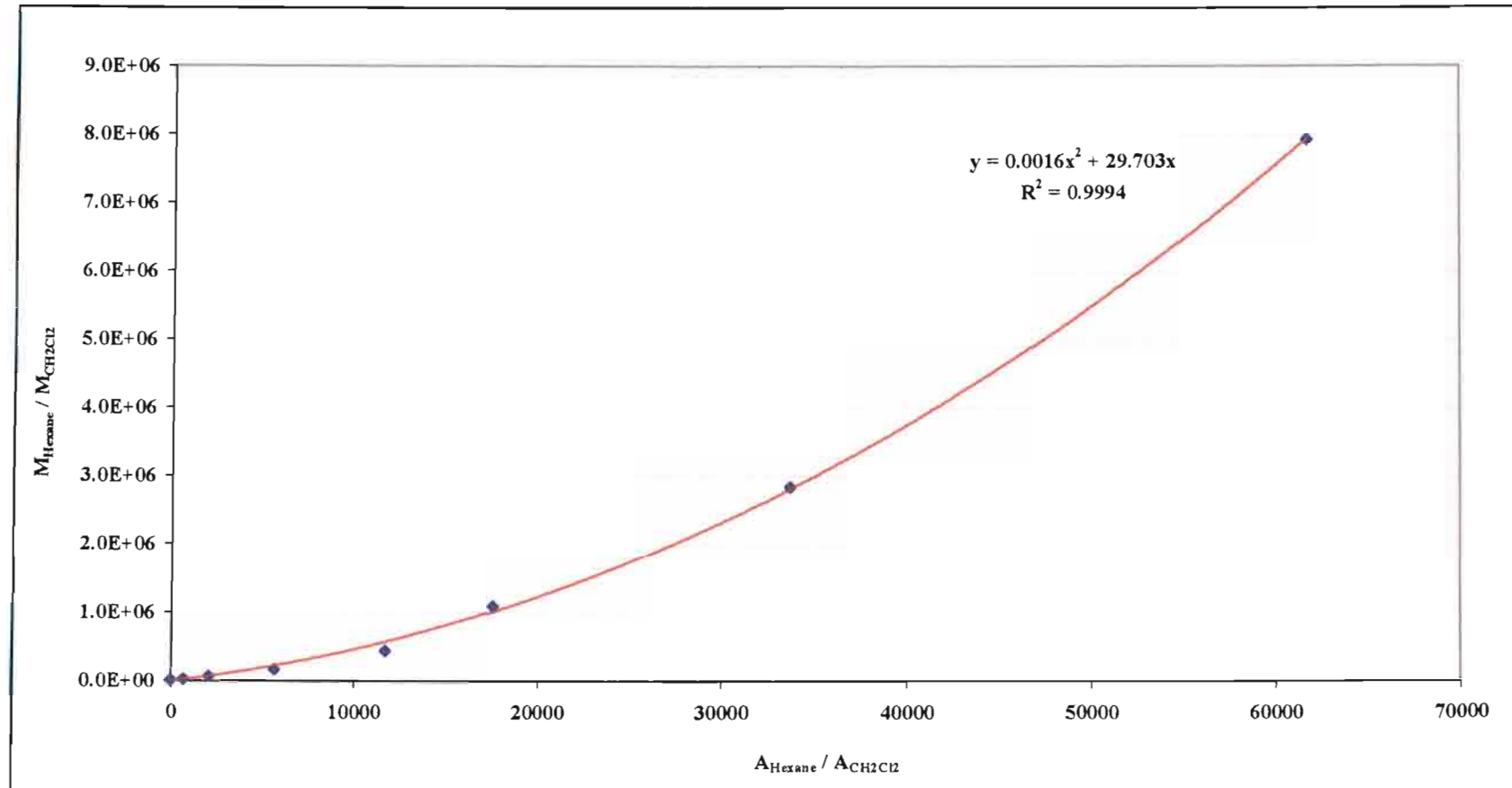
Figure D-1: GC/MS Calibration curve for dichloromethane in a hexane solvent

$$y = -0.027x^2 + 11.549x$$
$$R^2 = 0.9998$$
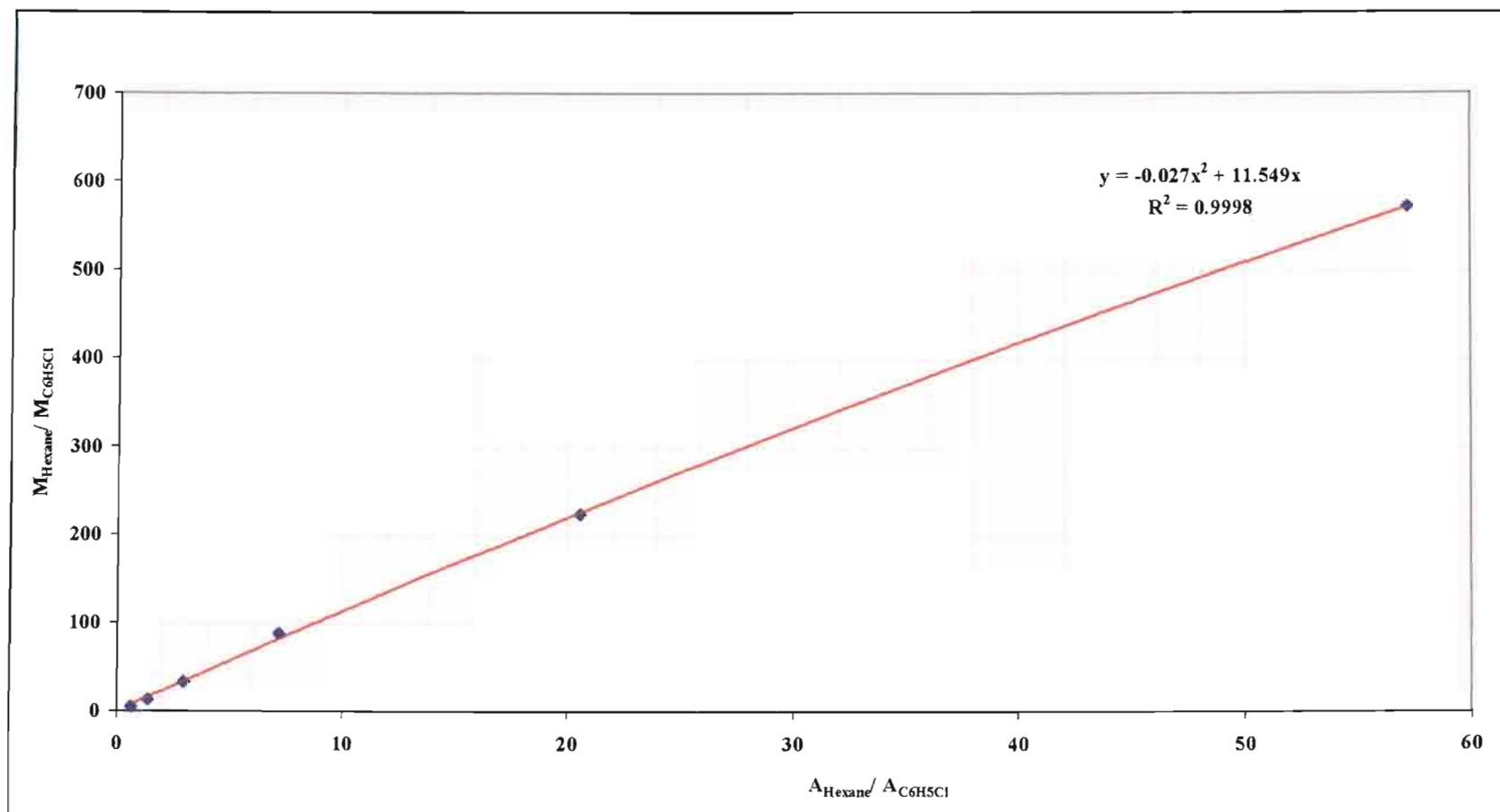
Figure D-2: GC/MS Calibration curve for chlorobenzene in a hexane solvent

$$y = 0.1293x^2 + 12.091x$$
$$R^2 = 0.9994$$
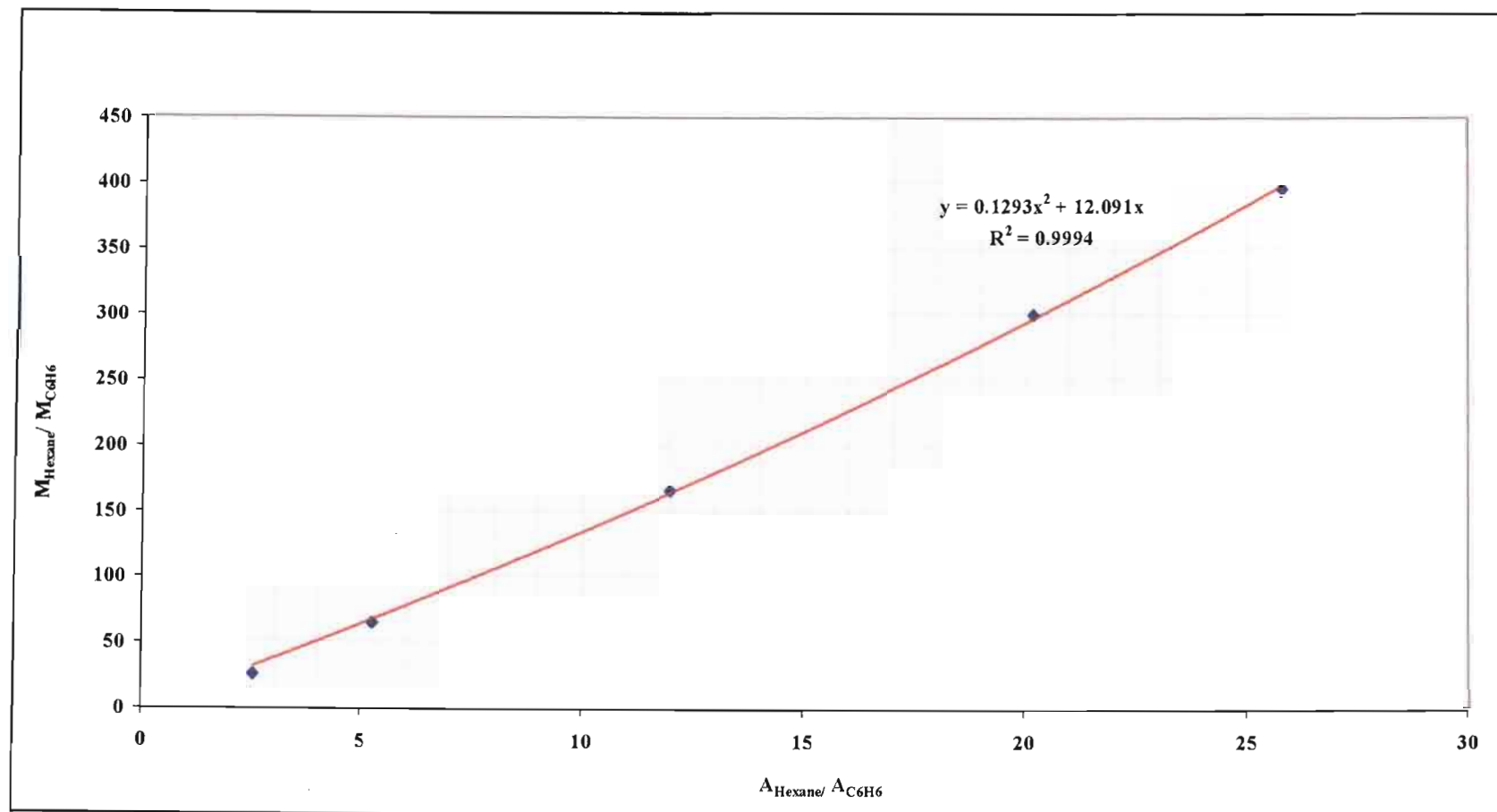
Figure D-3: GC/MS Calibration curve for benzene in a hexane solvent
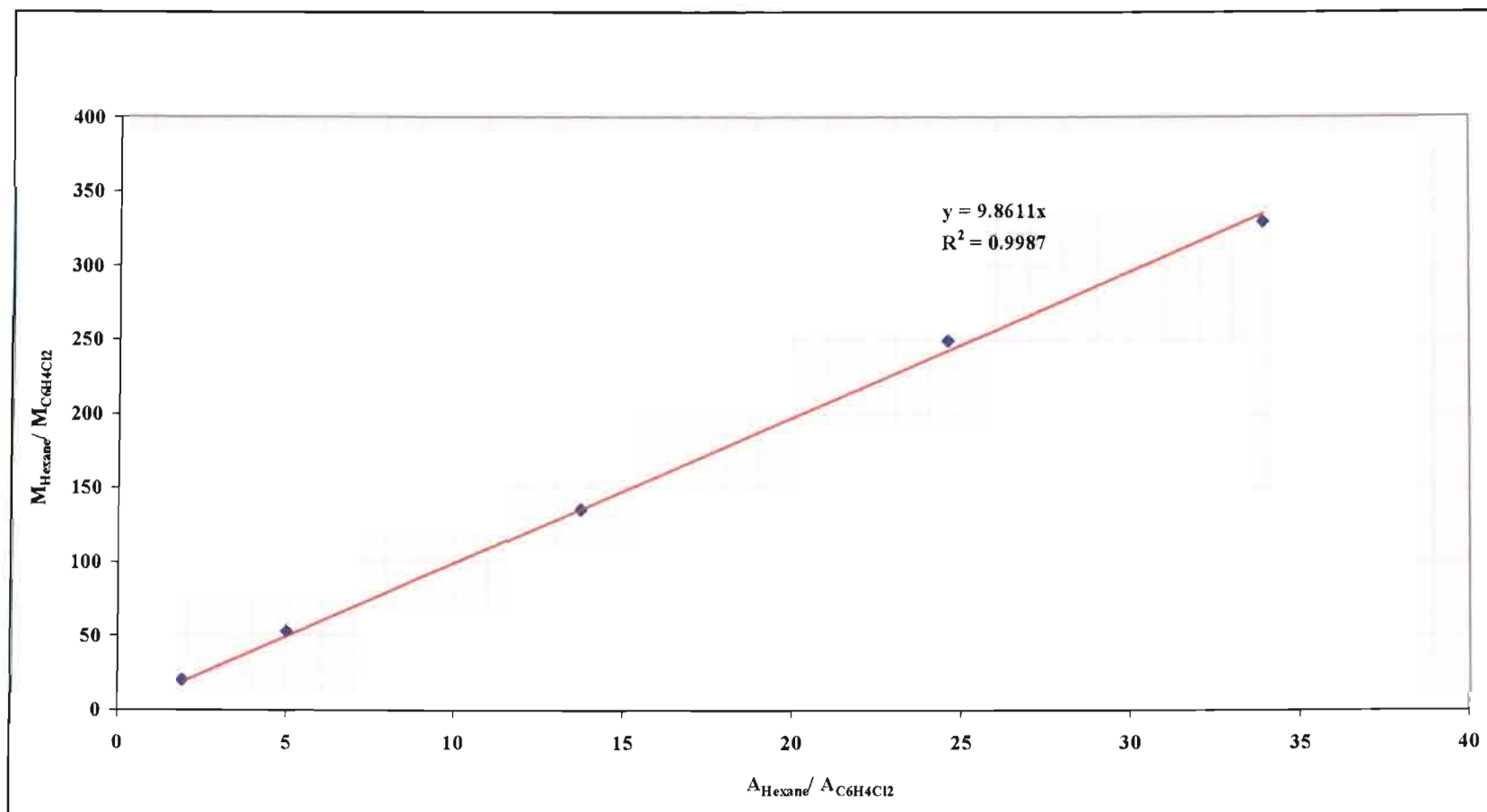
Figure D-4: GC/MS Calibration curve for dichlorobenzene in a hexane solvent
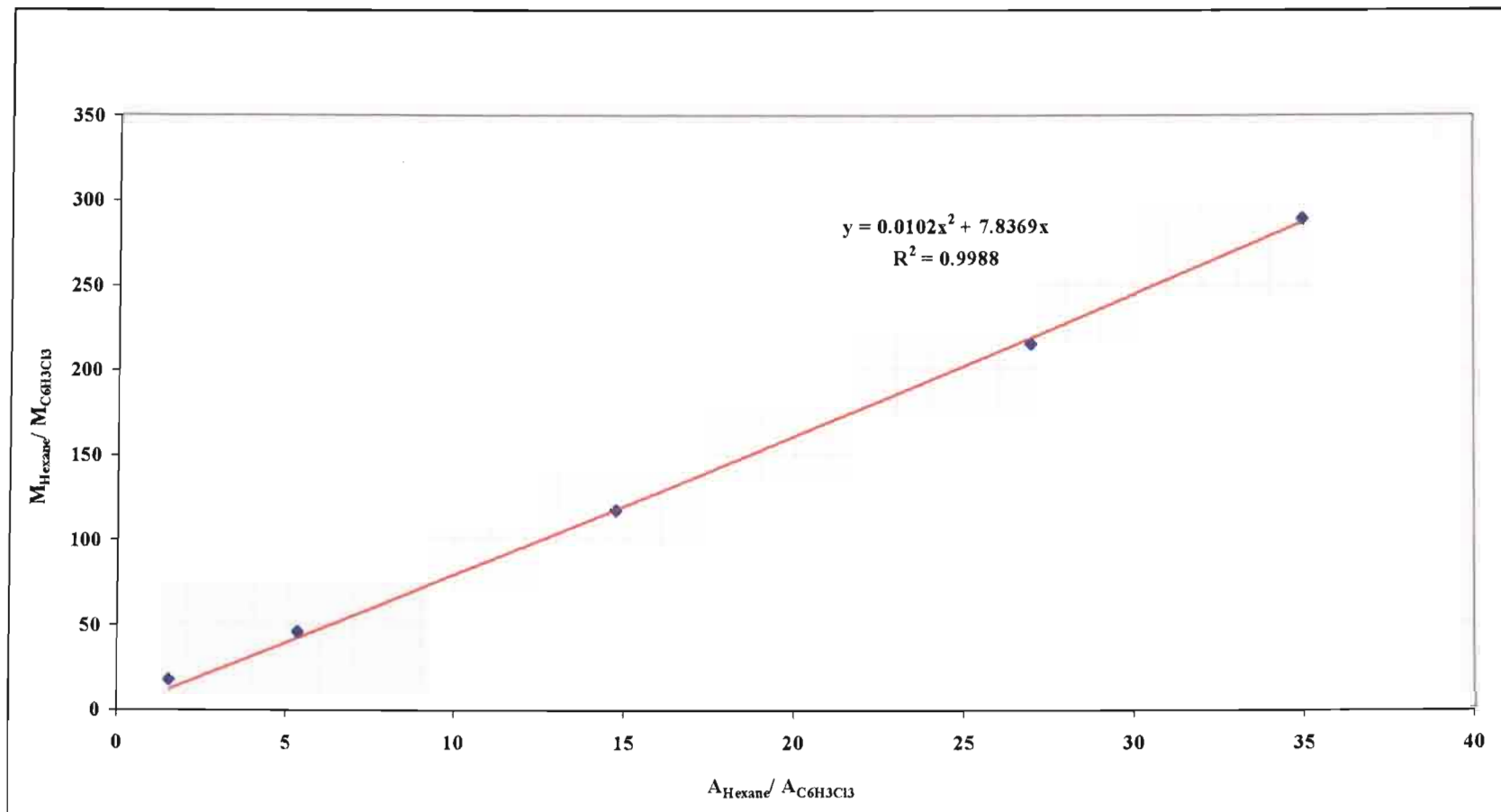
Figure D-5: GC/MS Calibration curve for trichlorobenzene in a hexane solvent

Appendix E: Comparison of experimental and predicted data
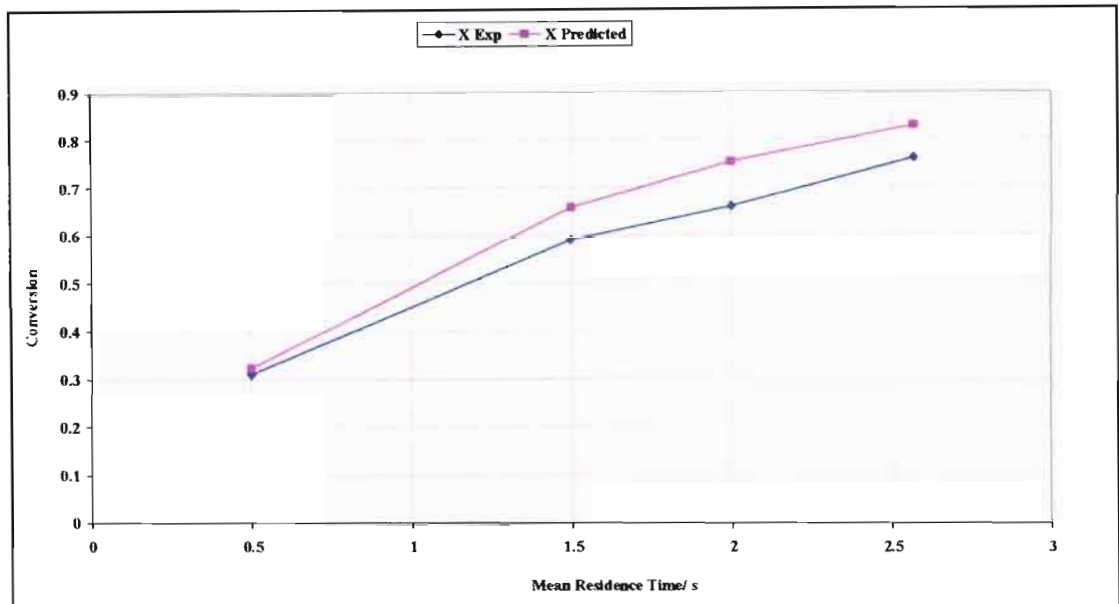
Figure E-1: Showing the predicted values for the rate constant for dichloromethane at a destruction temperature of 873K.
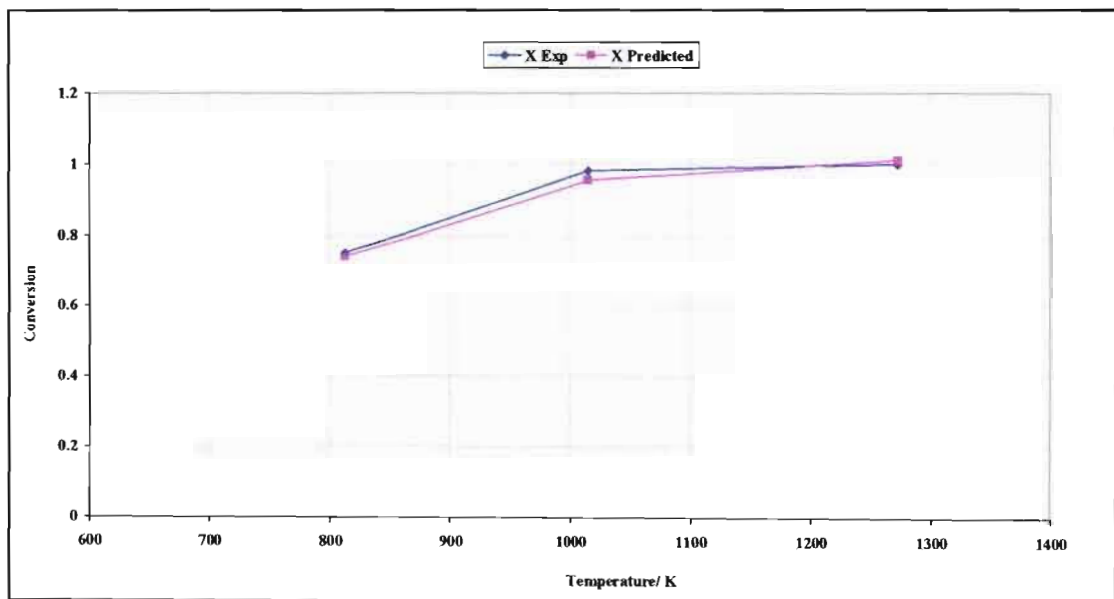
Figure E-2: Showing the prediction of the activation energy for dichloromethane for 813K to 1273K
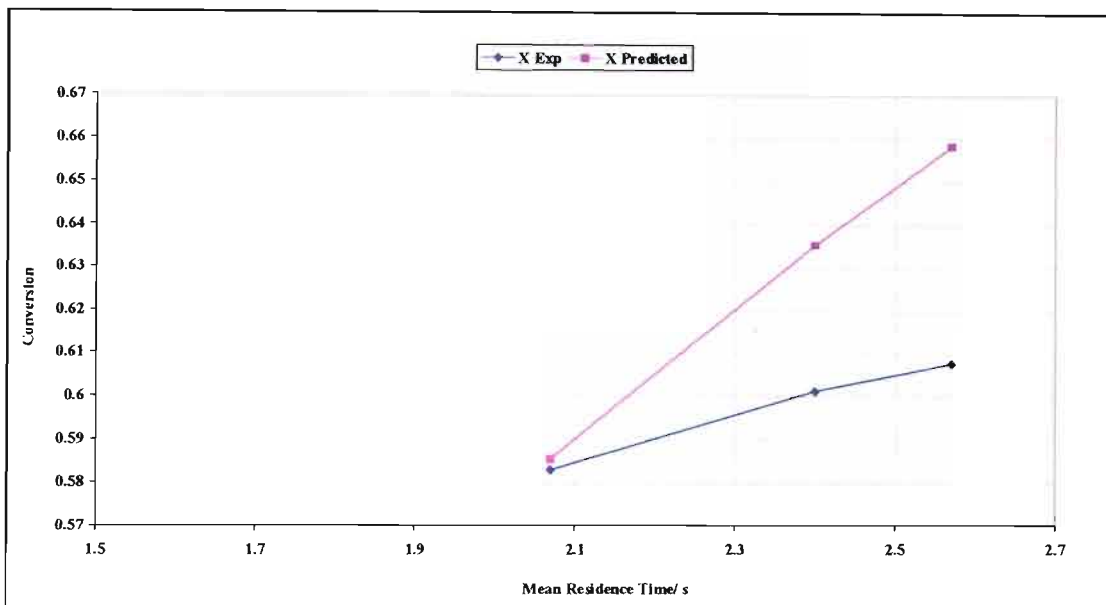
Figure E-3: Showing the predicted values for the rate constant for chlorobenzene pyrolysis at a reactor temperature of 923K
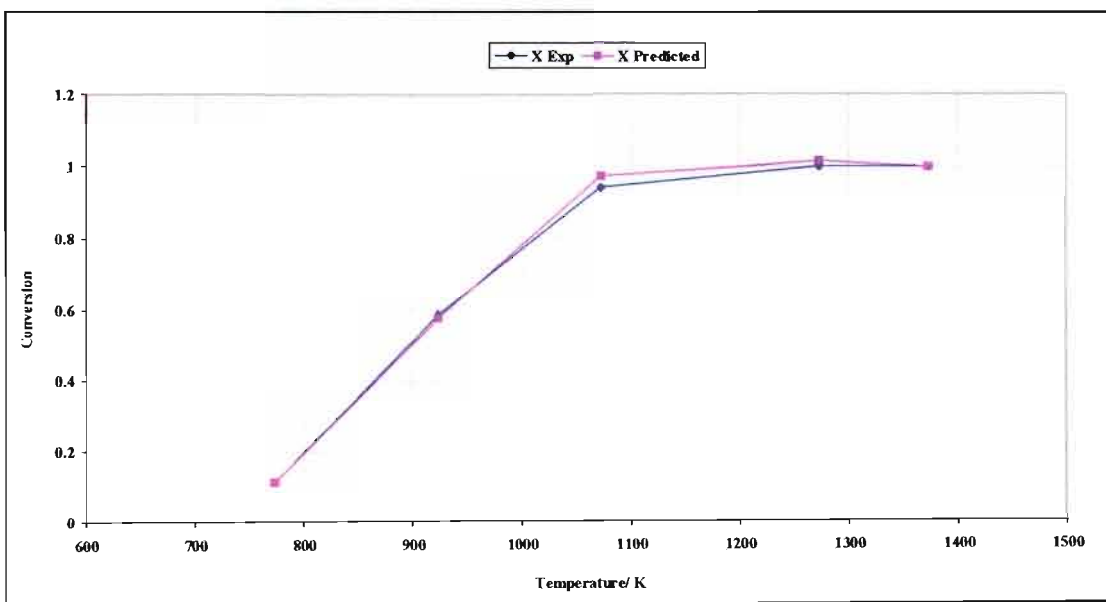
Figure E-4: Showing the prediction of the activation energy for chlorobenzene from 773K to 1373K

Appendix F: Material Safety Data Sheets

Appendix F1: Dichloromethane

1. Product Identification

Synonyms: MC; Dichloromethane (DCM); Methylene dichloride; Methylene bichloride; Methane dichloride
CAS No.: 75-09-2
Molecular Weight: 84.93
Chemical Formula: CH2Cl2

2. Composition/Information on Ingredients

Ingredient	CAS No	Percent	Hazardous
Methylene Chloride	75-09-2	> 99%	Yes

3. Hazards Identification

Emergency Overview

WARNING! HARMFUL IF SWALLOWED, INHALED OR ABSORBED THROUGH SKIN. AFFECTS CENTRAL NERVOUS SYSTEM, LIVER, CARDIOVASCULAR SYSTEM, AND BLOOD. CAUSES IRRITATION TO SKIN, EYES AND RESPIRATORY TRACT. SUSPECT CANCER HAZARD. MAY CAUSE CANCER. Risk of cancer depends on level and duration of exposure.

Health Rating: 3 - Severe (Cancer Causing)
Flammability Rating: 1 - Slight
Reactivity Rating: 2 - Moderate
Contact Rating: 3 - Severe
Lab Protective Equip: GOGGLES & SHIELD; LAB COAT & APRON; VENT HOOD; PROPER GLOVES
Storage Color Code: Blue (Health)

Potential Health Effects

Inhalation:
Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes formation of carbon monoxide in blood which affects cardiovascular system and central nervous system. Continued exposure may cause increased light-headedness, staggering, unconsciousness, and even death. Exposure may make the symptoms of angina (chest pains) worse.

Ingestion:
May cause irritation of the gastrointestinal tract with vomiting. If vomiting results in aspiration, chemical pneumonia could follow. Absorption through gastrointestinal tract may produce symptoms of central nervous system depression ranging from light headedness to unconsciousness.

Skin Contact:
Causes irritation, redness and pain. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.

Eye Contact:
Vapors can cause eye irritation. Contact can produce pain, inflammation and temporal eye damage.

Chronic Exposure:
Can cause headache, mental confusion, depression, liver effects, kidney effects, bronchitis, loss of appetite, nausea, lack of balance, and visual disturbances. Can cause dermatitis upon prolonged skin contact. Methylene chloride may cause cancer in humans.

Aggravation of Pre-existing Conditions:
Persons with pre-existing skin disorders, eye problems, impaired liver, kidney, respiratory or cardiovascular function may be more susceptible to the effects of this substance.

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4. First Aid Measures

Inhalation:
Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

Ingestion:
If swallowed, DO NOT INDUCE VOMITING. Give large quantities of water. Never give anything by mouth to an unconscious person. Get medical attention immediately.

Skin Contact:
Immediately flush skin with plenty of soap and water for at least 15 minutes while removing contaminated clothing and shoes. Get medical attention. Wash clothing before reuse. Thoroughly clean shoes before reuse.

Eye Contact:
Immediately flush eyes with plenty of water for at least 15 minutes, lifting lower and upper eyelids occasionally. Get medical attention immediately.

5. Fire Fighting Measures

Fire:
Autoignition temperature: 556C (1033F)
Flammable limits in air % by volume:
lel: 12; uel: 23
Forms flammable vapor-air mixtures above 100C (212F).

Explosion:
Concentrated can be ignited by a high intensity ignition source. Vapor may form flammable mixture in atmosphere that contains a high percentage of oxygen. Sealed containers may rupture when heated.

Fire Extinguishing Media:
Dry chemical, foam or carbon dioxide. Water spray may be used to keep fire exposed containers cool.

Special Information:
In the event of a fire, wear full protective clothing and NIOSH-approved self-contained breathing apparatus with full facepiece operated in the pressure demand or other positive pressure mode. Combustion by-products include phosgene and hydrogen chloride gases. Structural firefighters' clothing provides only limited protection to the combustion products of this material.

6. Accidental Release Measures

Ventilate area of leak or spill. Remove all sources of ignition. Wear appropriate personal protective equipment as specified in Section 8. Isolate hazard area. Keep unnecessary and unprotected personnel from entering. Contain and recover liquid when possible. Use non-sparking tools and equipment. Collect liquid in an appropriate container or absorb with an inert material (e. g., vermiculite, dry sand, earth), and place in a chemical waste container. Do not use combustible materials, such as saw dust. Do not flush to sewer.

7. Handling and Storage

Keep in a tightly closed container, stored in a cool, dry, ventilated area. Protect against physical damage. Isolate from any source of heat or ignition. Outside or detached storage is recommended. Containers of this material may be hazardous when empty since they retain product residues (vapors, liquid); observe all warnings and precautions listed for the product. To minimize decomposition, all storage containers should be galvanized or lined with a phenolic coating. This material may corrode plastic and rubber. Wear special protective equipment (Sec. 8) for maintenance break-in or where exposures may exceed established exposure levels. Wash hands, face, forearms and neck when exiting restricted areas. Shower, dispose of outer clothing, change to clean garments at the end of the day. Avoid cross-contamination of street clothes. Wash hands before eating and do not eat, drink, or smoke in workplace. Odor Threshold: 205 - 307 ppm. The odor threshold only serves as a warning of exposure; not smelling it does not mean you are not being exposed.

8. Exposure Controls/Personal Protection

Airborne Exposure Limits:
Methylene Chloride (Dichloromethane):
- OSHA Permissible Exposure Limit (PEL) -
25 ppm (TWA), 125 ppm (STEL), 12.5 ppm (8-hour TWA - Action Level)
- ACGIH Threshold Limit Value (TLV) -
50 ppm (TWA), A3 - suspected human carcinogen.
Ventilation System:
A system of local and/or general exhaust is recommended to keep employee exposures below the Airborne Exposure Limits. Local exhaust ventilation is generally preferred because it can control the emissions of the contaminant at its source, preventing dispersion of it into the general work area. Please refer to the ACGIH document, *Industrial Ventilation, A Manual of Recommended Practices*, most recent edition, for details.
Personal Respirators (NIOSH Approved):
If the exposure limit is exceeded, wear a supplied air, full-facepiece respirator, airlined hood, or full-facepiece self-contained breathing apparatus. The cartridges recommended for this material have a predicted service of less than 30 minutes at concentrations of ten times (10x) the exposure limits. Actual service life will vary considerbly, depending on concentration levels, temperature, humidity, and work rate. This substance has poor warning properties.
Skin Protection:
Wear impervious protective clothing, including boots, gloves, lab coat, apron or coveralls, as appropriate, to prevent skin contact. Neoprene is a recommended material for personal protective equipment. Natural rubber and polyvinyl chloride ARE NOT recommended materials for personal protective equipment.
Eye Protection:
Use chemical safety goggles and/or a full face shield where splashing is possible. Maintain eye wash fountain and quick-drench facilities in work area.
Other Control Measures:
Do not use closed circuit rebreathing system employing soda lime or other carbon dioxide absorber because of formation of toxic compounds capable of producing cranial nerve paralysis. See OSHA Standard for medical surveillance, record keeping, and reporting requirements for methylene chloride (29 CFR 1910.1052).

9. Physical and Chemical Properties

Appearance:
Clear, colorless liquid.
Odor:
Chloroform-like odor.
Solubility:
1.32 gm/100 gm water @ 20C.
Specific Gravity:
1.318 @ 25C
pH:
No information found.
% Volatiles by volume @ 21C (70F):
100
Boiling Point:
39.8C (104F)
Melting Point:

-97C (-143F)
Vapor Density (Air=1):
2.9
Vapor Pressure (mm Hg):
350 @ 20C (68F)
Evaporation Rate (BuAc=1):
27.5

10. Stability and Reactivity

Stability:
Stable under ordinary conditions of use and storage.
Hazardous Decomposition Products:
Emits highly toxic fumes of phosgene when heated to decomposition. Decomposes in a
flame or hot surface to form toxic gas phosgene and corrosive mists of hydrochloric acid.
Carbon dioxide and carbon monoxide may form when heated to decomposition.
Hazardous Polymerization:
Will not occur.
Incompatibilities:
Strong oxidizers, strong caustics, plastics, rubber, nitric acid, water + heat, and chemically
active metals, such as aluminum and magnesium powder, sodium, potassium, and lithium.
Avoid contact with open flames and electrical arcs. Liquid methylene chloride will attack
some forms of plastics, rubber, and coatings.
Conditions to Avoid:
Moisture, heat, flames, ignition sources and incompatibles.

11. Toxicological Information

Toxicological Data:
Dichloromethane: Oral rat LD50: 1600 mg/kg; inhalation rat LC50: 52 gm/m3; investigated
as a tumorigen, mutagen, reproductive effector.
Reproductive Toxicity:
Dichloromethane has been linked to spontaneous abortions in humans.

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--------\Cancer Lists\--------------------------------------------------------
                          ---NTP Carcinogen---
Ingredient                Known    Anticipated   IARC Category
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Methylene Chloride (75-09-2)       No       Yes          2B
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12. Ecological Information

Environmental Fate:
When released into the soil, this material may leach into groundwater. When released into
the soil, this material is expected to quickly evaporate. When released into water, this
material may biodegrade to a moderate extent. When released to water, this material is
expected to quickly evaporate. This material has a log octanol-water partition coefficient of
less than 3.0. This material is not expected to significantly bioaccumulate. When released

into the air, this material may be moderately degraded by reaction with photochemically produced hydroxyl radicals. When released into the air, this material is expected to have a half-life of greater than 30 days. When released into the air, this material may be removed from the atmosphere to a moderate extent by wet deposition.
Environmental Toxicity:
The LC50/96-hour values for fish are over 100 mg/l. This material is not expected to be toxic to aquatic life.

13. Disposal Considerations

Whatever cannot be saved for recovery or recycling should be handled as hazardous waste and sent to a RCRA approved incinerator or disposed in a RCRA approved waste facility. Processing, use or contamination of this product may change the waste management options. State and local disposal regulations may differ from federal disposal regulations. Dispose of container and unused contents in accordance with federal, state and local requirements.

14. Other Information

NFPA Ratings: Health: **2** Flammability: **1** Reactivity: **0**
Label Hazard Warning:
WARNING! HARMFUL IF SWALLOWED, INHALED OR ABSORBED THROUGH SKIN. AFFECTS CENTRAL NERVOUS SYSTEM, LIVER, CARDIOVASCULAR SYSTEM, AND BLOOD. CAUSES IRRITATION TO SKIN, EYES AND RESPIRATORY TRACT. SUSPECT CANCER HAZARD. MAY CAUSE CANCER. Risk of cancer depends on level and duration of exposure.
Label Precautions:
Do not breathe vapor.
Keep container closed.
Use only with adequate ventilation.
Wash thoroughly after handling.
Keep away from heat and flame.
Do not get in eyes, on skin, or on clothing.

Label First Aid:
If swallowed, DO NOT INDUCE VOMITING. Give large quantities of water. Never give anything by mouth to an unconscious person. If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Wash clothing before reuse. In all cases, get medical attention.

Appendix F2: Chlorobenzene

1. Product Identification

Synonyms: Monochlorobenzene; Chlorobenzol; Phenyl chloride; Benzene chloride
CAS No.: 108-90-7
Molecular Weight: 112.56
Chemical Formula: C6H5Cl

2. Composition/Information on Ingredients

Ingredient	CAS No	Percent	Hazardous
Chlorobenzene	108-90-7	99 - 100%	Yes

3. Hazards Identification

Emergency Overview

WARNING! FLAMMABLE LIQUID AND VAPOR. HARMFUL IF SWALLOWED OR INHALED. CAUSES IRRITATION TO SKIN, EYES AND RESPIRATORY TRACT. AFFECTS CENTRAL NERVOUS SYSTEM AND LIVER.

Health Rating: 2 - Moderate
Flammability Rating: 3 - Severe (Flammable)
Reactivity Rating: 1 - Slight
Contact Rating: 2 - Moderate
Lab Protective Equip: GOGGLES; LAB COAT; VENT HOOD; PROPER GLOVES; CLASS B EXTINGUISHER.
Storage Color Code: Red (Flammable)

Potential Health Effects

Inhalation:
Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Affects central nervous system causing dizziness, incoordination and unconsciousness.

Ingestion:
Causes irritation to the gastrointestinal tract. Symptoms may include nausea, vomiting and diarrhea. Toxic! May cause systemic poisoning with symptoms paralleling those of inhalation.
Skin Contact:
Causes irritation to skin. Symptoms include redness, itching, and pain. May be slowly absorbed through the skin with possible systemic effects.
Eye Contact:
Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage.
Chronic Exposure:
Prolonged or repeated skin exposure may cause dermatitis or skin burns. Prolonged or repeated exposure may cause liver, kidney, or lung damage.
Aggravation of Pre-existing Conditions:
Persons with pre-existing skin, eye or central nervous system disorders, or impaired liver, kidney, or pulmonary function may be more susceptible to the effects of this substance.

4. First Aid Measures

Inhalation:
Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.
Ingestion:
Give large amounts of water to drink. Never give anything by mouth to an unconscious person. Get medical attention.
Skin Contact:
Immediately flush skin with plenty of soap and water for at least 15 minutes while removing contaminated clothing and shoes. Get medical attention. Wash clothing before reuse. Thoroughly clean shoes before reuse.
Eye Contact:
Immediately flush eyes with plenty of water for at least 15 minutes, lifting lower and upper eyelids occasionally. Get medical attention immediately.

5. Fire Fighting Measures

Fire:
Flash point: 28C (82F) CC
Autoignition temperature: 593C (1099F)
Flammable limits in air % by volume:
lel: 1.3; uel: 9.6
Flammable Liquid
Explosion:
Above flash point, vapor-air mixtures are explosive within flammable limits noted above. Reactions with incompatibles may pose an explosion hazard. Vapors can flow along surfaces to distant ignition source and flash back. Sealed containers may rupture when heated. Sensitive to static discharge.
Fire Extinguishing Media:
Dry chemical, foam or carbon dioxide. Water spray may be used to keep fire exposed containers cool, dilute spills to nonflammable mixtures, protect personnel attempting to stop leak and disperse vapors.

Special Information:
In the event of a fire, wear full protective clothing and NIOSH-approved self-contained breathing apparatus with full facepiece operated in the pressure demand or other positive pressure mode. This highly flammable liquid must be kept from sparks, open flame, hot surfaces, and all sources of heat and ignition. Combustion by-products include phosgene and hydrogen chloride gases.

6. Accidental Release Measures

Ventilate area of leak or spill. Remove all sources of ignition. Wear appropriate personal protective equipment as specified in Section 8. Isolate hazard area. Keep unnecessary and unprotected personnel from entering. Contain and recover liquid when possible. Use non-sparking tools and equipment. Collect liquid in an appropriate container or absorb with an inert material (e. g., vermiculite, dry sand, earth), and place in a chemical waste container. Do not use combustible materials, such as saw dust. Do not flush to sewer! If a leak or spill has not ignited, use water spray to disperse the vapors, to protect personnel attempting to stop leak, and to flush spills away from exposures. US Regulations (CERCLA) require reporting spills and releases to soil, water and air in excess of reportable quantities. The toll free number for the US Coast Guard National Response Center is (800) 424-8802.

7. Handling and Storage

Protect against physical damage. Outside or detached storage is preferred. Inside storage should be in a standard flammable liquids storage room or cabinet. Separate from oxidizing materials. Storage and use areas should be No Smoking areas. Containers should be bonded and grounded for transfers to avoid static sparks. Containers of this material may be hazardous when empty since they retain product residues (vapors, liquid); observe all warnings and precautions listed for the product.

8. Exposure Controls/Personal Protection

Airborne Exposure Limits:
-OSHA Permissible Exposure Limit (PEL):
75 ppm (TWA)

-ACGIH Threshold Limit Value (TLV):
10 ppm (TWA)

Ventilation System:
A system of local and/or general exhaust is recommended to keep employee exposures below the Airborne Exposure Limits. Local exhaust ventilation is generally preferred because it can control the emissions of the contaminant at its source, preventing dispersion of it into the general work area. Please refer to the ACGIH document, *Industrial Ventilation, A Manual of Recommended Practices*, most recent edition, for details.

Personal Respirators (NIOSH Approved):
If the exposure limit is exceeded and engineering controls are not feasible, a half-face organic vapor respirator may be worn for up to ten times the exposure limit, or the maximum use concentration specified by the appropriate regulatory agency or respirator supplier,

whichever is lowest. A full-face piece organic vapor respirator may be worn up to 50 times the exposure limit, or the maximum use concentration specified by the appropriate regulatory agency or respirator supplier, whichever is lowest. For emergencies or instances where the exposure levels are not known, use a full-face piece positive-pressure, air-supplied respirator. WARNING: Air-purifying respirators do not protect workers in oxygen-deficient atmospheres.

Skin Protection:
Wear impervious protective clothing, including boots, gloves, lab coat, apron or coveralls, as appropriate, to prevent skin contact.

Eye Protection:
Use chemical safety goggles and/or a full face shield where splashing is possible. Maintain eye wash fountain and quick-drench facilities in work area.

9. Physical and Chemical Properties

Appearance:
Clear, colorless liquid.
Odor:
Faint, almond like odor.
Solubility:
Insoluble in water.
Specific Gravity:
1.11 @ 20C/4C
pH:
No information found.
% Volatiles by volume @ 21C (70F):
100
Boiling Point:
132C (270F)
Melting Point:
-45C (-49F)
Vapor Density (Air=1):
3.9
Vapor Pressure (mm Hg):
11.8 @ 25C (77F)
Evaporation Rate (BuAc=1):
1.1

10. Stability and Reactivity

Stability:
Stable under ordinary conditions of use and storage.
Hazardous Decomposition Products:
May produce carbon monoxide, carbon dioxide, hydrogen chloride and phosgene when heated to decomposition.
Hazardous Polymerization:
Will not occur.
Incompatibilities:
Oxidizing agents, dimethyl sulfoxide, silver perchlorate, silver chromate.

Conditions to Avoid:
Heat, flames, ignition sources and incompatibles.

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11. Toxicological Information

For Chlorobenzene: Oral rat LD50: 1110 mg/kg; Inhalation rat LC50: 2965 ppm.
Investigated as a tumorigen, mutagen, reproductive effector.
--------\Cancer Lists\---
                              ---NTP Carcinogen---
Ingredient   Known   Anticipated   IARC Category
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Chlorobenzene (108-90-7)   No   No   None

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12. Ecological Information

Environmental Fate:
When released into the soil, this material may evaporate to a moderate extent. When released into the soil, this material is not expected to biodegrade. When released into the soil, this material may leach into groundwater. When released to water, this material is expected to quickly evaporate. When released into the water, this material is expected to have a half-life of less than 1 day. When released into water, this material is not expected to biodegrade. This material is not expected to significantly bioaccumulate. When released into the air, this material may be moderately degraded by reaction with photochemically produced hydroxyl radicals. When released into the air, this material is expected to have a half-life between 1 and 10 days.
Environmental Toxicity:
The LC50/96-hour values for fish are between 10 and 100 mg/l. This material is expected to be slightly toxic to aquatic life.

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13. Disposal Considerations

Whatever cannot be saved for recovery or recycling should be handled as hazardous waste and sent to a RCRA approved incinerator or disposed in a RCRA approved waste facility. Processing, use or contamination of this product may change the waste management options. State and local disposal regulations may differ from federal disposal regulations. Dispose of container and unused contents in accordance with federal, state and local requirements.

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14. Other Information

NFPA Ratings: Health: 2 Flammability: 3 Reactivity: 0
Label Hazard Warning:
WARNING! FLAMMABLE LIQUID AND VAPOR. HARMFUL IF SWALLOWED OR INHALED. CAUSES IRRITATION TO SKIN, EYES AND RESPIRATORY TRACT. AFFECTS CENTRAL NERVOUS SYSTEM AND LIVER.
Label Precautions:

Keep away from heat, sparks and flame.
Avoid breathing vapor.
Keep container closed.
Wash thoroughly after handling.
Avoid contact with eyes, skin and clothing.
Use only with adequate ventilation.

Label First Aid:

If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. If swallowed, give large amounts of water to drink. Never give anything by mouth to an unconscious person. In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes. Remove contaminated clothing and shoes. Wash clothing before reuse. In all cases, get medical attention.

Product Use:

Laboratory Reagent.