PYROLYSIS OF CHLORINATED

ORGANIC CHEMICALS

by

Kleantha Pillay

Submitted in fulfillment of the academic requirements for the degree of Master of Science in Engineering in the School of Chemical Engineering, University of Natal, Durban.

December 2001

Supervisor: Prof. D.R. Arnold

Co-supervisor: Prof. D. Ramjugernath

ABSTRACT

At present, South Africa has inadequate technology to destroy its hazardous waste, with approximately 18 000 litres of chlorinated hazardous waste stored in this country. Approximately 800 tons of banned or obsolete chemicals are to be sent to Pontypool, Wales, for incineration, at a considerable cost. Because of the toxic nature of chlorinated waste and their long-term effects on the environment, a sustainable method of dealing with this type of waste is essential.

Gas phase destruction of methylene chloride, trichlorobenzene and lindane by pyrolysis (i.e. heating in the absence of oxygen) was attempted. Destruction was effected by high temperature thermal degradation of molecules into free radicals. These radicals then combine to form hydrogen chloride and carbon as major products. This method was chosen so as to eliminate the possible formation of highly toxic oxygenated derivatives such as polychlorinated dibenzofurans and dibenzodioxins that can be formed during incineration if strict control is not excercised.

The reactor assembly was built in the Department of Chemical Engineering at the University of Natal. It incorporates aspects of many different previously designed reactors, as discussed in the text. Heat for the reactions was supplied by induction. A high frequency induction unit supplied current to a copper coil. The resulting magnetic field induced current to flow in a susceptor housed within the copper coil. The susceptor in this case was a graphite tube, which served as both the heating element and the thermal radiation source, in addition to forming the walls of the reaction zone. Up and down stream processes were designed and experiments were carried out in which reaction temperatures (348-1400°C) and residence times (1.3-5.6 seconds) were varied.

Destruction efficiencies of 100% and 99.99% were obtained for methylene chloride and trichlorobenzene respectively, with inert argon used as the carrier gas. These destruction efficiencies comply with the 99.99% stipulated by the United States Conservation and Recovery Act. A cause for concern was the formation of chlorinated benzenes and naphthalenes. Destruction of lindane proved unsuccessful due to limitations in the vapourisation and feed system and will have to be investigated further. The method of induction heating was evaluated to be 98.9% thermally efficient.

Raw material and utility consumption per ton of waste destroyed by the pyrolysis process was compared to values for incineration as well as the plasma arc and catalytic extraction processes.

Consumption for pyrolysis compares favourably with all three processes and suggests that the process could be competitive.

Claims to the success of the technology on a wide scale are limited by the small number of compounds that were successfully pyrolysed. Results do however indicate much promise for this technology to be used as a final chlorinated waste destruction unit on an existing process. Modifications to the existing reactor to improve product recovery and analysis will allow for temperature and residence time optimisation for a variety of wastes. Additional instrumentation and process control will allow for kinetic studies to be undertaken in future. This project should be considered as the first step in an ongoing series of research and subsequent improvements to the technology presented here.

PREFACE

The work presented in this thesis was performed at the University of Natal, Durban, from February 2000 to October 2001. The work was supervised by Prof. D.R. Arnold and Dr D. Ramjugernath.

This thesis is presented as the full requirement for the degree M.Sc. Engineering (Chemical). All the work presented is original, unless otherwise stated and has not, in whole or part, been submitted previously to any tertiary educational institution as part of a degree.

K. Pillay

19 Feb 2002

Date

I, the supervisor of this project, Professor D.R. Arnold, have accepted and approved the submission of this thesis for examination.

D.R. Arnold

19 Feb 2002

Date

ACKNOWLEDGEMENTS

I would like to acknowledge the following people and organisations for their contribution to this project:

- Prof. Arnold and Prof. Ramjugernath for their guidance, support and ideas.
- Deon van Staden and Gary Whelan from Quadro Engineering for sponsorship of the reactor and repairs to the induction unit.
- The workshop staff at the School of Chemical Engineering –Les, Ken, Kelly, Michael, Dudley and Colin.
- The 'hazop team' for their time and invaluable experience.
- The National Research Foundation for funding.

CONTENT

LIST OF FIGURES

LIST OF TABLES

LIST OF ACRONYMS AND SYMBOLS

ACRONYMS

ASTM	American Society for Testing of Materials
DE	Destruction Efficiency
DEAT	Department of Environmental Affairs and Tourism
DHHS	Department of Health ans Human Services
DRE	Destruction and Removal Efficiency
EEC	European Enviromental Council
EPA	Environmental Protection Agency
HCB	Hexachlorobenzene
PCB	Polychlorinated biphenyls
PCBz	Polychlorinated benzenes
PCDD	Polychlorinated dibenzodioxins
PCDF	Polychlorinated dibenzofurans
PCPh	Polychlorinated phenols
PIC	Product of incomplete combustion
POP	Persistent Organic Pollutant
TCDD	Tetrachlorodibenzodioxin
TCDF	Tetrachlorodibenzofuran
TEF	Toxicity Equivalency Factors
PAH	Polycyclic aromatic hydrocarbon

SYMBOLS

A	GC peak area
α	lumped parameter = (UA)
A	heat transfer area
Cp	specific heat
D	change
ΔG°	standard Gibbs energy change of reaction

ΔH°	standard enthalpy change of reaction
ΔS°	standard entropy change of reaction
ϕ	phase angle
ΔH_R	heat of reaction
I	current
m	mass
P	power
R	universal gas constant
T	temperature
t	time
U	overall heat transfer coefficient
V	voltage
wt	weight

SUBSCRIPTS

1	initial reactor condition
2	final reactor condition
a	ambient condition
e	ethanol
h	n-hexane
in	initial organic feed condition
o	organic feed
t	tube

1. INTRODUCTION

Persistent organic pollutants (POPs) are organic compounds that resist biological, chemical and photolytic degradation to varying degrees. Of these POPs, many organochlorine insecticides such as dieldrin, DDT and chlordane, and several industrial chemical products and byproducts including polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (PCDDs) and dibenzo-p-furans (PCDFs), are noted for their persistence and bioaccumulative characteristics.

Two important subgroups of POPs are polycyclic aromatic hydrocarbons (PAHs) and some halogenated hydrocarbons. Chlorinated organic compounds have become entrenched in society. They are widely used in the chemical industry for the production of polyvinyl chloride, solvents, pesticides, specialty chemicals and pharmaceuticals.

Carbon-chlorine bonds are very stable to hydrolysis and the molecule's resistance to biological and photolytic degradation increases with increasing chlorine substitution. Chlorine in an aliphatic structure is less stable to hydrolysis than chlorine attached to an aromatic ring. As a result, chlorinated POPs are generally ring structures with chain or branched chain frameworks.

Polychlorinated biphenyls (PCBs) are mixtures of chlorinated hydrocarbons that have been used extensively since 1930 in industrial applications. Since they were identified in fish in the late 1960's, they have been identified in diverse areas of the environment. Production of PCBs in the United States was stopped in 1977 because of the tendency of these products to bioaccumulate and persist in the environment, owing to low degradation rates and because of toxic effects. PCBs are still present in many of the capacitors and transformers in use today, and stores of PCBs all over the world await destruction by a suitable environmentally safe technology. Most sources of organochlorides are man-made. Hexachlorobenzene (HCB), dioxins and furans however, are unintentional byproducts of manufacturing and combustion processes. Dioxins and furans, in particular, are products of hazardous waste incinerators.

The aim of this project is to identify and bring to the fore a suitable technology to destroy such chlorinated organic waste by illustrating its successful operation. Attention will be given to the nature of the by-products formed.

1.1 Chemistry of PCBs

The PCBs form a class of chlorinated hydrocarbons and are manufactured by the progressive chlorination of biphenyl in the presence of a suitable catalyst. PCBs are also called chlorinated biphenyls, chlorobiphenyls and polychlorobiphenyls.

The empirical formula for this family of compound is $C_{12}H_{10-n}Cl_n$, with n = 1 – 10. Homologues exist and differ from each other in the number of chlorine atoms that the molecule contains. There are ten different homologues of PCBs and each homologue has a particular number of isomers. Theoretically, the formation of 209 different PCBs is possible [van der Westhuizen, 1994].

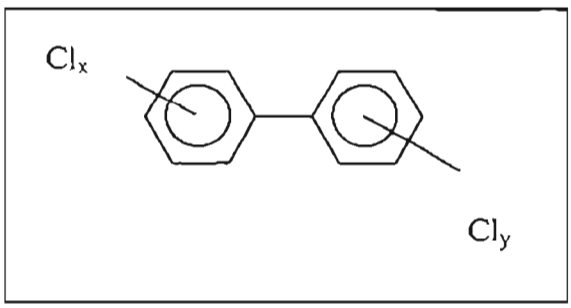


Figure 1-1: General PCB structure

Table 1-1: PCB Homologues and Number of Isomers

Homologue	Number of Isomers
Monochlorobiphenyl	3
Dichlorobiphenyl	12
Trichlorobiphenyl	24
Tetrachlorobiphenyl	42
Pentachlorobiphenyl	46
Hexachlorobiphenyl	42
Heptachlorobiphenyl	24
Octachlorobiphenyl	12
Nonachlorobiphenyl	3
Decachlorobiphenyl	1

PCBs are known by a variety of trade names:

Arochlor (USA)
Phenochlor (France)
Clophen (Germany)
Kanechlor (Japan)
Fenchlor (Italy)
Sovol (USSR)

The value of PCBs for industrial applications was related to their chemical inertness, thermal and oxidative stability, heat and fire resistance and high dielectric constant. They were used as dielectrics in transformers and large capacitors, as heat exchange fluids, as paint additives, in carbonless copy paper and in plastics.

Half lives for PCBs undergoing photodegradation range from approximately 10 days for a monochlorobiphenyl to 1.5 years for a heptachlorobiphenyl. Since the hazardous nature and overwhelming occurrence of PCBs were discovered, production of PCBs in the United States was banned by the EPA. Although the production of PCBs has become almost insignificant over the last 15 years, stores of PCB containing oil and equipment remain and some means of effective disposal is required.

1.2 Chemistry of Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) & polycyclic aromatic hydrocarbons (PAHs)

At present most chlorinated waste destruction is effected by incineration. This method, however, can lead to the formation of toxic oxygenated derivatives, namely dioxins. Dioxins include PCDDs and PCDFs. Dioxins and furans may contain between 1 and 8 chlorine atoms. There are 75 possible dioxin isomers and 135 furan isomers. Neither dioxins nor furans are produced commercially and they have no known use. They are by-products resulting from the production of other chemicals. Dioxins are released into the environment through the production of pesticides and other chlorinated substances, while furans are a major contaminant of PCBs. Both have been related to a variety of incineration processes and have been detected in emissions from the incineration of hospital waste, municipal waste and hazardous waste.

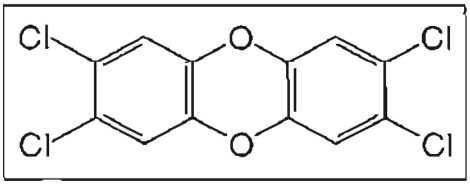


Figure 1-2: PCDD – 2,3,7,8 TCDD

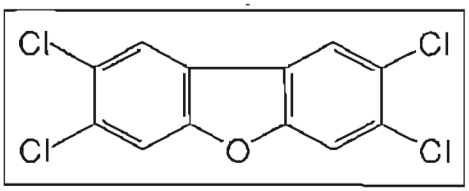


Figure 1-3: PCDF – 2,3,7,8 TCDF

Polycyclic aromatic hydrocarbons (PAHs) are a group of over 100 different chemicals formed during the incomplete combustion of organic matter and are known to be precursors to more complex soot particles. PAHs are usually found as a mixture containing two or more of these compounds, such as soot. Soot formation increases with increasing chlorine : hydrogen ratio in the feed as a result of chlorine catalysed pyrolysis and increased abstraction of aromatic hydrogen by chlorine [McKinnon & Howard, 1990; Marr *et al*, 1992]. PAHs are formed by fusion of several benzene rings with each other, or with cyclopentadiene.

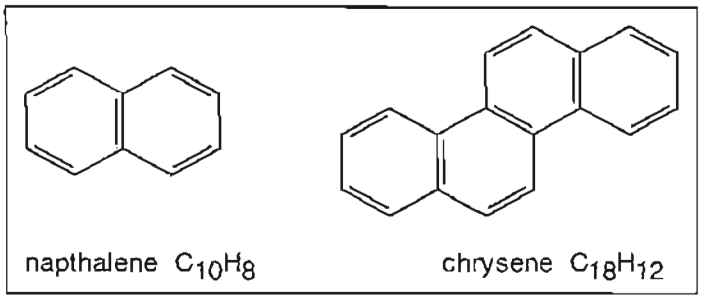


Figure 1-4: Some PAH molecules

1.3 Toxicology of PCBs, PCDD/Fs and PAHs

1.3.1 PCBs

The chemical stability of PCBs allows them to be resistant to biodegradation. They are persistent and concentrate upwards in the food chain.

The toxicology of PCBs increases with the number of substituted chlorine atoms. PCBs have been detected in various tissues of individuals with no known occupational or unique environmental

exposure. High PCB exposure has been linked to alterations in liver enzymes, and dermatological effects such as rashes and acne have been reported [UNEP, 1995].

Incidents of mass PCB poisoning have also occurred in Japan (1968) and Taiwan (1979) through contaminated rice oil. Children born up to 7 years after maternal exposure in the Taiwan incident exhibited hyperpigmentation, deformed nails and teeth and delayed intrauterine growth. Fetuses are potentially more sensitive to PCBs than adults. PCBs accumulate in breast milk, placing nursing infants at additional risk.

Excretion of PCBs is slow and the higher the chlorination, the longer it takes to be excreted from the body. People exposed in the Japan incident suffered from low immunity and thus a variety of infections.

Cancer deaths in both male and female workers involved in the manufacture of electrical capacitors increased significantly. Carcinogenecity of PCBs in humans has not yet been reliably proven, but there is some suggestion that PCBs are associated with malignant melanoma, leukemia and cancers of the liver, gall bladder and the billary tract in people occupationally exposed. The U.S. Department of Health and Human Services has determined that PCBs may reasonably be anticipated to be carcinogens. While the role of PCBs in producing cancer, reproductive, and developmental defects in humans cannot be clearly delineated, the suggestive evidence provides an additional basis for public health concern about humans who may be exposed to PCBs. PCBs have been shown to promote, but not initiate cancers [UNEP, 1995].

1.3.2 PCDD/Fs

Seventeen of the 210 dioxins and furans contribute most significantly to the toxicity of complex mixtures. Toxicity Equivalency Factors (TEFs) have been assigned to individual dioxins and furans based on a comparison to the toxicity of 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD). These compounds, like PCBs, are concentrated by food chains and bioaccumulate.

The only persistent effect associated with dioxin exposure in humans is chloroacne. Effects such as enlarged liver, abnormal enzyme levels, hepatitis, neuropathies, fatigue and depression have been reported [UNEP, 1995]. Results of a study of 1520 workers exposed to 2,3,7,8-TCDD for a period of one year and with a latency of at least twenty years between exposure and diagnosis of a disease,

revealed a significantly higher mortality from soft tissue sarcoma and cancers of the respiratory system. The interpretation of these results was limited by the small number of deaths and possible cofounders such as smoking and other occupational exposures.

While there is inadequate evidence for the carcinogenicity of 2,3,7,8-TCDD in humans, there is sufficient evidence in experimental animals. 2,3,7,8-TCDD has been classified as a possible human carcinogen.

There is currently no health value for furans, but they appear to be less potent that 2,3,7,8-TCDD.

Studies of carcinogenesis associated with occupational exposure to 2,3,7,8-TCDD seem to indicate that high exposure of humans does elevate overall cancer incidence [UNEP, 1995, 1999]. Laboratory studies provide convincing supporting evidence that selected dioxins and furans may have carcinogenic effects and act as strong tumor promoters.

1.3.3 PAHs

The Department of Health and Human Services (DHHS) in the United States, has determined that some PAHs may reasonably be expected to be carcinogens. Benzo (a) pyrene, (BaP) was identified as a strong animal and human carcinogen as early as 1933 [UNEP, 1995].

Mice that were fed high levels of one PAH during pregnancy had difficulty reproducing and so did their offspring. These offspring also had higher rates of birth defects and lower body weights. It is not known whether these effects occur in people.

1.4 International requirements for hazardous waste destruction

A certain degree of destruction has to be achieved before a material can be described as destroyed. The effectiveness of a waste destruction system is based on the percentage of the initial hazardous component destroyed. The efficiency of waste destruction is commonly described by two similar terms: destruction efficiency (DE) and destruction and removal efficiency (DRE).

The Conservation and Recovery Act (1976) in the United States stipulates a DRE of 99.99% for halogenated material. However, the Environmental Protection Agency (EPA) requires a DRE of 99.9999% for highly chlorinated organic substances. PCBs are classified as either chlorinated or highly chlorinated organics, depending on the make-up of the material. By ASTM standards, a material is considered PCB free if the PCB content is less than 100ppm. For waste containing PCCD/Fs, the EPA standard is 99.9999% DE, while that of the ASTM is 99.99999% DE. Thus, the process can allow for less than 1ppm (EPA) or 0.1ppm (ASTM) of unconverted source material. Waste that does not contain PCDD/Fs, but are converted to these compounds during incineration must contain less that 1ppb (EPA) or 0.1ppb (EEC).

Hydrochloric acid is another major byproduct of the destruction process of chlorinated organics. The maximum emission level of hydrogen chloride in South Africa is $10g/m^3$. In the United States, the regulatory standards governing the emission of hydrogen chloride range from outlet emissions of 30-50ppb in some states, to 90% removal requirement in other states.

The South African Department of Environmental Affairs and Tourism [National waste management strategies and action plans, 1999] undertook to develop

- A classification system for waste treatment facilities
- A register of waste treatment facilities
- Regulations and standards for waste treatment facilities
- Revised air emission standards for waste incineration facilities

They have estimated that the activities necessary to achieve these outputs will take as long as 3 years and should be completed by December 2002.

Currently, the Department of Environmental Affairs and Tourism is responsible for establishing and maintaining a register of waste disposal facilities, as well as for permitting, monitoring and auditing of hazardous waste disposal facilities.

1.5 Motivation & Objective

Inefficient incineration techniques for the destruction of hazardous waste leads to the formation of PCBs, PCDD/Fs and other products of incomplete combustion (PICs). The following compounds have been identified as principal organic hazardous constituents and PICs by the EPA (1989):

- Chlorinated inorganics
- Chlorinated alkanes
- Chlorinated alkenes
- Chlorinated benzenes
- Chlorinated phenols
- Chlorinated dioxins and furans

Incinerator emissions result from substances in waste feedstock or products that are not completely removed by emission control. The products of incomplete combustion (PICs) usually form from recombination or reformation processes in the post-combustion section of the incinerator.

Presently there are approximately 18 000 litres of Askerel fluid (mixtures of commercial PCB mixtures and trichlorobenzene) stored in South Africa, with another approximately 255 000 litres of PCB containing capacitor oil still in use. Incineration is the most widely used destruction technique overseas, but an alternative to this technology will be welcomed because of the disadvantages it poses.

The National Department of Agriculture has announced that approximately 800 tons of banned and obsolete chemicals in South Africa were to be collected and sent to Pontypool, Wales, for disposal [Boon, 2000]. There, a company called ReChem is to incinerate the waste in a plant that now produces no dioxins and furans at measurable levels (0.1 ng /cm^3). South Africa is a signatory to the Basel Convention, which aims to restrict the shipment of hazardous waste across boundaries. However, countries with inadequate technology may export their hazardous waste to other countries, provided that the final method of disposal is environmentally sound. At present, South Africa does not have any suitable destruction facilities available and a sustainable method of dealing with the waste is necessary.

At present, destruction by incineration is proven technology and meets the emission standards. The are many operational plants, although not in South Africa. Very high capital costs are necessary to meet the emission standards. In comparison, the newer plasma arc technology requires a lower capital expenditure as well as lower operation costs. Again, few plants are operational and the power costs are high. High capital costs and unknown operating costs as well as the fact that there are currently no operating plants are disadvantages to the molten metal extraction process (see Chapter 3).

The fully absorbed operating and capital costs of three of the more established processes are compared in table 1-2 [Arnold, personal communication, 2000].

Table 1-2: Comparative costs for waste destruction methods based on a plant capacity of 7440 tpa in 1997

	Incineration	Plasma Arc	Molten Metal	Encapsulation
Capital Cost (Rm)	94.00	42.39	72.43	NIL
Operating Cost (R/t)	5788.00	3001.00	5086.90	4000.00

Van der Westhuizen [1994] carried out a series of high temperature, reductive pyrolysis experiments at the University of Stellenbosch. The reactor consisted mainly of graphite and was heated by electrical impedance. Destruction efficiencies of typically 99.9999%, not only for PCB, but also for a number of other chlorinated hydrocarbons were achieved. Eskom has developed a pyrolysis process in which the DRE of lindane and trichlorobenzene apparently meets standards. The technology suffered from the blocking of the reactor. This problem was solved and Quadro Engineering presently uses this technology to synthesize hydrogen cyanide. It is possible that the destruction of chlorinated waste by pyrolysis could have lower capital and operating costs than the other alternatives. This method is also interesting because it produces two valuable byproducts: carbon black and hydrogen chloride. It is also fairly simple as compared to incineration and plasma arc technology and is a compact process.

The primary objective of this project is to illustrate that technology similar to that used by Quadro Engineering can be successfully used for the destruction of chlorinated chemical compounds. This is to be done by:

- Constructing a suitable reactor assembly
- Designing equipment up and down stream of the reactor
- Identifying reaction products, as well as the changes in the product spectra with temperature and residence time variations.
- Successfully destroying both an aliphatic and an aromatic compound
- Successfully destroying a sample of actual industrial waste
- Evaluate the efficiency of the chosen method of heat transfer to the reactants

A secondary objective is to destroy wastes which occur both in the liquid and solid state and to investigate the economic viability of the proposed process.

2. PYROLYSIS EXPERIMENTS, RESULTS AND PROPOSED REACTION MECHANISMS

2.1 Introduction

Although there is some controversy about the importance of the different possible mechanisms of hydrocarbon pyrolysis, it is generally agreed that the reactions occur by a radical chain mechanism. A mechanism to account for first order kinetics of organic pyrolysis mechanisms was proposed by Rice and Herzfeld [1934]. Their proposal is summarised below:

Step 1 - Initiation:	The molecule splits at its weakest link, initiating free radicals.
Step 2 – Propagation:	One of these radicals abstracts a hydrogen atom from the parent molecule, forming a saturated molecule and a new free radical. Both radicals may react in this manner.
Step 3 – Termination:	Chain ending occurs through disproportionation or association of radicals.

Savage [2000] summarised the elementary reaction families in hydrocarbon pyrolysis, as shown in Figure 2-1. These reversible free-radical reactions provide opportunities both for molecular degradation (breaking chemical bonds) as well as molecular growth (forming chemical bonds). Often multiple bonds are available to be broken, but the path that involves cleavage of the weakest bond is expected to occur most quickly. Typically, C-H bonds are stronger than C-C bonds. Bond strengths can be affected by the presence of double bonds and aromatic rings [Benson, 1960].

Much experimental work on hydrocarbon and more specifically, chlorinated hydrocarbon pyrolysis has been carried out since the Rice-Herzfeld mechanism was proposed, and the some of the results and proposed pyrolysis mechanisms are discussed in this chapter.

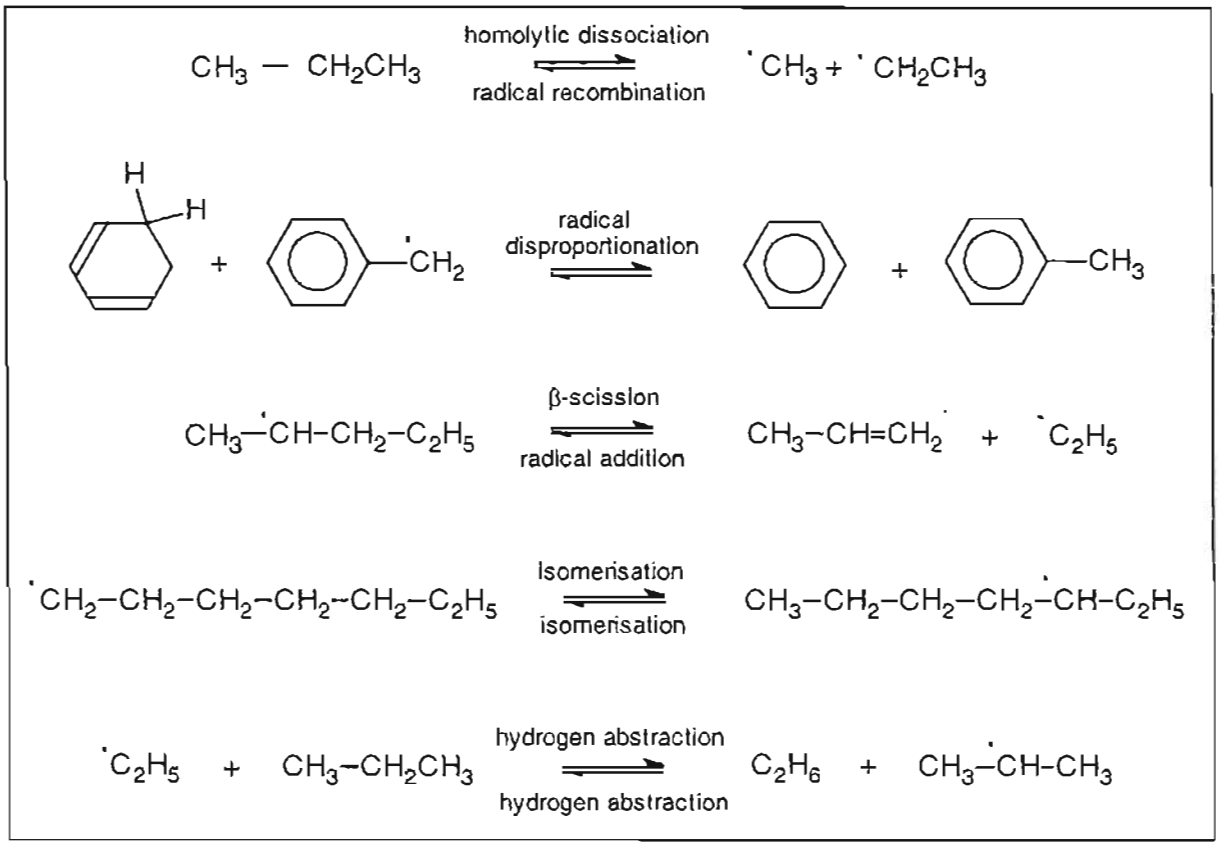


Figure 2-1: Main reaction families for hydrocarbon pyrolysis

2.2 Pyrolysis of Chlorinated Aliphatic Compounds

Barton and Howlett [1950] pyrolysed 1,1,2,2- and 1,1,1,2-tetrachloroethane overnight at temperatures between 263 - 382°C, to give trichloroethylene and hydrogen chloride. It was found that the addition of propylene to the reactant caused a directly proportional increase in the length of the decomposition time. No decomposition occurred during this time, and it was concluded therefore that the decomposition proceeded entirely by chain mechanism.

The reaction mechanism was represented by the following steps; similar to those proposed by Rice and Herzfeld:

Initiation: First order decomposition of 1,1,2,2-tetrachloroethane to furnish chlorine atoms.

Propagation: (i) $Cl + CHCl_2{}^{\bullet}CHCl_2 \rightarrow HCl + {}^{\bullet}CCl_2{}^{\bullet}CHCl_2$

(ii) ${}^{\bullet}CCl_2{}^{\bullet}CHCl_2 \rightarrow CCl_2{:}CHCl + Cl$

Termination: $Cl + {}^{\bullet}CCl_2{}^{\bullet}CHCl_2 \rightarrow HCl + CCl_2{:}CCl_2$

Tirey *et al* [1990] conducted high temperature gas phase pyrolysis of tetrachloroethene (C_2Cl_4) in a 0.97 mm inside diameter quartz tube with length of 980 mm. Helium was used as a carrier gas and residence times of 2 seconds were achieved over a temperature range of 300 - 1050°C. Significant yields of chlorinated olefinic and aromatic species were observed, with hexachlorobenzene being the major product.

A simplified reaction set accounting for the formation of Cl_2, CCl_4 and C_6Cl_6 is presented in Table 2-1.

In addition to reactions 1 and 2, the reaction below was also considered as a step in the decomposition of C_2Cl_4:

$$C_2Cl_4 + Cl \Leftrightarrow C_2Cl_3 + Cl_2$$

However, the abstraction of chlorine by another chlorine atom is highly endothermic. This reaction was thus eliminated. The trichlorovinyl radical (C_2Cl_3) produced in reaction 1 is subject to carbon-chlorine bond homolysis to yield C_2Cl_2. Rapid elimination of C_2Cl_2 to form C_2 and Cl_2 is unlikely. This reaction, although exothermic, has activation energies much larger than the heat of reaction [Benson, 1960]. Thus, instead of C-Cl bond scission (high bond energy), the only pathway open to C_2Cl_2 is molecular growth reactions. These will be discussed later.

Table 2-1: Partial reaction scheme for C_2Cl_4 pyrolysis

(non-aromatic species)

1.	$C_2Cl_4 = C_2Cl_3 + Cl$
2.	$C_2Cl_4 = C_2Cl_2 + Cl_2$
3.	$C_2Cl_3 + M = C_2Cl_2 + Cl + M$
4.	$C_2Cl_4 + Cl = C_2Cl_5^{\bullet} \rightarrow CCl_3 + CCl_2$
5.	$2\,CCl_2 + M = C_2Cl_4 + M$
6.	$C_2Cl_3 + Cl + M = CCl_4 + M$
7.	$CCl_3 + Cl_2 = CCl_4 + Cl$
8.	$2\,Cl + M = Cl_2 + M$
9.	$C_2Cl_4 + CCl_3 = C3Cl7^{\bullet} \rightarrow C_3Cl_6 + Cl$
10.	$C_2Cl_4 + C_2Cl_3 = C_4Cl_7^{\bullet} \rightarrow C_4Cl_6 + Cl$
11.	$C_4Cl_6 = n\text{-}C_4Cl_5 + Cl$
12.	$C_2Cl_3 + C_2Cl_2 = n\text{-}C_4Cl_5^{\bullet} \rightarrow n\text{-}C_4Cl_4 + Cl$
13.	$n\text{-}C_4Cl_4 = n\text{-}C_4Cl_3 + Cl$
14.	$C_2Cl_4 + n\text{-}C_4Cl_5 = C_6Cl_9^{\bullet} \rightarrow C_6Cl_8 + Cl$
15.	$C_4Cl_6 + C_2Cl_3 = C_6Cl_9^{\bullet} \rightarrow C_6Cl_8 + Cl$

Pathways to the formation of aromatic products generally involve cyclisation of acetylenic species:

$$Cl_2C{=}ClC\text{-}CCl{=}^{\bullet}CCl + ClC{\equiv}CCl \leftrightarrow C_6Cl_6 \text{ (cyclic)} + Cl$$

A continuation of this work was carried out by Taylor *et al* [1996]. Detailed analyses were carried out on the products of tetrachloroethene pyrolysis from 300 – 1000°C and 1.83 atm. The effects of reactor surface area to volume (S/V) were investigated in two fused-silica tubular flow reactors of 1mm and 10mm inside diameters. At high S/V ratios, C_2Cl_4 decomposition was initiated at 700°C and included products of Cl_2, CCl_4, C_4Cl_6 and C_6Cl_6 (cyclic). Under low S/V ratios, decomposition was initiated at 900°C with products of C_2Cl_2 and C_6Cl_6 (cyclic). The hexachlorobenzene yields at lower S/V ratios were a factor of 4 larger than those at higher S/V ratios. These results are in line with those of Tirey *et al* [1990].

Earlier, Taylor *et al* [1994] used the experimental set-up mentioned above to pyrolyse trichloroethene (C_2HCl_3) at a residence time of 1.7 seconds. Initial decomposition occurred at 727°C, with C_2Cl_2 and hydrogen chloride being the major observed products. Molecular growth was observed at higher temperatures with C_2Cl_2, C_2Cl_4 and C_6Cl_6 being produced.

Analyses showed that C-Cl bond fission is the dominant initiation step. The hydrogen atom in C_2HCl_3 is then abstracted by the chlorine atom produced in the first step, yielding trichlorovinyl radical and hydrogen chloride. C_2Cl_3 then either loses a chlorine atom to form C_2Cl_2, or reacts with Cl_2 to form C_2Cl_4. The trichlorovinyl radical can also add to other radicals present to give higher molecular weight compounds. Rapid abstraction of hydrogen by chlorine inhibits the formation of high molecular weight hydrocarbons, and any hydrogen-containing C_1 and C_2 species that form are rapidly destroyed by chlorine abstraction of hydrogen.

Based on the absence of production of chlorinated aromatics from methyl chloride and methylene chloride as compared with carbon tetrachloride and chloroform, it was proposed by Taylor and Dellinger [1999] that condensation reactions are promoted by chlorine radicals. This accounts for the formation of chlorinated aromatic species.

Taylor and Dellinger [1988] investigated the thermal degradation characteristics of chloromethane mixtures. Under pyrolytic conditions, methylene chloride was 99% destroyed at approximately 850°C and a residence time of 2 seconds.

The formation mechanisms of high molecular weight polycyclic aromatic hydrocarbons (PAH) are discussed later in this chapter.

2.3 Pyrolysis of Chlorinated Aromatic Compounds

The most well documented chlorinated aromatic compound to be pyrolysed is chlorobenzene. The high temperature pyrolysis of chlorobenzene is important as it serves as a prototype chlorinated aromatic hydrocarbon of interest for studies of toxic waste destruction.

Louw *et al* [1973] interpreted chlorobenzene pyrolysis as a radical chain reaction, with the radicals C_6H_4Cl, chlorine (Cl) and hydrogen (H) as carriers. Their experiments were carried out in nitrogen gas at 500°C, with a residence time between 105 and 120 seconds. Biphenyl, chlorobiphenyls and bichlorophenyls were produced. The effect of different additives, namely chlorine, formaldehyde and azobenzene, on product formation was monitored. These additives were sources of chlorine, hydrogen and phenyl radicals respectively, and had a marked effect on the amounts and compositions of the biaryls formed.

A more recent investigation by Ritter *et al* [1990] on the thermal decomposition of a chlorobenzene-hydrogen mixture in a tubular flow reactor at conditions of 1050 – 1275°C, 1 atm total pressure and 0.02 – 2.5 seconds residence time indicated that hydrogen chloride, benzene and solid carbon were the major products. Methane, toluene, naphthalene and biphenyl were produced in smaller amounts. Subsequent pyrolysis of chlorobenzene in helium resulted in significantly lower conversion to recoverable products and increased soot formation.

Kern *et al* [1992] undertook a shock tube study of chlorobenzene pyrolysis in neon. Temperatures between 1307 - 1727°C were employed at 0.3 – 0.5 atm, with reaction times of 700μs. Acetylene, hydrogen chloride and diacetylene were the major products, with trace amounts of benzene, C_6H_2 and C_8H_2 detected. Only phenyl radicals were detected by mass spectrometry, and the only chlorine-containing product detected was hydrogen chloride. No traces of oxygenated compounds were observed.

An interesting chain carried by chlorine atoms was identified. The initial decomposition reaction,

$$C_6H_5Cl \leftrightarrow C_6H_5 + Cl \qquad (1)$$

produces the chlorine radicals, which then propagate the following chain steps:

$$Cl + C_6H_5Cl \leftrightarrow C_6H_4Cl + HCl \qquad (2)$$

$$C_6H_4Cl + C_6H_5Cl \rightarrow C_{12}H_9Cl + Cl \qquad (3)$$

$$C_{12}H_9Cl + Cl \rightarrow C_{12}H_8Cl + HCl \qquad (4)$$

$$C_{12}H_8Cl + C_6H_5Cl \rightarrow C_{18}H_{13}Cl + Cl \qquad (5)$$

These reactions illustrate the importance of chlorine in producing higher molecular weight species. The activation energies for reactions (1) and (2) are 85 kcal/mol and 12 kcal/mol respectively [Kern *et al*, 1992], while the activation energies for the analogous reactions carried by H atoms are 110.5 kcal/mol and 18.6 kcal/mol [Ritter & Bozzelli, 1990].

Van der Westhuizen [1994] carried out pyrolysis experiments at approximately 2000°C with chloroform, carbon tetrachloride, polychlorinated biphenyls, Lindane and Dieldrin as feedstock.

Destruction efficiencies of at least 99.9999% were obtained for all of these compounds. Trace quantities of chlorinated benzenes were found in the products.

Kloster and Reisinger [1990] pyrolysed trichlorobenzene, tetrachlorobenzene and hexachlorobenzene (HCB) in closed ampoules between 200 - 550°C for 24 hour periods. Formation of compounds containing more chlorine atoms than the starting materials was observed. Polychlorinated biphenyls were produced from both $C_6H_3Cl_3$ and $C_6H_2Cl_4$. At 450°C, C_6Cl_6 remained stable, with 82.2% of the feed recovered unchanged.

The decomposition of HCB in nitrogen was studied in a tubular flow reactor at 1 atm and 900 - 1200°C, with residence times of 2 seconds by Mejdoub *et al* [1998]. Initial decomposition occurred at 900°C with the formation of Cl_2 and $C_{12}Cl_{10}$ (decachlorobiphenyl). Noticeable decomposition and molecular growth was observed at higher temperatures, with CCl_4, C_2Cl_4, C_2Cl_6, C_4Cl_6, C_8Cl_8 (cyclic), $C_{12}Cl_8$ (cyclic), $C_{18}Cl_{10}$ (cyclic) and soot detected in the product. A reaction mechanism similar to that of Kern *et al* [1992] and Taylor *et al* [1994, 1996] was proposed.

2.4 Mechanisms of Formation of Polycyclic Aromatic and High Molecular Weight Hydrocarbons

The formation of soot during the thermal degradation of hydrocarbons is the result of competition between destruction mechanisms involving free radicals and molecular weight growth. In pyrolysis systems, the presence of chlorine, e.g. in PCB's, increases the conversion of carbon to soot [McKinnon & Howard, 1990].

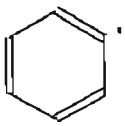
The soot formation process consists of four basic mechanisms: mass growth, coagulation, oxidation and pyrolysis, each of which is dependent on the free radical concentration. Polycyclic aromatic hydrocarbons (PAH's) are considered the molecular intermediates to soot. This is supported by the rapid rise in the PAH's concentration prior to soot nucleation. The chemical structure of soot is also very similar to that of PAH on an atomic level. The main difference between soot particles and large PAH molecules is not chemical structure, but the discreet changes in molecular weight and geometrical structure. These differences result from the reactive coagulation of large PAH molecules.

Frenklach and Warnatz [1987] recognised the formation of the first aromatic ring and the subsequent growth of aromatic rings as the two basic parts of PAH formation. Acetylene is regarded as the species causing mass addition to the PAH and soot system. In systems where no aromatic structures exist, the first aromatic ring is usually formed by the addition of acetylene to vinyl, resulting in vinylacetylene and a hydrogen atom at high temperature:

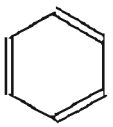
$$^{\bullet}C_2H_3 + C_2H_2 \rightarrow C_4H_4 + H^{\bullet}$$

Abstraction of a hydrogen atom from vinylacetylene occurs. The vinylacetylene radical, C_4H_3, has been proposed as the key intermediate in the formation of aromatic hydrocarbons through addition to C_2H_2, followed by cyclisation to phenyl radical.

$$C_4H_4 + H^{\bullet} \rightarrow n\text{-}C_4H_3 + H_2$$

$$n\text{-}C_4H_3 + C_2H_2 \rightarrow$$ 

Benzene and phenyl molecules are converted from one to the other by the abstraction or addition of a hydrogen molecule:

 $+ H^{\bullet} \leftrightarrow$  $+ H_2$

Hydrogen abstraction from an aromatic ring activates the aromatic molecule for acetylene addition, which propagates molecular growth as well as cyclisation to PAH. Several mechanisms have been identified in which acetylene can react to form an aromatic ring and then continue to form larger aromatic structures. The following mechanism for ring closure was presented [Frenklach & Warnatz, 1987]:

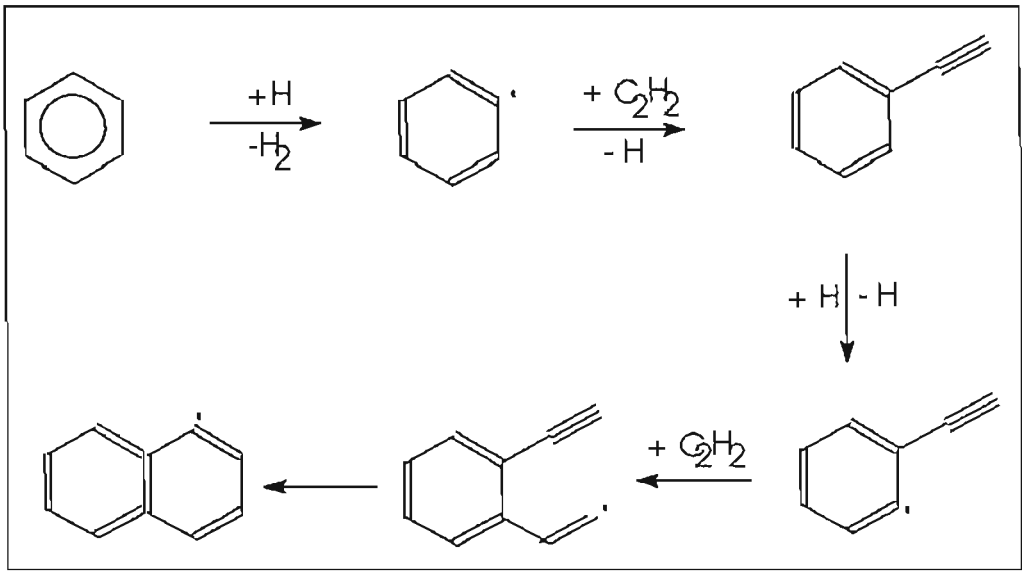


Figure 2-2: Ring closure mechanism in soot formation model

Direct condensation of aromatic rings is also important. In the high temperature pyrolysis of benzene, the reaction sequence below dominates the initial stages of PAH growth.

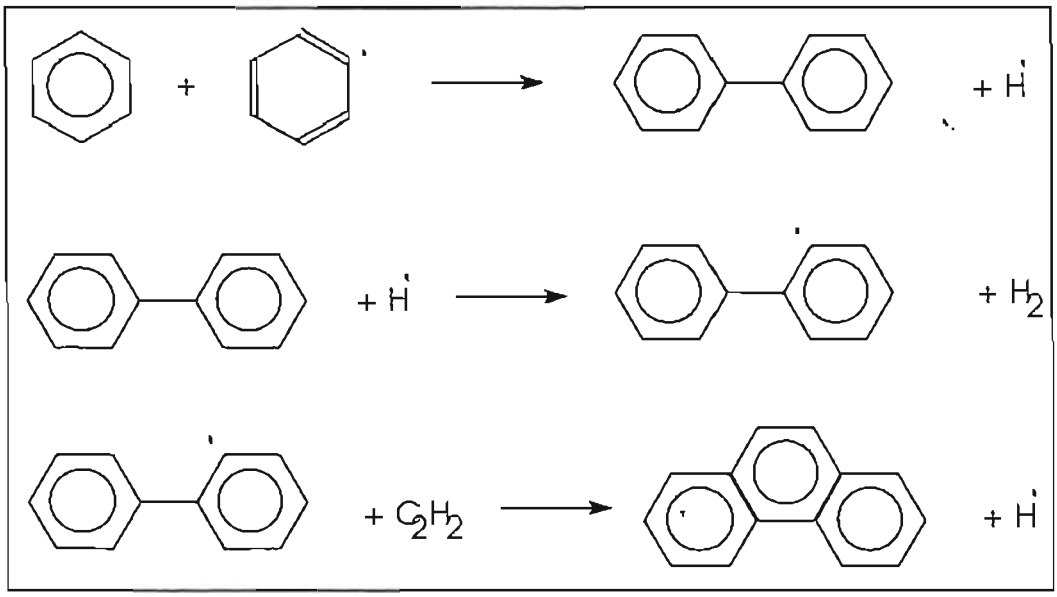


Figure 2-3: Aromatic ring condensation

Feedstock benzenoid molecules decompose primarily into acetylene as the reaction progresses, and when the concentration of acetylene approaches that of benzene, PAH growth occurs via the acetylene addition mechanism for non-aromatic fuels, as discussed above. The free energy change for the formation of certain PAH molecules such as coronene, pyrene and anthracene is so large

that the reactions are practically irreversible. Thus sooting nucleation is halted and carcinogenic PAH's persist.

Tirey *et al* [1990] have devised a series of olefinic and acetylenic pathways for the formation of higher molecular weight aromatic species. Molecular growth pathways involving secondary C_4 radicals are also presented by Taylor *et al* [1994].

Investigations into the effect of chlorine on PAH and soot formation have also been carried out by McKinnon and Howard [1990] and Marr *et al* [1992]. During pyrolysis, chlorine present in the reactant can be liberated as hydrogen chloride, or can be lost through attack by hydrogen atoms:

$$C_xH_yCl_z \rightarrow C_xH_{y-1}Cl_{z-1} + HCl$$

$$CxH_yCl_z \rightarrow C_xH_yCl_{z-1} + Cl^{\bullet}$$

As mentioned earlier, chlorine abstraction by chlorine is unlikely due to the large endothermicity and the high strength of the C-Cl bond.

It was observed that larger amounts of soot formed from chlorinated hydrocarbons than from non-chlorinated hydrocarbons. Sooting tendency and PAH production increased with increasing chlorine : hydrogen ratio. This trend, based on kinetic analysis and modeling was attributed to enhanced chlorine-catalysed molecular degradation. This promotes the formation of aromatic ring compounds and the large concentration of chlorine atoms accelerates the abstraction of H from stable PAH molecules, thus activating them for further growth. These results were mirrored by Marr *et al* [1992] and McKinnon and Howard [1990]. Marr *et al* [1992] also found that the yields of cyclopenta(cd)pyrene and benzo(a)pyrene, two PAH's that are major contributors to biological activity in human cell mutagenicity and carcinogenicity testing, are greatly suppressed with chlorine present.

Ritter and Bozzelli [1990] carried out experiments on the pyrolysis of chlorobenzene in hydrogen and helium make-up gases. It was suggested that the reason for chlorobenzene's acceleration of soot formation is the role of the chlorine product in the reaction system. The ability of soot to capture high molecular weight PAH is increased in the presence of chlorine. Kern *et al* [1992] came to the same conclusion in their study of chlorobenzene pyrolysis.

It is thus conclusive that, during the high temperature treatment of organic waste, higher chlorine : hydrogen ratios promote sooting and PAH formation. It follows that chlorine : hydrogen ratios less than one are required to inhibit sooting.

2.5 Mechanisms of Formation of Polychlorinated Dibenzofurans and Polychlorinated Dibenzodioxins

The major source of PCDD/F's in the environment is the combustion process. Their formation during incineration has been attributed to *de novo* synthesis from activated carbonaceous material, oxygen and Hydrogen chloride or Cl_2 as well as from reactions of chlorinated precursors such as chlorophenols, chlorobenzenes and polychlorinated biphenyls [Tayler & Dellinger, 1998; Weber & Hagenmaier, 1999]. However, the detailed mechanisms of PCDD/F formation are still unresolved.

Theories discussing the thermal formation of dioxins have generally dealt with gas-phase reactions. Dickson and Karasek [1987] found that chlorinated dioxins form from pentachlorophenols and trichlorophenols by surface catalysed reactions on flyash particulates present in the incineration process. In these heterogeneous gas-solid reactions, precursor molecules become chemisorbed onto the flyash, which has many Lewis and Bronsted acid and base sites. Gas phase radicals abstract hydrogen or chlorine from the bound precursors, resulting in highly reactive molecules.

Weber and Hagenmaier [1999] investigated PCDD/F formation in fluidised bed incineration. They found three main pathways of PCDD/F formation with regard to the isomers formed in their investigation:

- Condensation of intermediates, in which the PCDD/F substitution pattern reflects the substitution of the intermediates;
- Direct formation of the dibenzodioxin and dibenzofuran from chlorinated carbon;
- Chlorination and dechlorination of the resulting PCDD/F in both the gas phase as well as by heterogeneous catalysis on flyash.

Formation of chlorobenzenes can occur via pyrolysis of polymers, through chlorination of benzene, and via cyclisation of chlorinated C_1 and C_2 units. Chlorophenols are formed from chlorobenzenes

via a reaction of a chlorophenyl radical with an •OH radical. Alternatively, the reaction of a chlorophenyl radical with the O_2 / R• -RO• reaction steps results in the formation of a chlorophenoxy radical, and is discussed by Ballschmiter *et al* [1988]. One of the reaction pathways open to the chlorophenoxy radical is the abstraction of a hydrogen radical to form a chlorophenol.

A reaction scheme with polychlorinated benzenes and polychlorinated phenols as intermediates and end products in high temperature chemistry is presented in Figure 2-4.

Based on the results of their investigations and those previous, Taylor and Dellinger [1999] have devised an extended mechanism of PCDD/F formation from particulate carbon and inorganic chlorine, and this is presented in Figure 2-5. The formation of chlorinated benzenes is by copper-catalysed chlorination and molecular growth of acetylene. The conversion of chlorobenzenes to PCDD/F does not involve the formation of the intermediate chlorophenol, but rather involves chemisorption of chlorinated benzenes on silica to form chemisorbed chlorophenoxy species.

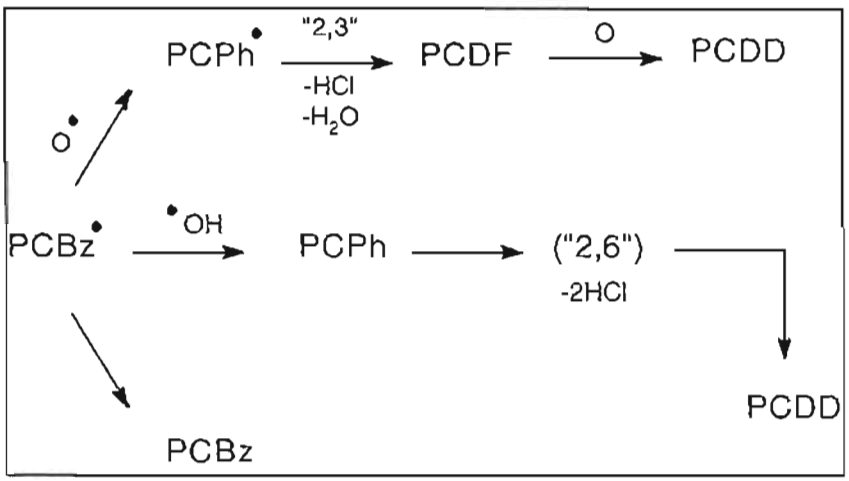


Figure 2-4: Polychlorinated benzenes and polychlorinated phenols as intermediates and end products in high temperature chemistry of polychlorophenyl- and polychlorophenoxy-radicals

PCBz• - polychlorophenyl-radical

PCPh• - polychlorophenoxy radical

PCBz - polychlorobenzenes

PCPh - polychlorophenols

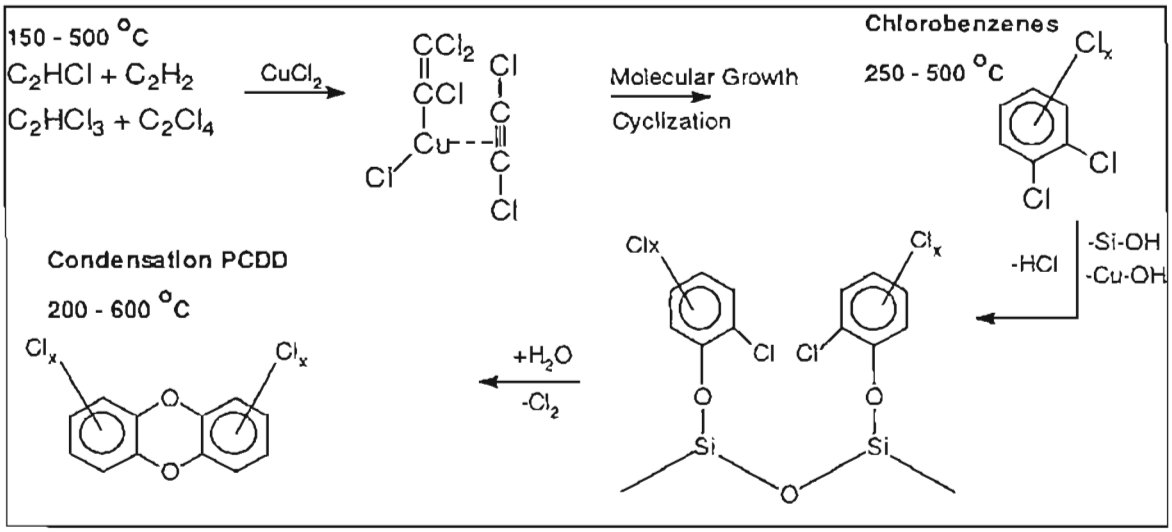


Figure 2-5: Pathway of formation of PCDD/F in combustion and thermal sources

Chagger *et al* [2000] found that the dioxin concentration is a function of oxygen concentration and the unburned hydrogen in the reactor. They proposed a furan and dioxin formation mechanism based on benzene, phenol and dibenzyl as precursors. This mechanism then assumes chlorination of the furans and dioxins via a fly-ash catalysed reaction with Hydrogen chloride.

Table 2-2: Proposed Dioxin and Furan Formation Mechanism [Chagger et al, 2000]

Dioxin Formation	Furan Formation
$C_6H_4OH + C_6H_5O = C_{12}H_9O_2 + H$	$C_{12}H_{10} + OH = C_{12}H_{10}O + H$
$C_6H_4OH + C_6H_5O = C_{12}H_9O_2 + H_2$	$C_{12}H_{10}O + H = C_{12}H_9O + H_2O$
$C_6H_5O + C_6H_5O = C_{12}H_9O_2 + H$	$C_{12}H_9O = C_{12}H_8O + H$
$C_6H_5O + C_6H_5O = C_{12}H_9O_2 + H_2$	$C_6H_5O + C_6H_5O = C_{12}H_8O + H_2O$
$C_{12}H_9O_2 = C_{12}H_8O_2 + H$	$C_6H_5OH + C_6H_6 = C_{12}H_8O + H_2 + H_2$
$C_{12}H_9O_2 + OH = C_{12}H_8O_2 + H_2O$	$C_6H_5O + C_6H_5OH = C_{12}H_{10}O_2 + H$
$C_{12}H_9O_2 + H = C_{12}H_8O_2 + H_2$	$C_6H_4OH + C_6H_5O = C_{12}H_8O + H_2O$
$C_{12}H_9O_2 + O = C_{12}H_8O_2 + OH$	

Lenoir *et al* [1998] concluded from their investigations on the relevant pathways of PCDD/F formation that the traditional distinction between the precursor and the *de novo* synthesis is becoming more and more irrelevant. They found that the precursor theory can be extended to

compounds such as like acetylene, which is chemically less similar to PCDD. Thus PCDD formation depends on the stability of the PCDD isomer and not on the precursor.

2.6 Conclusions

The survey above has highlighted some of the factors governing chlorinated hydrocarbon pyrolysis. Among them are reaction temperatures and pressures, residence times and reactor surface/volume ratios.

Chlorine, hydrogen and phenyl radicals play important roles in pyrolysis reactions, and acetylene is an important intermediate. The major dechlorination reactions are listed in Table 2-3.

Table 2-3: Major dechlorination reactions in pyrolysis:

Reaction	Example
Decomposition	$C_6H_4CH_3Cl \rightarrow {}^{\bullet}C_6H_4Cl + {}^{\bullet}CH_3$
Displacement	$C_6H_5Cl + H^{\bullet} \rightarrow C_6H_6 + {}^{\bullet}Cl$
Abstraction	$C_6H_5Cl + H^{\bullet} \rightarrow {}^{\bullet}C_6H_5 + HCl$
1,2 elimination leading to ring rupture	$C_6H_5Cl \rightarrow :C_6H_4 + HCl$ $:C_6H_4 \rightarrow C_4H_2 + C_2H_2$

A sufficient hydrogen : chlorine ratio must be maintained in order to render the chlorination of aromatic molecules and radicals infeasible. This is because recombination with hydrogen rather than with chlorine is thermodynamically favoured. Hydrogen radicals accelerate the dechlorination process, as well as deactivating phenyl and chlorine radicals which are the precursors to soot formation. Thus a suitable hydrogen : chlorine ratio will inhibit both the formation of soot as well as noxious chlorine (Cl_2) gas.

Benzene, phenol and chlorobenzenes have been identified as precursors in PCDD/F formation. Chlorobenzenes have been identified in the product stream of both aliphatic and aromatic chlorinated hydrocarbon pyrolysis. It is thus clear that even small quantities of oxygen in the pyrolysis process can result in the formation of PCDD/F, thus highlighting the necessity of an oxygen-free environment.

3. EXISTING TECHNOLOGIES FOR HAZARDOUS WASTE DESTRUCTION

The method of disposal of hazardous waste by landfill has become questionable since it was found that this had a significant effect on the contamination of the immediate environment. Most of the toxic substances remain harmful longer than the landfill sites can contain them.

A number of technologies have been proposed for the destruction of hazardous waste, in particular for the destruction of chlorinated waste. The two major methods of destruction are:

- Thermal methods
- Non-thermal methods

These technologies can be classified under the general categories as listed in Table 3-1. The corresponding destruction and removal efficiencies (DRE) are provided.

The biggest problem with non-thermal methods is that most are laboratory scale models, and the data available is limited. This presents a problem in evaluating these methods.

3.1 Thermal methods of waste destruction

The thermal destruction methods can be categorised as either boilers or incinerators. Rotary kilns, fluidised beds, multiple chambers, catalytic combustion, pyrolysis and combustion in oxygen starved combustors are all considered to be incineration systems. Boilers include oil, gas and coal fired boilers.

3.1.1 Rotary kiln incineration

Rotary kiln incineration is the most common commercial on-site thermal treatment [Rey de Castro, 1989; Lee & Huffman, 1989]. One of the features of the kiln is that it can accept diverse feeds: any liquids that can be atomised, heavy tars, sludges and solids.

Table 3-1: Categories of hazardous waste destruction technology

Category	Technology	DRE (%)
Thermal Oxidation	• Rotary Kiln Incineration	≥ 99.99
	• Circulating bed combuster	
	• Westinghouse / O'Connor combuster	
	• Fluidised Bed Incineration	≥ 99.99
	• Cement Kilns	≥ 99.99
	• Multi-purpose municipal waste incinerator	≥ 99.99
	• Waste Gasification	Unknown
	• Controlled Combustion (Burn boxes)	≥ 99.99
	• Gaseous Liquid Thermal Oxidation	≥ 99.99
Catalytic Process	• Oxidation	≥ 99
	• Hydrogenation	80 – 100
Chemical Process	• Catalytic Extraction Process	≥ 99.99
Supercritical Water Oxidation	• Supercritical water hydrolysis	≅ 100
	• Supercritical water oxidation	≥ 97
Wet Air Oxidation		≥ 99
Plasma Destruction	• Thermal Plasma	Unknown
	• Plasma Arc	≥ 99.9999
UV Photolysis	• Photochemical Degradation	Unknown
	• UV Decomposition	Unknown
	• Irradiation	Unknown
	• Photo-dechlorination	Unknown
	• Photocatalytic Degradation	≥ 95.99
	• Photochemical Oxidation	
Biological Process	• Microbial treatment	≅ 100
	• Activated sludge method	
	• Trickling filter method	
High Energy Radiation	• Conversion by ionic radiation	Unknown

Feed is burned to ash and gases in rotating refractory-lined cylinders, at temperatures from 650 to 980 °C. The rotary nature of the kiln allows for new surfaces of the waste to be constantly exposed to high temperatures. Gaseous products pass to into a secondary combustion chamber (the afterburner), and incineration is then completed at temperatures between 870 and 1315 °C. The exhaust gases are scrubbed before being released into the atmosphere. Heat is often recovered from the exhaust gas.

The capital cost of installation is high, thus it is impractical for low feed rates. Also, the motion of the kiln causes the refractory to be susceptible to thermal shock damage. This can be prevented by

continuous operation. Large portions of the kilns require rebricking annually, and the support and alignment of the system are of paramount importance.

This method generally meets or exceeds the 99.99% DRE for hazardous organic constituents. In a test burn of waste fuel containing 20% (vol) dichlorobenzene in a rotary kiln, a DRE of 99.999% was achieved [Rey de Castro, 1989]. This is a significant result, since dichlorobenzene is considered a good surrogate for PCBs.

To completely oxidise hazardous waste molecules, 150% excess air is required to provide the necessary quantity of oxygen. Because 79% of air is nitrogen, extra energy is required to raise the nitrogen to combustion temperature. Also, additional product gas handling and cleaning processes are required. Thus the majority of the excess air used does not contribute to the effectiveness of incineration.

3.1.2 Rotary barrel combustor

At the centre of this system is a water-cooled rotary barrel. It is constructed of alternating longitudinal water tubes and flat perforated steel plates which, welded together, form the perimeter [Lee & Huffman, 1989]. The perforations control the distribution of the combustion air, while the heat is removed from the barrel by the cooling water. The combuster is slightly inclined and is rotated by a chain and roller driver. Feed dries and progressively burns as it moves down the length of the barrel. A tenth of the original feed volume exits the combustor as ash, while the remaining material is further combusted in an afterburner grate. Gases produced during combustion flows through the radiant, superheater and convective sections of the boiler. This gas then exits through a heat exchanger which preheats the incoming combustion air.

This technology is able to handle liquids, solids and semi-solids, as well as sludges and residual oils. Energy recovery is high. The siftings from the combustion chamber may, however, contain some material that is not completely combusted. Also, the introduction of air into the combustor increases the chances of dibenzofurans and dioxins being formed.

3.1.3 Circulating bed combustor

Ogden Environmental Services offers the option of a circulating bed combustor (CBC). The CBC's use much higher air velocities than those used in conventional fluidised beds. Circulating sand flows up the combustion reactor and down a cyclone that redirects the sand to the bottom of the combustor.

Liquid or solid hazardous waste is fed into the bottom of the combustor, and heat is transferred by means of the hot circulating sand. This efficient form of heat transfer allows for the temperature throughout the combustion loop to be within 10°C of the combustion temperature, eliminating the need for an afterburner and allowing for temperatures lower than that of the rotary kiln. Residence times vary from 2 seconds (for gases) to 30 minutes (for larger feed material).

Ash is removed periodically by means of a water-cooled ash removal system. Energy released by the exothermic reactions is removed by cooling. In the combustion zone, solid particles make contact with the cooling tubes, enhancing heat transfer. Heat is further removed from the flue gas with conventional heat exchangers.

The CBC has performed so well that it is one of the seven incinerators licensed to destroy PCBs in the United States. A DRE of > 99.9999% was achieved for a liquid PCB feed carried out at the Ogden Environmental Inc. pilot plant [Rey de Castro, 1989].

One advantage of the CBC is that waste can be combusted at lower temperatures than in other incinerators. Lower vessel temperatures prevent the formation of significant amounts of NO_x. Also, the bed material acts as a scrubber to capture acid gas from the flue gas, reportedly resulting in a non-toxic solid residue.

Disposal of the supposedly inert residual bed material is a potential problem. Also, large amounts of fine particles in the flue gas could require large and costly pollution control devices. The waste feed particle size has to be controlled in order to maintain a constant fed rate.

3.1.4 Infrared systems

Infrared systems consist of three main components. The primary combustion chamber (PCC) can achieve temperatures of up to 1010°C by exposure to infrared radiant heat. This is provided by rows of electrically powered silicon carbide rods. The secondary combustion chamber (SCC) is gas fired, reaching temperatures of up to 1260°C. Air pollution control equipment includes an emissions control system consisting of a venturi section for particulate removal, a packed scrubber in which acid gas is neutralised and an induced draft blower which draws cleaned gases from the scrubber into the exhaust stack.

An investigation into the disposal of PCB containing waste using the infrared system was carried out in 1988 [Lee & Huffman, 1989]. The unit achieved a DRE in excess of 99.99% for PCBs, but exceeded the limit for particulate emissions. Emission control modifications were then effected. Analyses of the waste, ash, scrubber waters, scrubber solids and the stack gases were undertaken to investigate the presence of any dioxins and furans. Results are summarised in the Table 3-2.

This technology can control residence time and temperature more accurately in the PCC than other technologies. The feed however requires pretreating to conform to recommended size limitations. Also, liquid waste needs to be mixed with solid material, such as sand in order to be effectively destroyed in the PCC.

Table 3-2: Infrared System – Results of Product Analysis

Sample	TCDD	PCDD	TCDF	PCDF	Detection Limit
Waste feed matrix	ND	ND	ND	ND	1.1 ppb
Ash after treatment	ND	ND	ND	ND	1.4 ppb
Scrubber water	ND	ND	ND	ND	0.000022 ng / l
Stack gas	ND	ND	0.47**	ND	340 µg / l

TCDD = tetrachlorodibenzodioxin
PCDD = polychlorodibenzodioxin
TCDF = tetrachlorodibenzofuran
PCDF = polychlorodibenzofuran
ND = non detectable
** reported for one out of four tests

3.1.5 Plasma arc technology

Plasma is a high-energy atomised gas. Electric power across a reverse polarity electrode assembly produces an electric arc. This arc causes a low pressure injected air stream to form a thermal plasma. The air molecules are excited into higher energy states, and release heat as they relax to lower energy states, providing temperatures between 2000 and
8000 °C. As the activated components of the plasma decay, their energy is transferred to the waste materials exposed to the plasma field. Thermochemical and photochemical dissociation of the waste occur, producing atoms and ions that recombine according to kinetic equilibrium theory. The recombination products are non-toxic gases consisting of mainly hydrogen, carbon monoxide, nitrogen and hydrogen chloride. The breakdown of the waste into atoms occurs almost instantaneously, and no large molecular intermediary compounds are formed during recombination.

The off-gases are condensed and caustically treated to neutralise acids. Residual carbon is removed by filtration before the gas is discharged. The scrubber water from the acid emissions control contains only halogenated and sulphonated salts which reduces the need for emissions control equipment. Residual gases and scrubber water are free of organic contaminants.

In tests carried out on PCBs, DRE of > 99.9999% were obtained [Lee & Huffman, 1989].

3.1.6 Electric pyrolyser

Pyrolysis is thermal destruction in the absence of oxygen. Since oxidation (burning) is minimised, the only destructive force is heat. The heat provides energy for dissociating chemical bonds, eventually producing simpler, non-toxic molecules. The absence of oxygen eliminates the possibility of dioxin and furan formation.

Pyrolysis reactors can be directly heated by fuel-fired burners or indirectly heated by, for example, electric resistance heating elements [Rey de Castro, 1989]. The latter method is useful when the gas stream leaving the primary burner contains a valuable product that can be recovered rather than burned. The gas product stream would become diluted with burner flue gas if the reactor were heated directly.

Van der Westhuisen [1994] achieved typical DRE's of 99.9999% for chlorinated hydrocarbons in an electric pyrolysis reactor.

3.2 Non-thermal methods of waste destruction

Non-thermal methods can be subdivided further into physicochemical and biological processes. However not much conclusive information is available on the biological processes being investigated.

3.2.1 Adsorption processes

These processes are used for removing chlorinated hydrocarbons from aqueous waste streams. The stream is passed through an activated carbon slurry, and the impurities are adsorbed onto the carbon. Carbon regeneration is achieved with the use of a furnace. Information on the use of adsorption for PCB destruction is unavailable.

3.2.2 Catalytic dehydrochlorination

PCB is reacted with hydrogen gas under 2-5 MPa pressure, in the presence of a catalyst. The catalyst is 61% nickel or 10% palladium on charcoal. Temperatures vary between 100-120°C. A laboratory scale model indicated full conversion of PCB to dechlorinated biphenyls, thus resulting in a non-toxic product. At the Electrical Power Research Institute seminar in 1987, UOP Incorporated claimed a 99.9% conversion with a pilot plant.

3.2.3 Chlorinolysis

In this process chlorine is added to the waste under high / low temperature and low / high pressure. Conversion to chlorinated hydrocarbons occurs uncatalysed, in the vapour phase. If only carbon and chlorine are present, the product is carbon tetrachloride, while toxic phosgene ($COCl_2$) and hydrogen chloride are formed from waste containing hydrogen and oxygen [Arnold, 2000]. The reactor is prone to corrosion and needs to be constructed from resistant materials.

3.2.4 Ozonation

In this technique, PCB is destroyed by UV radiation and ozone to form carbon dioxide, water and hydrochloric acid. Akerman *et al* [1983] reported the DRE in the order of 93%. Extensive research on this technology is still required.

3.2.5 Catalytic extraction process (CEP)

This method, also know as the molten metal method, uses the catalytic and solvent properties of molten iron to break waste into its elements. Hazardous waste is introduced into a bath of molten metal which causes the waste to dissociate into its elements. On addition of a chemical reactant such as lime, the elements reconfigure into H_2, CO and HCl gas, ceramics and metals. The following reactions are important in this process:

$$2C + O_2(g) = 2CO(g)$$

$$2Fe(l) + O_2(g) = 2FeO(l)$$

$$2Fe(l) + O_2(g) = 2Fe(l) + 2O$$

$$FeO(l) + C = CO(g) + Fe(l)$$

3.2.6 Sunohio process

In this process, the PCB is separated into biphenyl and chlorine. Organically bound chlorine is converted into chloride and the biphenyl molecule is converted into polymeric solids. The unit handles 100-10 000 ppm PCB contaminated oil, with a DRE of 94.4% - 99.9%. Moisture has to be removed before treatment.

Oil treated using this method was found to have a high pH and was thus considered hazardous. It was also found that the colour and interfacial tension of the treated oil deviated from acceptable norms. The electrical properties of the treated oils were also not acceptable for reuse.

3.2.7 Catalysed wet air oxidation

This process has been developed by Enviroscience Inc. The PCB is oxidised in air or oxygen in an acidic aqueous medium at high temperature. DRE was reported as 99% on a laboratory scale model.

3.2.8 Electrochemical process

This process, based on the electrochemical dehalogenation of PCB, was reported by Environmental Research and Technology Inc. Non-noble metal electrodes were used in an electrochemical solution consisting of the PCB contaminated fluid and a proprietary reagent, at 5-15 volts. Chloride salt and substituted biphenyls were formed.

3.2.9 Supported liquid phase reagent process

Chemical degradation of PCB is effected by an optimised mixture of polyethyleneglycol, polypropyleneglycol, a base and a radical initiator in a fixed bed reactor. Levels of 350 ppm PCB were degraded to 50 ppm in 1.5 hours in a batch reactor.

3.2.10 Supercritical water oxidation

This process has so far been used most successfully in wastewater treatment. At temperatures near 600°C and pressures between 2.8 x 10^4 and 3.1 x 10^4 kPa, organic contaminants of wastewater become completely soluble in supercritical water. The solubility allows for the organic contaminants to be cracked into carbon dioxide and water [Fairley & Chynoweth, 1994].

Halogenated organics, especially organochlorines, are highly corrosive at supercritical temperatures and pressures. Also, inorganic salts precipitate out of solution in supercritical water and clog reactors. These problems have been overcome through reactor design and materials of construction.

3.3 Conclusion

When excess air is used for incineration, the oxidising condition results in exothermic reactions which are difficult to control and require a large downstream afterburner and pollution prevention equipment. The pyrolytic condition results in endothermic reactions which are easier to control, resulting in a smaller downstream afterburner and pollution abatement equipment.

During incineration, most of the combustion occurs in the primary chamber, with the secondary chamber functioning to heat the gas streams for the required residence time. The secondary chamber has no influence on the operating characteristics in the primary chamber. In pyrolysis however, most of the degradation occurs in the secondary chamber, which is capable of using pyrolysis products as fuel.

Table 3-3 summarises the comparison between excess air and pyrolytic incineration.

Table 3-3: Comparison of Pyrolytic and Excess Air Incineration

FACTOR	EXCESS AIR	PYROLYSIS
Reaction type	Exothermic	Endothermic
Reaction rate	Difficult to control	Easy to control
Primary chamber atmosphere	Oxidising	Non-oxidising
Equipment size	Larger	Smaller
Furnace sealing	Not critical	Critical
Particulate carry-over	Likely	Unlikely
Heating rate	Faster	Controlled slower
Fouling of heat recovery equipment	Rapid	Slow
Furnace temperature	Higher (> 1090°C)	Lower (< 760°C)
Furnace refractory life	Shorter	Longer
Product recovery from residue	Not recoverable if oxidised	Recoverable
Secondary chamber atmosphere	Oxidising	Oxidising
Secondary chamber temperature	980 - 1090°C	980 - 1090°C

Critical evaluation of most of the non-thermal methods mentioned is difficult as very little data is available

As mentioned in Chapter 1, the capital and operational costs of the various alternatives are either high, or the technology has not yet been proven to meet required destruction and removal standards. While incineration has been proven, there are presently no plants operating in South Africa for the destruction of chlorinated waste. Table 3-3 highlights some of the advantages of pyrolysis over

incineration and shows that pyrolysis could be a suitable and possibly more simple alternative to incineration.

4. EQUIPMENT

This chapter firstly summarises reactors and processes already patented for the purposes of pyrolysis. A discussion of equipment used for this project follows.

4.1 An Overview of Pyrolysis Reactors and Processes

A high temperature chemical reaction process using fluid-wall reactors was patented in the United States by Matovich [1977a]. He patented a process in which a shell of refractory material that could reflect radiation enclosed a volume constituting a black body cavity. A reaction chamber was formed by enveloping the black body cavity with an inert fluid, with the black body cavity constituting the reactor tube. This fluid was transparent to radiation. The reactor tube was heated to incandescence and in turn radiated energy inwards to initiate and sustain the chemical reaction.

Matovich [1977b] further modified this reactor later in the same year. Figure 4-1 is an elevation of the inlet end of one embodiment of the reactor.

Matovich specified the reactor tube to be made of a porous, refractory material and the reactor tube to be enclosed by a stainless steel pressure vessel, 70. Suitable materials for the reactor tube must have a low absorption coefficient and be substantially transparent to radiation. These included glass, quartz, hot sintered aluminium oxide, borosilicate glass; organic polymers such as Plexiglass, polyethylene, polypropylene; and inorganic salts such as the halides of sodium, lead and potassium. Cooling coils, 87, surround the outside of the stainless steel shell. By introducing an inert fluid under pressure into the pressure vessel, a protective blanket was provided to the outside of the reactor tube. This fluid must also be substantially transparent to thermal radiation, and included simple gases such a neon, argon, helium, krypton and xenon as well as complex gases such as hydrogen, nitrogen and oxygen that do not decompose into solid products. The choice of inert fluid depends on the particular reaction.

Heat for the reactions was provided by radiation coupling, with electrical elements being housed in the reaction chamber. The radiant energy source may be a plasma arc, a heated filament, a flame or any other suitable means. The radiant energy generated was collected by a reflector and directed through the reactor tub to coincide with the flow path of the reactants.

The reactants were introduced into the reaction zone, 65, at the inlet end, 62. The reactants entered at 91, flowed past a tangential baffle, 92, and then flowed through a porous carbon diffuser, 95 before passing through the reaction chamber, 65. Heating was provided by carbon electrodes, 100a-100f

A second embodiment of the reactor made used of a carbon or graphite tube which itself generated high intensity radiant energy which coincided with the flow path of the reactants. Here, heat was provided by carbon electrodes, 100a-100f, suitable for use with a three phase power source. The heat generated by the electrodes is transferred to the tube. The tube could also be heated directly be electrical resistance.

The reactor could be used in virtually any high temperature chemical reaction, including in the production of carbon black and hydrogen by the pyrolysis of natural gas, dissociation and partial dissociation of hydrocarbons, and the conversion of organic waste into fuel gas.

Previous to this invention, high temperature reactors transferred heat to the reactants by convection and/or conduction. This produces two major problems that limit the scope and the nature of the reactions that can be carried out. The highest temperature in these reactors is at the interface between the inside wall of the reactor and the reactant stream and the available reaction temperature is thus limited by the temperature to which the reactor tube can be safely heated. Secondly, the reactions tend to take place on the walls of the reactor at the highest temperatures, causing product build-up on the walls. This causes blockages and further impairs the heat transfer to the reactant stream, making the process inefficient.

A number of reactors and processes for high temperature chemical reactions, specifically for pyrolysis reactions, were developed between 1980 and 1997. A down draft pyrolysis reactor with a fixed catalytic bed was designed by Chittick [1986] and included an infrared radiation shield. The primary motivation for the reactor was to convert the off-gas of a carbonaceous materials oxidiser to fuel gas, comprising carbon monoxide, hydrogen and methane at temperatures between 800 and 1400°C.

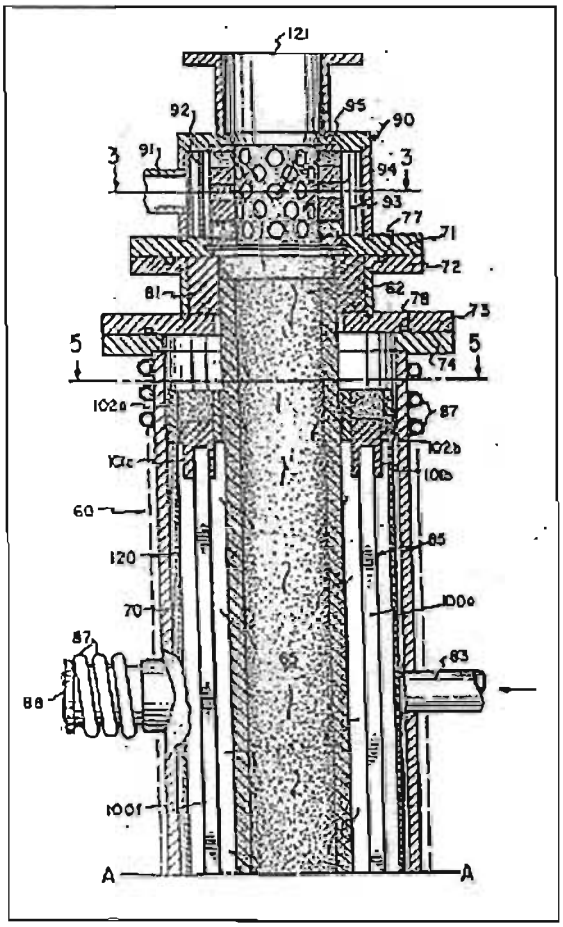


Figure 4-1: Inlet end elevation of one embodiment Matovich's [1977] reactor

An attempt to improve the pyrolysis process and apparatus including reducing investment costs as well as reduced purification costs for the pyrolysis gas, led Christmann [1988] to design a pyrolysis reactor coupled with an incinerator plant. The gases from the incinerator were pyrolysed, with the heat for the pyrolysis reactions provided by the hot flue gases from the incinerator.

Benson *et al* [1991] developed a method specifically for the gas phase pyrolysis of chlorinated organic compounds in a reducing atmosphere to produce hydrogen chloride. The temperature and the reducing atmosphere in the reaction zone were produced by combusting an excess of methane or hydrogen with oxygen. Carbon tetrachloride, chloroform, or tetrachloroethylene was contacted with the hydrogen rich reductive atmosphere in the reaction chamber. Carbon that accumulated within the reactor was oxidised and removed partially by passing air through the reactor at temperatures above 675°C.

Figure 4-2 is a shows the invention of Benson *et al* [1991]. The reactor, 10, was enclosed by a gas impervious casing that was coated internally with a ceramic to prevent corrosion by the hydrogen chloride produced in the reaction zone, 14. Flowmeters are indicated encircled V symbols. A methane / oxygen mixture entered the reactor tube at a burner tip, 26. Electrical conducting wires, 30 and 32, were connected to a resistance wire, 34 through a bushel, 28 as a means of ignition for the methane / oxygen mixture. An insulation zone, 58, was incorporated to maintain the reactor temperature. This zone could also include electrical or methane heaters.

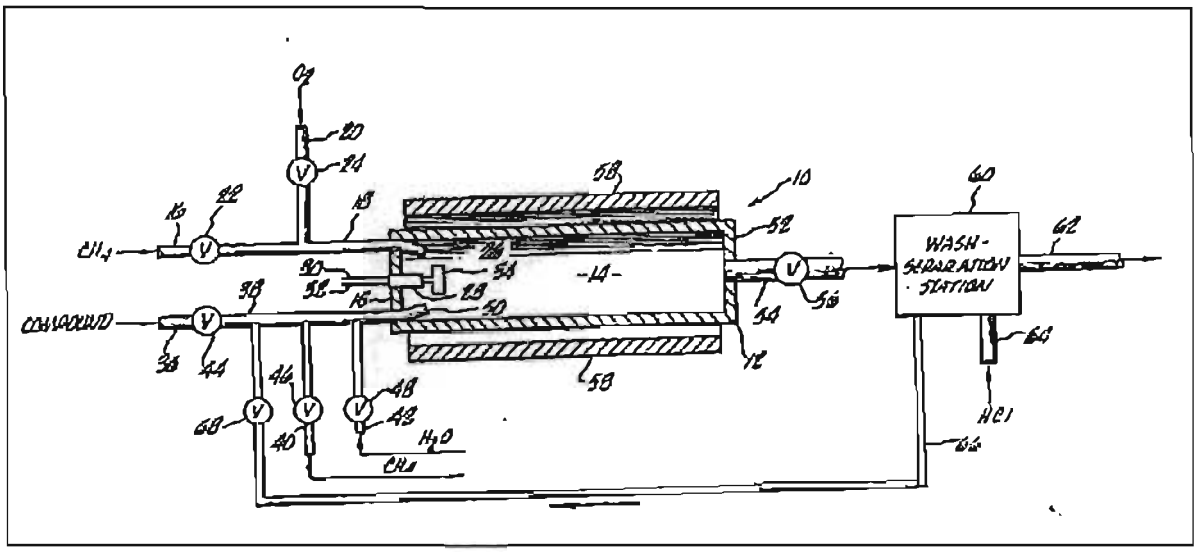


Figure 4-2: Pyrolysis reactor of Benson *et al* [1991]

Agarwal [1992] invented a pyrolysis apparatus and process for the decomposition of material containing organic as well as inorganic constituents. The inorganic component was continuously recovered in a carbon-free form and the organic component in a gaseous decomposition product. The feed was moved from one end of the reactor to the other by a mechanical conveyor. The reactor housing was heated by a furnace, which included a burner. The burner was initially fired with natural gas and later by the pyrolysis product gases. Figure 4-3 is cross sectional view of the pyrolysis reaction assembly and gas treatment portion of the materials recovery system.

Feed enters through conduit 26. Organic gaseous products are exhausted through 28, while solid residues exit the reactor, 16, through conduit 30. The central shaft, 18, is rotated by a motor and the spiral flight assembly, 20, is designed to force material through the reactor towards the exit. The

reactor is inclined at 30 degrees to the horizontal to aid the flow of material. The reactor is heated by furnace, 36, which includes a burner, 38.

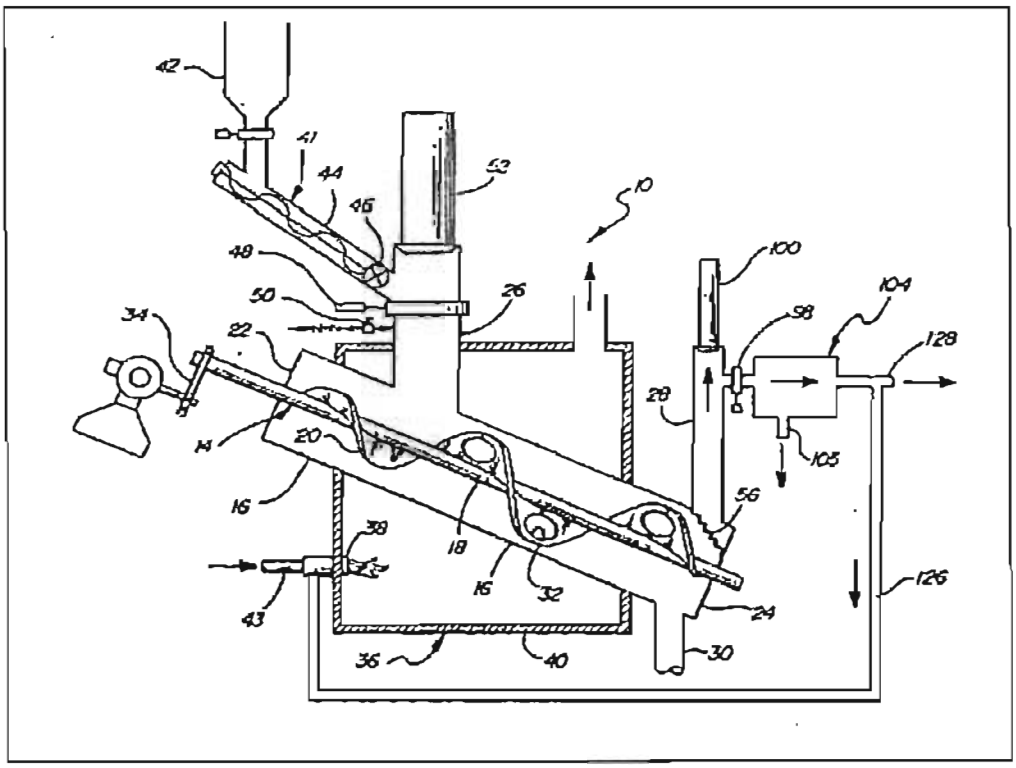


Figure 4-3: Pyrolysis reactor of Agarwal [1992]

An alternative heating method and pyrolysis apparatus was proposed by Holland [1995]. Waste material which is not susceptible to microwave irradiation was contacted with pulverised carbonaceous material (such as scrap tyres) which is susceptible to irradiation by microwave. The pulverised material was heated by microwave irradiation and the thermal energy was transferred to the waste material, causing it to pyrolyse. Figure 4-4 is a schematic illustration of the apparatus.

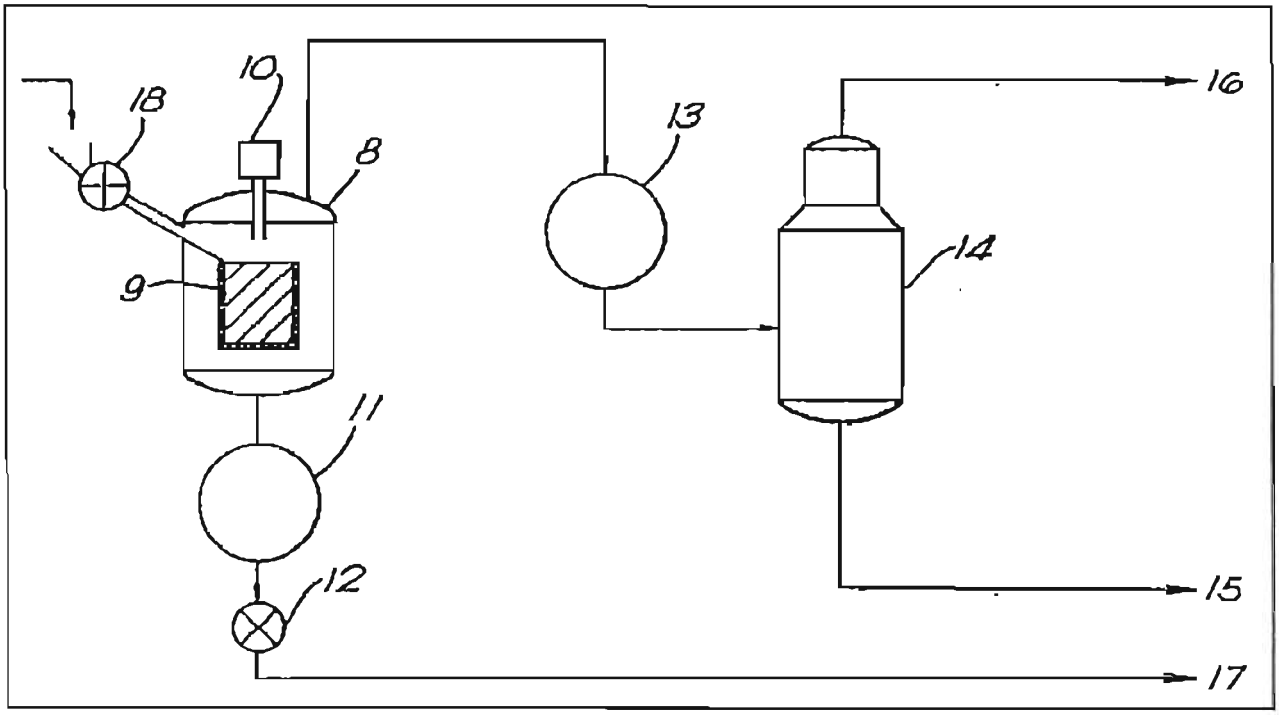


Figure 4-4: Apparatus for waste pyrolysis by microwave radiation, Holland [1995]

The waste material and pulverulent carbonaceous material entered a refractory lined stainless steel pyrolysis chamber, 9, through an air lock, 18. The material in the chamber was exposed to microwave irradiation from a microwave generator, 10. Solid products were passed through a carbon cooler, 11, while the gases evolved were cooled before entering a gas / liquid separator.

Wu & Chen [1995] proposed a thermal conversion pyrolysis reactor system for a continuous flow pyrolysis reaction. The reactor system utilised a diffusion material, preheated by exhaust gases, to transport the waste material through the reactor and to partially catalyse the reactions. Heating was provided in a furnace space with combustive heating provided by turbulent burners. Combustible gas reaction products were used in the turbulent burners.

A reactor for the chemical destruction of heavy molecular weight organic compounds, semi-volatile organic compounds or hydrogen sulphide contained in a gaseous feed was patented by Wang in [1977]. This reactor contained a hollow core surrounded by several ceramic walls and insulating zones to minimise energy losses from the reactor core. A number of electrical heating elements were arranged within the hollow reaction zone, directly heating the gaseous material. Temperatures of up to at least 1900 °C can be obtained. The physical contact of the heating elements and the

waste stream offers the added advantage of a plasma formation near the surface of the heating element. The plasma enhanced the speed at which the chemical bonds of the hazardous waste are destroyed (see section 3.1.5 on Plasma Arc Technology).

Electromagnetic fields were also set up within the central reaction zone. These fields expelled dissociated gases or particles away from the reaction area. Dissociated gases and ionised particles were grouped according to mass by the electromagnetic fields. The dissociated gases were separated and thus recombination at the reaction sites was avoided. The rapid movement of the dissociated gases from the reaction site resulted in non-equilibrium conditions, thus driving the desired reactions to high conversion rates. Figure 4-5 is a vertical sectional view of the thermoelectric reactor.

The central reaction zone is surrounded by an inner ceramic wall, 26, an energy retaining zone, 27, high temperature insulating blankets, 29 and 30, and a steel casing, 31. The ceramic walls, 26 and 28, could be silicon carbide or graphite. Section 35 is a turbulent heating zone made of porous ceramic fibres. The energy retaining zone and the turbulent heating zone contained layers of heat retaining porous ceramic fibres such as alumina, silica, mullite, titanate or some combination thereof. The physical properties of thermal emissivity, absorptivity, reflectivity, conductivity and porosity of the ceramic fibres have a large impact on energy efficiency. The creation of multiple energy 'trapping' zones allowed for high uniform temperatures, leading to uniform product formation. Energy sources, 25, are contained in the hollow core reactor, 36. These sources are typically electric resistance heating elements, electric arcs or plasma torches.

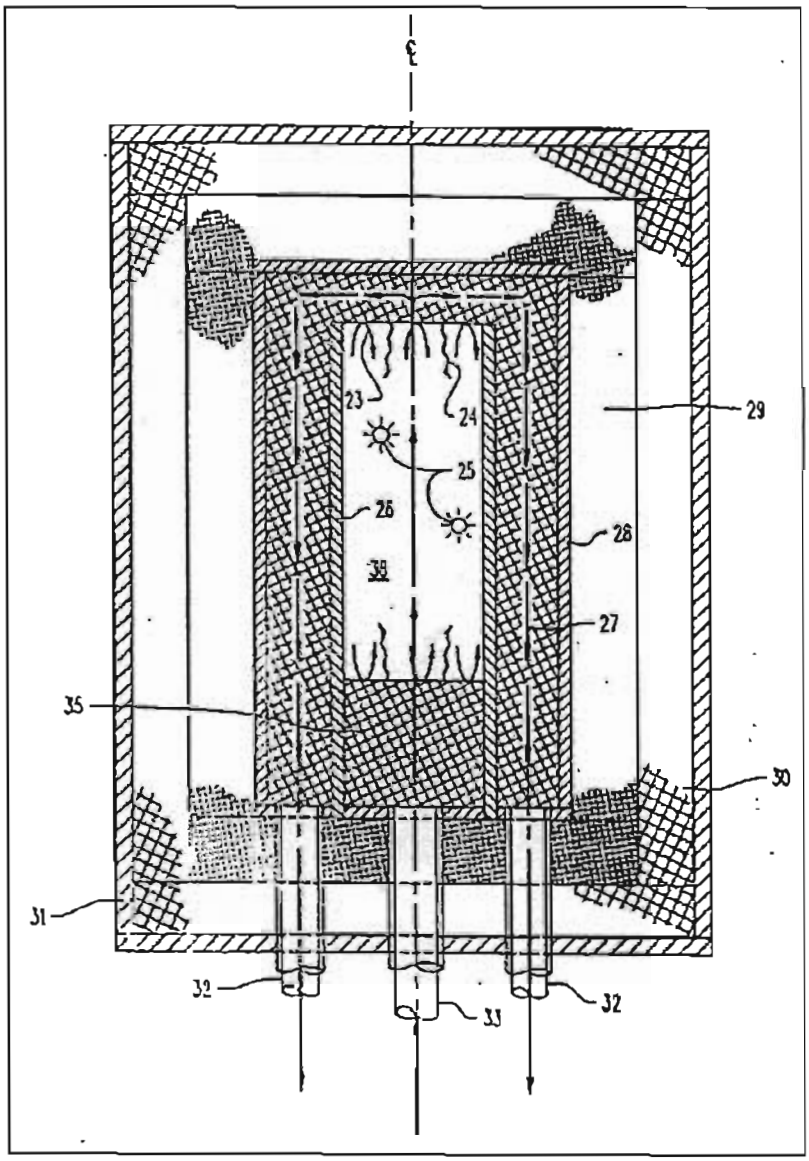


Figure 4-5: Thermoelectric reactor of Wang [1997]

Welgemoed [1996] patented a reactor specifically for the production of hydrogen cyanide gas from a saturated hydrocarbon (methane) reactant and a nitrogen containing (ammonia) reactant. One embodiment of the reactor was a block of graphite, into which a number of holes (tubes into which the reactants are introduced) are drilled. Current was induced to flow in the graphite block under the influence of a high frequency magnetic field produced by a high frequency electrical current flowing in a coil which surrounds the graphite block. Heat was generated by the current flowing in the graphite and this heat was then radiated and/or convected into the tubes, thus supplying the heat of reaction for the production of the hydrogen cyanide.

Figure 4-6 is a schematic section through a second embodiment of the reactor as invented by Welgemoed [1996]. In this design, a number of graphite conduits, 14, were arranged in nests of three and contained in a furnace, 12. The side wall of each graphite tube was thickened at its upper, 18 and bottom, 20 ends, thus allowing for energy to be concentrated in the reaction zone, 21. The side walls could contain graphite, or a composite material comprising of a refractory material and a conductive layer. The inner surfaces of the graphite tubes could be coated with a layer of platinum to catalyse the reaction. This would also have the effect of concentrating the electrical current and enhancing the efficiency of the reactor. Each graphite tube in the nest of three was connected to one phase of a three phase power supply, 24. Reactants were supplied to the tubes by a manifold, 30, and the product gas stream was removed via a water-cooled manifold, 32. Temperatures in the reaction zones were monitored by thermocouples, 26. A viewing port, 28 was located in the furnace wall to allow for the measurement of the side wall temperature by an optical pyrometer.

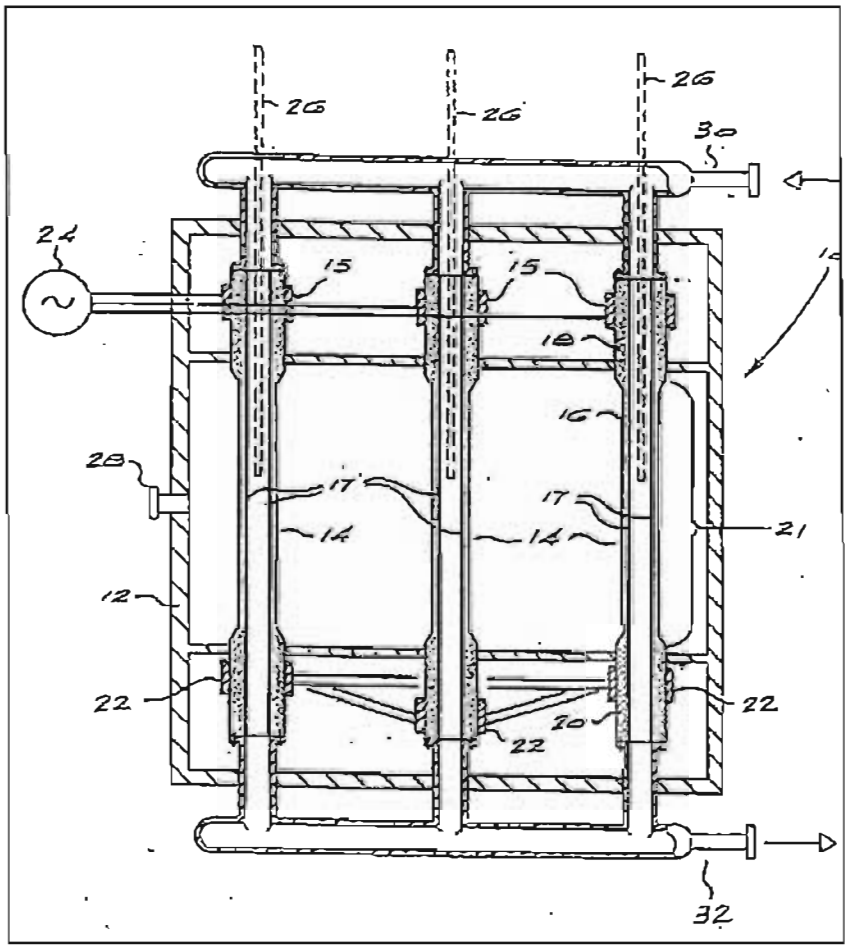


Figure 4-6: Reactor as invented by Welgemoed [1996]

The reactor used for this project is drawn from a combination of the technology described above and is discussed in detail in the next section.

4.2 Equipment and Process for the Pyrolysis of Chlorinated Hydrocarbon Waste

It was expected that chlorinated organic feed material would be pyrolysed to form primarily hydrogen chloride and solid carbon, as well as other minor components. This was further confirmed on use of a web-based tool [EQUILIB-Web, 1999] which predicts reaction products. Product concentrations and phases were predicted based on the assumption that the reaction reaches chemical equilibrium. An example of the products expected from the pyrolysis of CH_2Cl_2 at 1200°C is given below:

Table 4-1: EQUILIB-Web results

EQUILIB-Web Results (incorporating the thermochemical functions of ChemSage developed by GTT- Technologies GmbH, Aachen, Germany).		
CH_2Cl_2 =		
MOLS	**COMPOUND**	**TEMPERATURE, PRESSURE & PHASE**
0.99898	HCl	1473.00 K, 1.0000 atm, ideal gas
0.52270E-03	Cl_2	1473.00 K, 1.0000 atm, ideal gas
0.37851E-03	H_2	1473.00 K, 1.0000 atm, ideal gas
0.11728E-03	Cl	1473.00 K, 1.0000 atm, ideal gas
0.24473E-06	H	1473.00 K, 1.0000 atm, ideal gas
0.40826E-08	C_2HCl	1473.00 K, 1.0000 atm, ideal gas
0.28551E-08	C_2H_2	1473.00 K, 1.0000 atm, ideal gas
0.90156E-09	CH_3Cl	1473.00 K, 1.0000 atm, ideal gas
0.78980E-09	C_2Cl_2	1473.00 K, 1.0000 atm, ideal gas
0.76198E-09	CH_2Cl_2	1473.00 K, 1.0000 atm, ideal gas
0.40959E-09	CH_4	1473.00 K, 1.0000 atm, ideal gas
0.16038E-09	$CHCl_3$	1473.00 K, 1.0000 atm, ideal gas
1.0000	C	1473.00 K, 1.0000 atm, solid
The cut-off concentration has been specified to 1.000E-10		

Product phase distributions were also provided by EQUILIB-Web. The downstream process was thus designed with these predictions in mind.

The process can be divided into the following sections:

- Vapourisation of feed material
- High temperature destruction in the reactor
- Separation of carbon dust from the gas product
- Collection of samples for analysis
- Collection of hydrogen chloride formed in the reaction

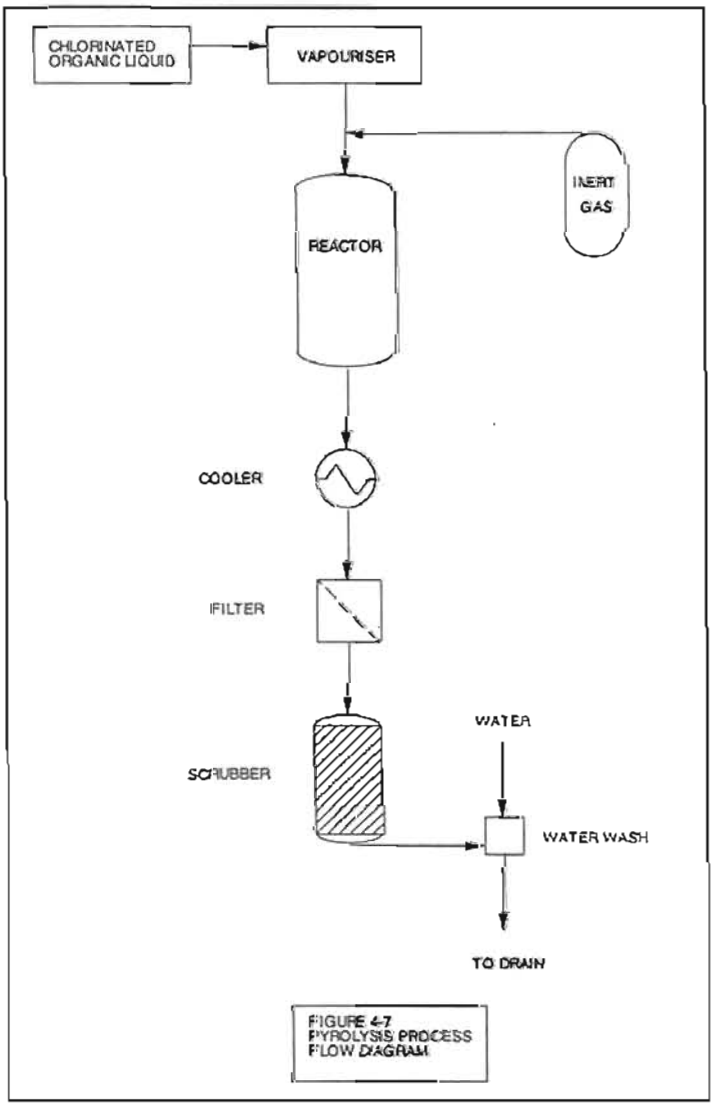


FIGURE 4-7
PYROLYSIS PROCESS
FLOW DIAGRAM

The initial process flow sheet is illustrated in Figure 4-7. The chlorinated feed was to be vapourised and then mixed with an inert gas before being fed into the reactor. The reaction products were to pass through a cooler and then through a solids filter to effect carbon removal. The hydrogen chloride portion of the product was to be scrubbed with caustic soda, with any remaining gases being dissolved in water and flowing to drain.

The chlorinated organic liquid flow was to be regulated by a dosing pump, and then allowed to vapourise in a heated section of tubing through which the feed enters the reactor. This tubing was to be externally heated with nichrome wire with power supplied from a variac.

The alternatives described above for the generation of heat for the reaction have several disadvantages. The method of electrical elements housed in the reaction zone could lead to corrosion and damage of these elements by the chemical compounds present. The ease of removal of these elements, if necessary, is questionable. Heat generation by the combustion of excess methane and oxygen as described by Benson *et al* [1991] requires precise control, failing which oxygen enters the pyrolysis process. This could lead to the formation of toxic dioxins and furans. Furnaces have been used extensively as heating sources; thus the method of induction heating was selected. The efficiency of this method for chlorinated waste destruction was also incorporated as a secondary objective of this project.

Materials for the reactor were sponsored by Quadro Engineering and the reactor was constructed in the School of Chemical Engineering. A sectional view of the reactor used is shown in Figure 4-8. The reactor consists of a vertical graphite tube, A. The inside of the tube is the reaction zone. Graphite was chosen as it has a high thermal conductivity and is capable of emitting radiant energy to the reactants. Graphite is also able to withstand temperatures of up to 2800°C [Perry *et al*, 1984] in a non-oxidising atmosphere, as would be expected in the pyrolysis process. Graphite is also porous, and will permit the flow of an inert gas through the walls of the tube to provide a protective blanket against the occurrence of the reaction on the tube walls. This is desirable to prevent blockage of the reactor. Graphite exhibits all of the mechanical, chemical and thermal properties required for this process, while other chemically stable materials such as high alumina and zirconia are too brittle. Silicon and boron carbides meet all the requirements, but are very expensive when compared to graphite. The thermal and electrical conductivities, as well as the mechanical strength of graphite increase with temperature.

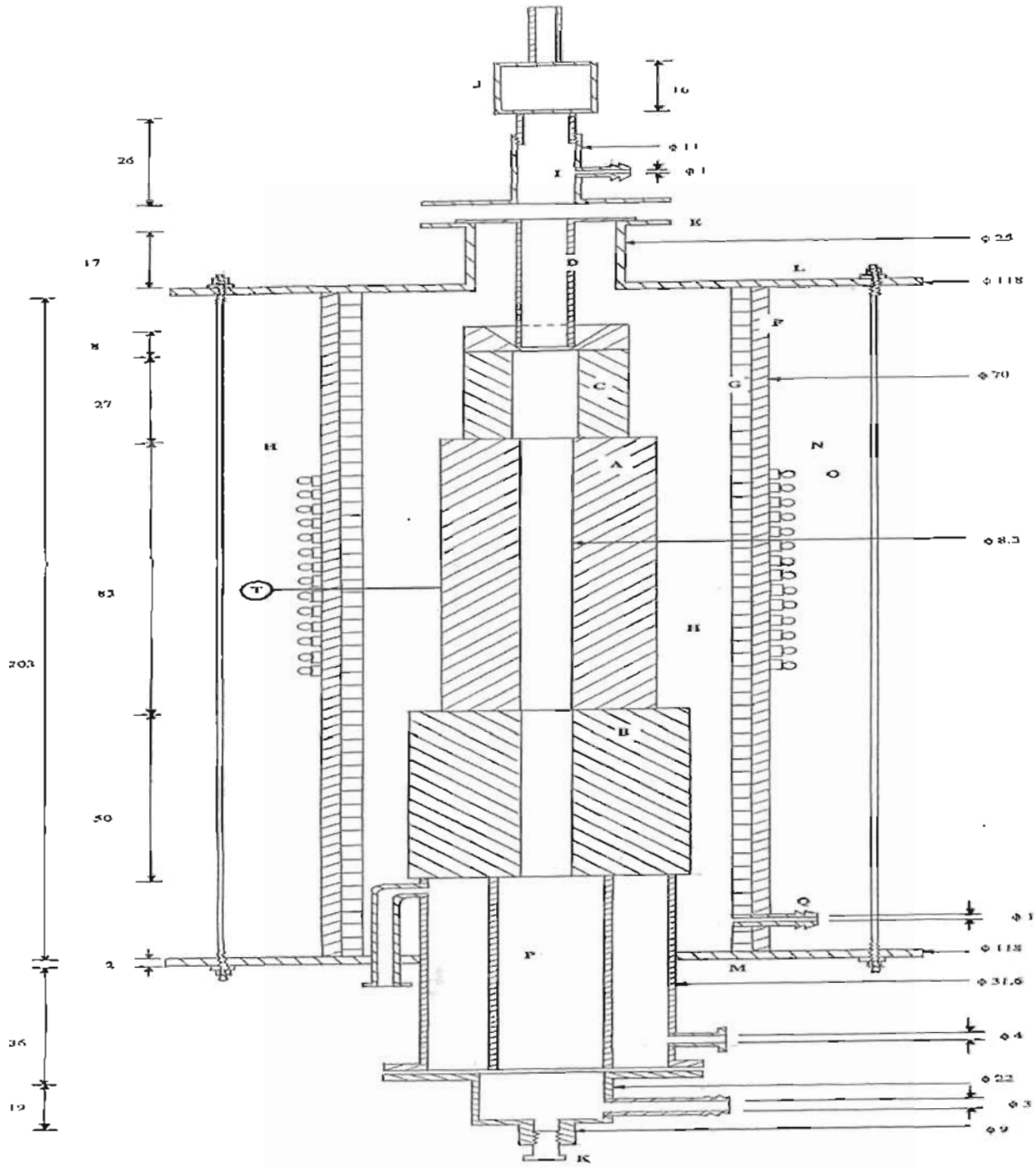


Figure 4-8
Cross sectional view of pyrolysis reactor
Scale 1 : 6
Dimensions in mm

J5. Comparative raw material and utility consumption

Table J-5

	Unit / t	CEP [a]	Plasma arc [a]	Incineration [a]	Pyrolysis	Comments on pyrolysis data
Raw materials						
Oxygen	t	0.5				
100% Caustic soda	t		0.005			
100% HCl	t		0.001			
Process chemicals	t			2		
Utilities						
Process water	m^3			94	1.94	For HCl recovery in scrubber.
Cooling water	m^3		230		187.48	Required only when induction unit is running.
Nitrogen	m^3		510		9.55	Recycled, estimated as 10% of non-recycled requirement.
Electricity	MWh	0.5	1.55	0.23	16.08	Induction heating only. Excludes pumps, variacs, etc.
Natural gas	t	0.23	1.77	2.84		
Steam	t	0.91				

a Arnold, D.R. (2000). Personal communication

Graphite is suitable for induction heating, thus becoming the heating element and thermal radiation source itself, in addition to forming the reactor wall. The inside diameter of the reactor tube was chosen to be fairly large, 50mm in a further attempt to prevent reactor blockage. The wall thickness, 79mm, is fairly large, as required for induction heating. The tube length is 500mm, providing for a reaction zone volume of $0.987dm^3$.

The graphite tube rests on a ceramic pipe, B, of identical internal diameter to prevent heat losses from the tube. A similar piece of ceramic pipe, C, rests on the top end of the graphite tube, also serving as heat insulation. This method of preventing heat loss from the top and bottom ends of the reaction zone was used as ceramic has a very low thermal conductivity and is relatively cheap. Resting on ceramic tube C, is another section of ceramic tubing, 40mm in length. The conical shape directs the flow of reactants towards the reaction zone. A section of steel pipe, D, rests on a lip on flange E to ensure that the feed enters the reaction zone and does not absorb into the carbon black in the shell. This assembly is housed in a larger 1.2m long ceramic pipe, F, with a diameter of 450mm. This outer pipe is lined inside with alumina wool insulation, G, and the space between the inner assembly of tubes and the wool insulation is filled with powdered carbon black, H. The carbon black is an excellent and cheap insulator, and seals the outer surface of the graphite reactor tube at high temperatures, thus preventing the flow of reactants out through the wall of the reactor tube. The reactor is orientated vertically, with the feed entering at the top end via conduit I. This orientation and flow direction was employed mainly to overcome blockages arising from the deposition of solid carbon product in the reaction zone. The top of the reactor is fitted with a device, J, that allows for the viewing of the reaction zone. It consists of a horizontal square of quartz and a mirror angled to reflect the reaction zone. The bottom end of the reactor is fitted with a removable plug, K, through which any carbon deposits can be emptied. The assembly described above rests on an iron framework and additional supports are provided by six steel rods that are bolted through plates L and M. This effectively holds the assembly together.

Argon was selected as the inert carrier gas. It is more expensive than using nitrogen, but it was felt that the presence of nitrogen might lead to the formation of nitrogen-containing hydrocarbons. Also, argon is transparent to thermal radiation, thus allowing all heat emitted from the graphite tube to be available for the reaction and minimising the energy carried out by the carrier gas.

Copper electrical coils, N, surround the outer ceramic pipe over an area aligned with the inner graphite reactor tube. A high frequency Pillar induction unit supplies current to these coils. The

resulting magnetic field induces a current to flow in a susceptor – in this case the graphite tube. The heat of the electrical coils is removed by cooling water flowing in surrounding tubes, O. The capacitors and other components of the induction unit are also water-cooled. The maximum power output of the induction unit is 67 kW and the unit is supplied by a three-phase power source.

The reaction products flow through a stainless steel jacketed water-cooled section, P. The products then pass through a horizontal section of 60mm diameter stainless steel pipe and through a carbon filter. Ideally this section of piping should be vertical to aid carbon flow, but was not feasible owing to spatial limitations. The carbon filter is essentially a cylindrical steel vessel 240mm in length and 155mm in diameter and closed with a gasket and flange. Glass wool resting on a steel wire grid mid-way in the vessel acts as the filter, catching the solid carbon entering from above and the gas product is allowed to flow through the exit below the grid and filter. Glass wool was used as it is successfully able to impede the flow of solid carbon particles.

As it was estimated that the product material would exit the reactor at a fairly high temperature in the region of 300°C, gasket material was chosen accordingly. Compressed asbestos-rubber sheeting was selected as its maximum service temperature is 370°C and it has excellent sealing properties combined with good chemical resistance [Perry *et al*, 1984].

The product gas, expected to consist primarily of hydrogen chloride, then flows through a set of caustic soda scrubbers. The scrubbers consist of a set of three $25dm^3$ plastic containers filled with caustic soda solution and phenolphthalein indicator. The scrubber containers are linked via 4mm diameter poly-flow tubing threaded through rubber bungs in the openings of the containers.

It was decided to take a gas sample as well as a carbon sample for analysis. Two sampling points were set up on the section of pipe between the water-cooled jacket and the carbon filter vessel, to be used alternately. Two glass sampling tubes were designed to act in series. The first tube contained glass wool to trap a carbon sample, with the gas being passed on into the second tube. Both tubes could be shut off with high vacuum stopcocks and the samples isolated. The tubes were to be evacuated first to aid the collection of the sample.

A hazard analysis was carried out on the initial design. The ensuing report can be found in Appendix A. It was felt that the hazards associated with pumping and heating wire failure used for the vapourisation of chlorinated liquids did in fact eliminate this option. As a result, the design was

modified. It was decided to contain the chlorinated liquid in dreschel bottles, held in a water bath at a set temperature. Argon gas is bubbled through the liquid, becomes saturated and carries the chlorinated organic vapour into the reactor. The concentration of the chlorinated organic in argon can be varied by adjusting the temperature of the waterbath. The tubing between the vapourisation system and reactor inlet is heated by nichrome wire to prevent condensation of the organic. Power is supplied by a variac.

A flow sheet of the process is presented in Figure 4-9. The flow rate of argon through the chlorinated organic is monitored by means of a calibrated rotameter. Two dreschel bottles connected by polyethylene tubing were used in series to ensure saturation of the argon. All piping upstream of the reactor is 6.35mm stainless steel tubing. Stainless steel was selected, as it is resistant to corrosion by chloride solutions. It was chosen over a cheaper material such as perspex because it has a higher thermal conductivity and offers for better heat transfer from the nichrome heating wire.

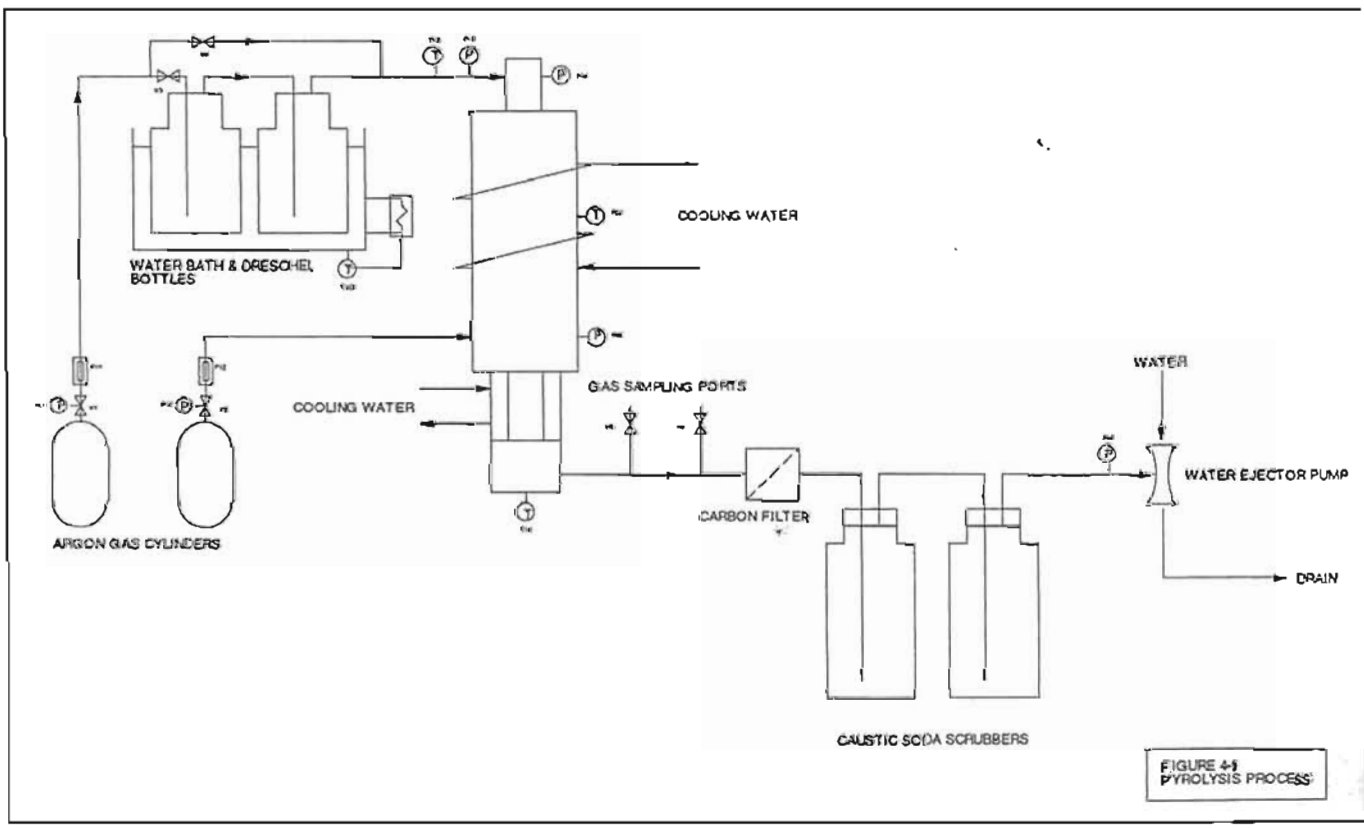


FIGURE 4-9
PYROLYSIS PROCESS

The space in the shell is kept slightly above atmospheric pressure with argon which enters via conduit Q. This prevents any gas components from escaping through the graphite walls and ensures that the feed flows directly into the reaction zone and not into the shell space.

The feed enters slightly above atmospheric pressure, emanating from the pressurised argon gas cylinder. The process is run under a slight vacuum that is attained by a water ejector pump attached to the end of the scrubber system. Operation slightly under atmospheric pressure prevents reactant flow out through the reactor walls into the shell, and induces the flow of the gas products through the process.

The section of piping between the reactor outlet and the carbon filter pot is stainless steel, 1.07m in length and 55mm in diameter. Two sampling points, 12mm in diameter and both fitted with stainless steel valves are located on the line. The outlet of the filter pot is 6.35mm, and is fitted with an attachment for polyethylene tubing. Gaseous hydrogen chloride does not attack polyethylene tubing thus it was selected as a cheap as well as a flexible material. The last scrubber is connected to the water ejector pump by polyethylene tubing.

Pressure is monitored at various points of the process by the use of water-filled manometers. The following pressures are monitored:

- Shell pressure
- Vacuum pressure
- Reactor inlet tube

Manometers are also placed in outlet lines from gas cylinders as a safety measure. In the case of a blockage arising further downstream, the gases can blow out through the manometers.

Three temperatures are monitored at the following points:

- Feed material
- Outside surface of graphite reactor tube
- Reactor product

Temperatures are measured with one 'K' and two 'R' type thermocouples respectively. Voltage readings are converted to temperature readings that are displayed or logged to a file by means of a PC73 C interface card. Aside from determining the actual temperature of the reaction, it was

necessary to carefully monitor the temperature of the graphite, as substantial sublimation losses occur above 2500°C.

The reaction temperature was manually controlled by monitoring the temperature of the graphite tube and turning the induction unit on and off as required. A more sophisticated control system can be considered once the technology is proven.

The entire rig is earthed, and valves and taps are insulated and earthed to prevent the build-up of static.

4.2.1 Commissioning Runs and Modifications

Before the graphite could be conditioned and the apparatus commissioned, calibrations of the following were carried out:

- Argon gas rotameter
- Thermocouples
- Vapourisation system (water bath temperature effect on feed composition)

It was decided to use the following compounds as reactants for the experimental runs:

- Aliphatic compound: methylene chloride (CH_2Cl_2)
- Aromatic compound: 1,2,4-trichlorobenzene ($C_6H_3Cl_3$)
- Industrial waste sample: lindane ($C_6H_6Cl_6$)

Hexane was selected for the test runs and commissioning of the process. Hexane has a boiling point (68.7°C) close to that of methylene chloride (40°C) and would be suitable to test the operation of the vapourisation system.

On first testing the induction unit, it was found that the unit was unstable and the power would regularly cut out. It was also found that a pressure switch on the inlet and outlet cooling water lines

did not function. On examination of the unit, a defective circuit board was found. The repair and return of the board halted further commissioning work on the reactor.

An electrician was consulted to advise and check on safe working conditions of the induction unit and reactor.

The first test was carried out to condition the graphite tube to high temperatures. The induction unit was turned on for 20 minutes at 10% of its rated power output (7kW). A temperature of 100°C was achieved in this time. It was important to raise the temperature very slowly to prevent the graphite from fracturing under sudden temperature fluctuations. The power output was then raised to 20kW and the graphite reactor tube heated to 1000°C. The heating rate for this period was 13°C per minute. Argon flow into the shell and reactor tube was introduced at a reactor temperature of 200°C. This was done to flush out the oxygen present in the system and to prevent the graphite from heating up too quickly. It was found that a large amount of water had collected in the space below the cooling water jacket. This water had been trapped in the graphite prior to its heating. The conditioning of the graphite was repeated until no more water was collected.

During these trials, it was found that the thermocouple signals to the PC card were very erratic while the induction unit was running. The strong magnetic fields around the electrical coils interfered with the signals and thus the temperature readings. The thermocouple cables were covered with aluminium tape and this reduced the interference caused by the magnetic field.

It was also found that the functionality of the variac was affected by the magnetic field. The variac was relocated away from the electrical coils and successfully heated the inlet pipe in this position.

The required cooling water pressure drop through the induction unit and the induction coil set-up is 1 atm and the induction unit is automatically shut down by a pressure switch if the this pressure drop is not met. It was found that the mains water pressure was insufficient for this purpose when it was used for other processes at the same time. A water-cooling tower was commissioned and used solely for the pyrolysis process. The set-up is such that water for the cooling of the induction unit and the electrical coils can be supplied either from water mains or from the cooling tower. The water ejector vacuum pump and the cooling jacket downstream of the reactor are supplied by mains only and the water runs to drain.

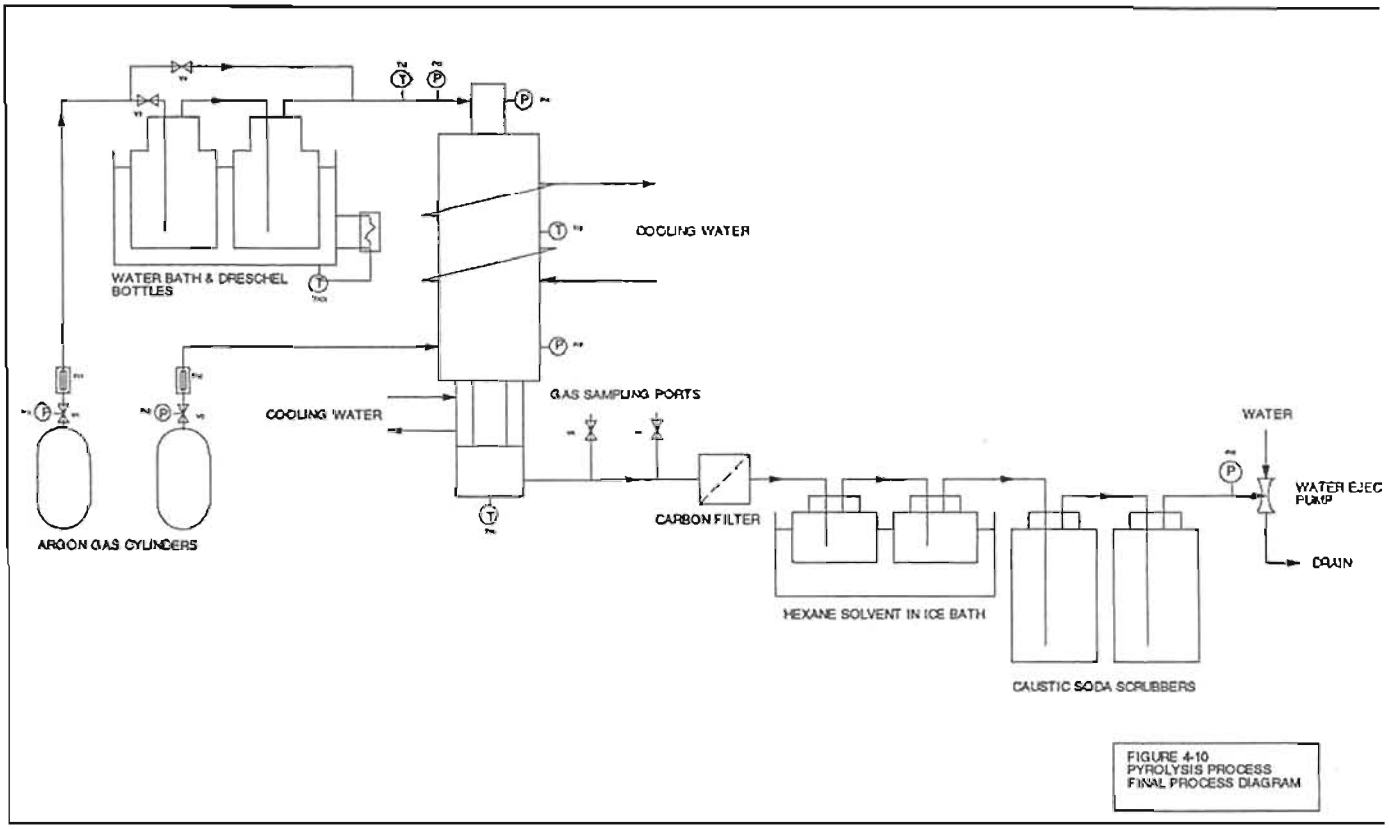
Three options were available for the evacuation of the sampling tubes. Repeat evacuations using two oil vacuum pumps showed that the pumps were erratic and that the vacuum attainable was insufficient. A compressed air vacuum pump was then used, and with this, a maximum vacuum of 80% was achieved. It became a concern that the oxygen remaining in the tube could react with the sample. Also, it was only possible to analyse samples once a week due to the availability of the instruments. Thus storage of the gas samples posed a problem. It was decided to modify the process such that the filtered product gas is bubbled through a hexane solvent before the hydrogen chloride is neutralised in the caustic soda scrubbers. A sufficient amount of solvent would dissolve all the other gases and can be easily stored in a refrigerator.

During the commissioning runs, a leak was located at the flange at the reactor inlet and merely required tightening of the bolts to solve the problem. The tape enclosing the nichrome wire on the inlet line to the reactor burnt out after the second run, causing a short circuit. The line was re-taped, this time with two layers of glass tape. There has been no need to replace this tape again.

It was also noticed that some of the carbon produced had passed through the glass wool filter and was deposited in the scrubber. On subsequent runs, a thicker layer of wool was used in the filter pot and only traces of carbon were found in the scrubber.

Larger amounts of carbon were found deposited at the end of the reactor, at the plug at the bottom end. This is dictated by the orientation of the reactor outlet pipe and could not be changed owing to spatial and time considerations. It was thus decided to use a vacuum on the end of the carbon filter and then at the reactor plug after each run to remove carbon that had settled in the horizontal section of pipe. It was noted that this set-up would affect the carbon mass balance.

The final process flow diagram is illustrated in Figure 4-10.



4.3 Experimental Procedure

The procedure below was devised for the destruction of methylene chloride, and deviations from this method for trichlorobenzene and lindane are discussed later. Valves referred to can be found in Figure 4-10.

- The scrubbers and solvent bottles were filled with caustic soda and hexane, respectively, and glass wool was placed in the filter pot.
- Cooling water flow to the induction unit, electrical coils and cooling jacket was started.
- Heating of the water bath and inlet line to the reactor was started.
- The induction unit was started at 30% of its maximum power rating of 67kW. It was found that this power output was sufficient to heat the reactor to above 1000°C within approximately 90 minutes.
- When the reactor tube temperature reached 200°C, argon gas was allowed to flow into the shell, and the shell pressure was maintained between 200 and 600 Pa gauge. A small argon flow was

also introduced into the reactor tube to blanket the tube wall. This was done with valve V4 opened, and valve V3 closed. At this time, valve V5 or V6 were opened, and argon was vented from the reactor and removed by an extractor fan situated in the ceiling above the reactor.

- When the reactor reached the required temperature, the induction unit was manually switched off, valves V5 and V6 were closed and a slight vacuum of between 600-1000 Pa gauge was induced by means of the water ejector pump.
- A known mass of methylene chloride was placed in the dreschel bottles and the required argon flowrate was set using V1 in conjunction with rotameter, FI1. Valve V4 was then closed with V3 simultaneously opened. Argon was thus allowed to bubble through the methylene chloride, carrying it into the reactor.
- During this period of feeding the reactants into the reactor, the temperatures of the reactor and the heated inlet line were monitored and increased by either running the induction unit or increasing the power output of the variac respectively. It was observed that the temperature of the reactor tube rose by approximately 50-80°C from the temperature at which the induction unit is switched off. Thus, for short runs of up to 60 minutes, it was rarely necessary for the unit to run after the initial heating period.
- The shell and tube pressures were monitored, and the argon flow to the shell was adjusted via valve V2 to ensure that the shell pressure, PI5, was at least 200 Pa higher than the tube pressure, PI4.
- During the run, ice was constantly replenished in the bath in which the hexane solvent bottles were contained, and the pink phenolphthalein colour in the scrubber was monitored. If the colour turned clear, the caustic soda was saturated with hydrogen chloride, which means that hydrogen chloride gas was escaping to drain.
- Once all, or the desired quantity of methylene chloride had been fed into the reactor, argon flow was again switched through valve V4, with V3 being closed. The argon flowrate was then increased to flush out all the products in the reactor into the solvent and scrubber, and the shell pressure was increased accordingly to be maintained at 200 Pa higher than the tube pressure. This was maintained for approximately 2 hours after feed to the reactor was stopped.
- At the end of the run, the hexane solvent bottles were sealed and refrigerated and the scrubber liquid could be titrated for hydrogen chloride concentration if desired.
- The argon flow to the shell was stopped, and only a small bleed of argon was allowed through the tube. This was to prevent any oxygen entering the reactor when the filter pot was opened.
- The filter wool was removed and any carbon settled in the bottom of the reactor or in the horizontal section of pipe was recovered with the aid of a vacuum cleaner.

- Argon flow to the tube was stopped when the reactor temperature reached approximately 400°C.

Note that all valve and other adjustments were made when the induction unit was not running, as all metal was considered live during induction.

The boiling points of trichlorobeneze and lindane are 213°C and 323°C respectively. An alternative method of vapourisation was devised for these two compounds. A steel vessel, illustrated in Figure 4-11 was fabricated and was heated by a 220V, 600W band heater surrounding the outside of the boiling vessel and powered by a variac. An inlet for argon gas and an outlet to the reactor were made in the lid. A thermocouple was also inserted into the centre of the vessel through the lid. A viton gasket was used to seal the flange between the lid and the vessel.

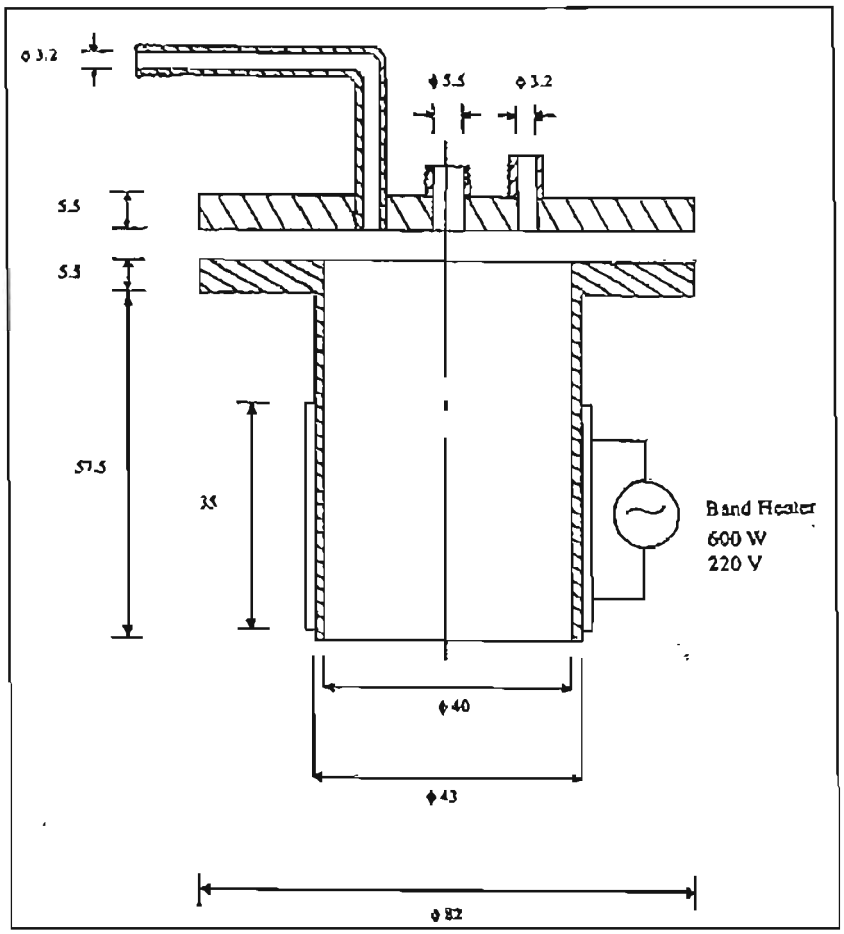


Figure 4-11: Boiling vessel

For experiments conducted with trichlorobenzene and lindane, known masses of the compounds were placed into the boiling vessel, which was then sealed and the heater turned on. The temperature in the vessel was logged to a file, and a simple plot of temperature versus time indicated the time taken for the compound to fully vapourise. This method was crude and offered no control over the rate of flow into the reactor. However, for the purposes of this project, i.e. illustrating that these products can be pyrolysed, this method was sufficient. A better system with accurate control can be implemented when optimisation of the process is investigated.

4.4 Sample Preparation & Analysis

The hexane solvent and compounds therein was analysed by a gas chromatograph (GC) with mass spectrometer (MS) detector located in the School of Chemistry at the University of Natal. The GC is an Aligent 6890, with an Agilent 5973 electron impact detector. The column used was a HP-Innowax polyethylene glycol column, P/N 1909N-133 (300mm x 0.25mm), with a film thickness of 0.25µm. The method can be found in Appendix C.

The solid product collected on the glass wool was washed off with acetone. The solid material recovered from the pipes and the bottom of the reactor was added to the acetone solvent. The solvent was then filtered to remove the solids. The filtrate was allowed to evaporate, and the remaining residue was dissolved in ethanol and analysed by GC/MS.

The initial set of samples were analysed qualitatively only, due to high costs of analyses. Once suitable experimental conditions had been found, quantitative analyses were carried out. For some of the later runs, the scrubber liquid was collected and a sample titrated with hydrochloric acid to determine the quantity of hydrogen chloride, and thus chlorine, recovered in the scrubber. In these later runs, a mass balance was also carried out on the carbon formed, and reaction products were quantified.

5. RESULTS AND DISCUSSION

This chapter provides details of experiments performed and the corresponding results. Both qualitative and quantitative results are investigated, and the destruction efficiency (DE) of the pyrolysis reactor is evaluated. The efficiency of transfer and use of energy supplied to the process is also evaluated and discussed.

5.1 Characterization of reactants and solvents

Suppliers of the reactants (methylene chloride, 1,2,4-trichlorobenzene) and solvents (ethanol and n-hexane) used in the pyrolysis process, as well as chemicals used for calibration of the GC can be found in Appendix G. The refractive indices of all the chemicals were measured and compared to literature values.

Reactants and solvents were analysed by GC/MS and the impurities found are tabulated below.

Table 5-1: Chemical impurities

Chemical	Impurities
ethanol	cyclohexane, methyl alcohol
hexane	pentane, methylcyclopentane, cyclohexane
methylene chloride	2-methyl-2-butene (stabiliser)
1,2,4-trichlorobenzene	cyclohexane, acetone, dichlorophenol
lindane (in ethanol solvent)	trichlorobenzene

5.2 GC calibration

The GC/MS was calibrated for the following compounds in hexane:

- methylene chloride
- chlorobenzene
- dichlorobenzene
- trichlorobenzene

- lindane,

as well as for trichlorobenzene in ethanol. Calibration curves can be found in Appendix H.

Many of the peaks of interest were very small as a direct result of the parts per million concentrations, and were not automatically integrated. These peaks had to be manually integrated, which immediately introduced errors by way of human judgement. This resulted in some points not fitting the general curve and being discarded. Errors in the calibrations were also expected due to the highly volatile nature of both solvent and solute. Ideally, four or more points are desirable when generating calibration curves, however, many of the calibration points had to be discarded as a result of the errors mentioned above,

It was decided to quantify only chlorinated pyrolysis products for mass balance purposes. It was also necessary to quantify the chlorinated products from an environmental point of concern, as many chlorinated hydrocarbons are toxic, as discussed earlier. Although tetra- and penta-chlorobenzene were detected products for some runs, they occurred in trace amounts, thus the GC/MS was not calibrated for these compounds. Since most of the solid product settled in the tube downstream of the reactor, attempts at carbon mass balances would prove futile.

5.3 Pyrolysis of Methylene Chloride

Initially, experiments on the pyrolysis of methylene chloride were conducted primarily to ascertain destruction efficiencies (or conversion) at different reaction temperatures and residence times. Mass balances were not attempted during this phase of the project, as the product analyses carried out were purely qualitative. These analyses were important as they served as an indication of the compounds the gas chromatograph had to be calibrated for. This became important during the second phase of the project, in which chlorine mass balances were attempted.

During the second phase, it became evident that collection of the hydrogen chloride product in the caustic soda scrubbers was inefficient. The second phase thus also deals with improvements to the collection system.

5.3.1 Phase One: Qualitative results

A set of 12 experiments was carried out to determine the effect of reaction temperature and residence time on the destruction efficiency and the product spectrum. The results are tabulated below. The mass of methylene chloride fed into the reactor ranged between 163g and 325g at a concentration of approximately 70 %(wt) with argon. Residence time was dependent on the flowrate of argon as well as on the reaction temperature. Short residence times of below approximately 1.2 seconds were impossible due to the nature of the feed system. Increasing the argon flow to allow for short residence times caused a pressure build-up in the dreschel bottles, resulting in the bottle heads being pushed off and oxygen being allowed into the system. Only products identified with over 80% certainty by the GC/MS database are reported. Starting material (i.e. methylene chloride) is not listed, but is implied for less than 100% destruction efficiency. Hydrogen chloride production is not listed, but was present for all runs.

Table 5-2: Products and DE of methylene chloride pyrolysis at different temperatures and residence times

Run	Temperature (°C)	Residence time (sec)	DE (%)	Chlorinated organic products	Other organic products
3a	1414	3.34	99.9999	none	hexane, cyclohexane, carbon
2c	1225	1.25	99.99	none	hexane, cyclohexane, carbon
2b	1221	3.78	100	none	hexane, cyclohexane, carbon
2a	1210	2.58	100	none	decane, hexane, cyclohexane, carbon
1c	1041	4.75	100	none	hexane, cyclohexane, carbon
1b	1040	2.12	100	none	hexane, cyclohexane, pentane, carbon
1a	1018	2.96	99.999	none	hexane, cyclohexane, 3-methyl-2-butanol, decane, carbon
4a	852	5.56	99.99	none	hexane, cyclohexane, carbon

Table 5-2 (continued): Products and DE of methylene chloride pyrolysis at different temperatures and residence times

Run	Temperature (°C)	Residence time (sec)	DE (%)	Chlorinated organic products	Other Organic products
5b	658	2.18	56.32	dichloroethene, trichloroethylene, tetrachloroethylene, chloroform, trichloropropene, tetrachloropropene, dichlorocyclobutene, chloromethylethyl-benzene, chlorobenzene, dichlorobenzene, trichlorobenzene, tetrachlorobutadiene, pentachlorobutadiene, tetrachloroethane, ethyl chloride, trichloronaphthalene, tetrachloronaphthalene	hexane, cyclohexane, octadecane, heptane, nonane, diiso-octyl phthalate, carbon
6c	488	2.55	99.9	dichloroethene, trichloroethylene, tetrachloroethylene, chloroform, chlorobenzene, dichlorobenzene, trichlorobenzene	pentane, hexane, cyclohexane, nonane, dibutyl phthalate, bis (2-ethylhexyl) phthalate, diiso-octyl adipate, carbon

Table 5-2 (continued): Products and DE of methylene chloride pyrolysis at different temperatures and residence times

Run	Temperature (°C)	Residence time (sec)	DE (%)	Chlorinated organic products	Other Organic products
6a	478	3.04	90.28	trichloroethylene, tetrachloroethylene, chloroform, dichlorocyclobutene, tetrachlorobutadiene, pentachlorobutadiene, dichloroethene, trichloropropene, tetrachloroethane, chlorobenzene, dichlorobenzene, trichlorobenzene	hexane, cyclohexane, nonane, linoleic acid ethyl ester, tetradecane, dibutyl phthalate, carbon
6b	348	3.52	63.56	trichloroethylene, chloroform, tetrachloroethane, tetrachlorobutadiene, chlorobenzene, dichlorobenzene, trichlorobenzene	hexane, cyclohexane, nonane, dibutyl phthalate, carbon

The first 8 runs, at temperatures between 850°C and 1420°C, produced no chlorinated hydrocarbons, signifying that all the chlorine had been converted to hydrogen chloride as expected. From runs 2a, b and c, it is clear that the residence time is an important variable. An increase in residence time by 1.33 seconds increased the DE from 99.99% to 100% at 1200°C. It can be seen from runs 1a-c, 2a-c and 4a that as the reaction temperature is decreased, the residence time needs to be increased to maintain high destruction efficiencies. A DE of 100% was expected at 1414°C and a residence time of 3.34 seconds, based on 100% DE at 1210 and 1221°C and residence times of 2.58 and 3.78 seconds respectively. Although this was not the case, an acceptable six nines (99.9999%) destruction was obtained.

Pentane, hexane and cyclohexane traces were found as residue on the carbon produced. It is suspected that rather than being a product of the pyrolysis reaction, the presence of these compounds is a direct result of evaporation of the solvent used in the process. The solvent was housed in closed containers located after the carbon filter pot. Process gas bubbled through the solvent through polyflow tubing. The hexane could quite conceivably evaporate, as it is very volatile. It was observed that at least 0.15 dm^3 of solvent was lost over the duration of each run, despite being kept at a temperature below its boiling point. In future, the use of a less volatile solvent could be investigated.

Traces of 3-methyl-2-butanol found in run 1a can be attributed to the impurities found in the ethanol solvent used to extract the products that formed as residues on the carbon.

Taylor and Dellinger [1988], observed products with no more than two carbon atoms in their study of methylene chloride pyrolysis at temperatures between 300-1050°C and a residence time of 2 seconds. However, as can be seen from the results tabulated, nonane, decane, octadecane, and tetradecane products were extracted from the carbon formed. These high molecular weight aliphatic compounds form as a result of decomposition and displacement dechlorination reactions and subsequent radical recombination and chain propagation, as discussed in Chapter 2.

Runs 5b and 6a-c were carried out specifically to observe the effect of lower temperatures on both the DE and the products of methylene chloride production. It can be seen that the destruction efficiencies between temperatures of 348-658°C are low and do not meet the 99.9999% value which was the objective of the project. The destruction efficiencies for this set of runs do not seem to follow any trend. At 658°C a DE of 56.3% is obtained, whereas higher destruction efficiencies are obtained at temperatures of 348, 478 and 488°C. This can be attributed to longer residence times at the lower reaction temperatures. It can be seen from Table 5-2 that for runs 6a and 6c, at similar temperatures and a residence time difference of 49 seconds, the lower residence time run in fact resulted in 9.7% higher destruction efficiency.

Chlorinated products included hydrocarbon chains with up to 4 carbon atoms, 4-carbon cyclic species (dichlorocyclobutene), and chlorinated benzene rings. Taylor and Dellinger [1988] observed an absence of production of chlorinated aromatics from methylene chloride, however results observed here are not in agreement. Chlorinated naphthalenes (10 carbon atoms) were also detected. A mechanism to explain the formation of these chlorinated compounds was attempted

and is based on the core pyrolysis and molecular growth mechanism for trichloroethane as presented by Taylor *et al* [1994]. Mechanisms leading to the formation of butadienyl radicals (reactions 11 and 13) and vinyl acetylene (reactions 10 and 12) can be found in Table 5-3.

Table 5-3: Core pyrolysis mechanism of methylene chloride leading to the formation of C_4 radicals

	Reaction
1.	$CH_2Cl_2 \leftrightarrow CH_2Cl + Cl$
2.	$CH_2Cl_2 + Cl \leftrightarrow CHCl_2 + HCl$
3.	$CHCl_2 \leftrightarrow CHCl + Cl$
4.	$CHCl_2 \rightarrow CHCl + Cl$
5.	$CHCl_2 + Cl_2 \rightarrow CHCl_3 + Cl$
6.	$CHCl_2 + Cl \rightarrow CCl_2 + HCl$
7.	$2\ CCl_2 \rightarrow C_2Cl_4$
8.	$C_2Cl_4 + Cl \rightarrow C_2Cl_3 + Cl_2$
9.	$C_2Cl_3 \leftrightarrow C_2Cl_2 + Cl$
10.	$2\ C_2Cl_2 \rightarrow C_4Cl_4$
11.	$C_2Cl_3 + C_2Cl_2 \leftrightarrow i\text{-}C_4Cl_5$
12.	$i\text{-}C_4Cl_5 \leftrightarrow C_4Cl_4 + Cl$
13.	$C_4Cl_4 \leftrightarrow i\text{-}C_4Cl_3 + Cl$

The formation of C_6 and higher molecular weight chlorinated PAH species involves the reaction of secondary vinyl acetylene radicals ($i\text{-}C_4Cl_3$) and secondary butadienyl radicals ($i\text{-}C_4Cl_5$) with vinyl acetylene (C_4Cl_4), for example:

$$i\text{-}C_4Cl_3 + C_4Cl_4 \leftrightarrow C_8Cl_7\ (I) \qquad (5\text{-}1)$$

$$i\text{-}C_4Cl_5 + C_4Cl_4 \leftrightarrow C_8Cl_9\ (I) \qquad (5\text{-}2)$$

The products of reactions (5-1) and (5-2) above each lose a chlorine atom, forming C_6Cl_5-CCl (cy) and C_6Cl_5-CCl=CCl_2 (cy) respectively. Figure 5-1 is a schematic of molecular growth pathways involving these secondary C_4 radicals [Taylor *et al*, 1994] and C_6Cl_5-CCl (cy). The reactions proceed through radical addition to the acetylene group, isomerisation and finally cyclisation. The

last step occurs via radical attack and chlorine displacement. This mechanism accounts for the formation of chlorinated naphthalenes and benzenes.

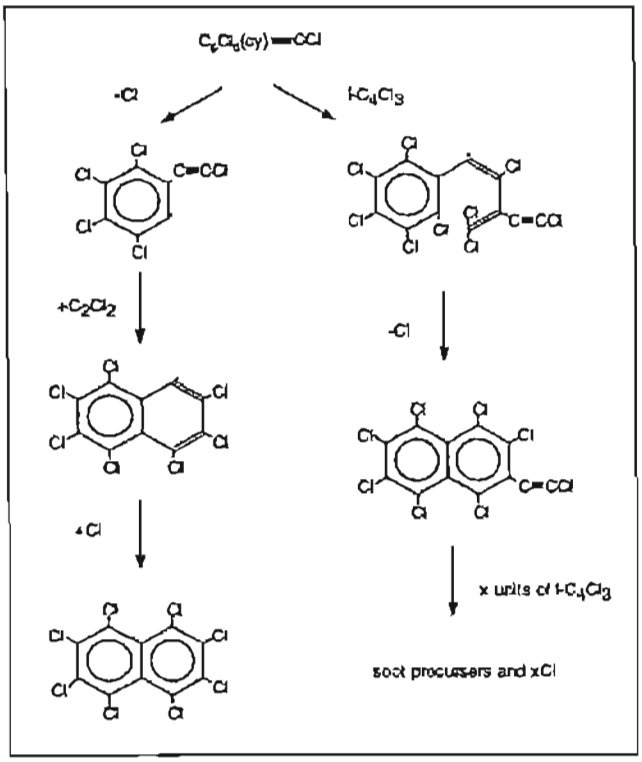


Figure 5-1: Schematic of molecular growth pathway involving C_4 radicals
(Taylor et al 1994, pg 89 fig 7)

Oxygenated compounds produced in runs 5 and 6a-c are causes for concern. Dibutyl phthalate ($C_{16}H_{22}O_4$) and bis (2-ethylhexyl) phthalate ($C_{24}H_{38}O_4$), as well as diisooctyl adipate and diisooctyl phthalate were produced. Figure 5-2 illustrates the structures of some of the phthalates formed. These experiments were carried out following the same procedure used for runs 1-4. The result suggests that there are traces of oxygen in the pyrolysis process, but that it only becomes visible in reaction products at lower temperatures. The dreschel bottles are only filled to half their capacity (0.25 dm^3), and this could be the one of the sources of oxygen. It is also possible that oxygen in the shell space and tube were not thoroughly flushed out between runs. During some of the later experiments, it was found that the silicone seal around the thermocouple inserted in the shell had become loose. As a result, oxygen leakage into the reactor could have occurred before the broken seal was detected. It is also possible that oxygen could have entered the system dissolved in the

hexane solvent. Degassing of the solvent could be considered for future work. These results highlight the importance of a completely oxygen-free atmosphere.

The compounds illustrated in Figure 5-2 are common plasticisers used in the formulation of polyvinylchloride (PVC). It is possible that these compounds could have been leached from the polyflow tubing in the process by the product gas stream.

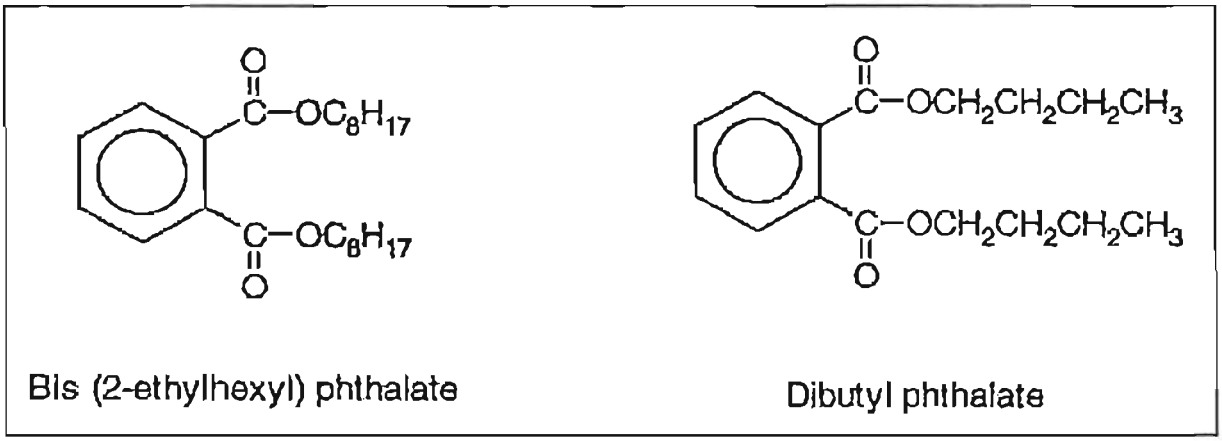


Figure 5-2: Oxygenated compounds found in runs 5a and 6a-c

5.3.2 Phase Two: Mass balance and collection system

Once temperatures and residence times for 100% destruction of methylene chloride had been established, chlorine and carbon mass balances were attempted.

The outlet tube from the reactor to the carbon filter was 1m long (to allow for the product to cool) and horizontally orientated due to spatial limitations, as mentioned earlier. Most of the carbon produced in the first 12 runs settled in this tube with less than 20% carbon recovery for some runs, and over 100% recovery for others. Also, after the first twelve runs, the reactor was opened out and a large amount of carbon was found collected in the bottom flange of the reactor near the plug. It was clear that the carbon collected after each run was not necessarily produced in that particular run. Thus, for runs 9b-l, the bottom flange was opened and cleaned out after each run, and a vacuum cleaner was used to recover as much carbon as possible from the horizontal outlet pipe. It was decided to focus on the chlorine mass balance, as this was the toxic component of the reactant,

thus maximum carbon recovery was important, as most of the heavy molecular weight chlorinated products were recovered from the solid carbon sample.

5.3.2.1 Reaction products

Table 5-4 is a summary of the results obtained. The destruction efficiency for all runs was 100%. Reaction temperatures and residence times are given. Also tabulated are the chlorinated and non-chlorinated hydrocarbons produced in the reactions. Feed masses ranged from 99.6 to 156.9g.

It was expected that products similar to those formed in the initial twelve runs would be obtained. Long chain hydrocarbons, namely tetradecane ($C_{14}H_{30}$), dodecane ($C_{12}H_{26}$), hexadecane ($C_{16}H_{34}$) and eicosane ($C_{20}H_{42}$) were formed, in agreement with those formed in runs 1-6c.

Between 1-2g of lindane was extracted from the carbon produced in runs 9d, 9k and 9f at reaction temperatures of 1032, 1031 and 854°C respectively. Lindane pyrolysis was carried out between runs 1-6d and 9b-l. As discussed later in Section 5.5, these experiments were unsuccessful, due to the condensation of the reactant on the inside of the inlet tube of the reactor. Results from runs 1-6d show no production of lindane. A possible explanation for the presence of lindane in runs 9d, 9k and 9f is that during cleaning of the tube, some lindane had been overlooked and become dislodged during these methylene chloride runs, collecting on the carbon produced. However, Van der Westhuizen [1994] found lindane traces in the pyrolysis product of trichloromethane and carbontetrachloride. Thus, in future, the reactor should be thoroughly cleaned and the reaction repeated to determine the source of the lindane. Repeat experiments were not carried out here, as lindane pyrolysis was aborted (see Section 5.5).

Table 5-4: Summary of conditions and products for 100% DE of methylene chloride

Run	Temperature (°C)	Residence time (secs)	Chlorinated organic products	Other Organic products
9e	1385	3.85	c, d, ethyl chloride	ethyl ether, 4-methyl-3-penten-2-one, tetradecane, acetic acid, butylated hydroxytoluene
9b	1222	3.57	c	h, butylated hydroxytoluene, diisopropylnaphthalene, eicosane, tetradecane, acetic acid, 4-methyl-3-penten-2-one
9i	1042	3.78	c, d, e, ethyl chloride,	h, acetaldehyde, 4-methyl-3-penten-2-one, tetradecane, hexadecane, butylated hydroxytoluene
9h	1033	4.73	c, d, e, f, ethyl chloride, hydrochloric acid, pentachlorobiphenyl, hexachlorobiphenyl, dichloronaphthalene, trichloronaphthalene, trichlorophenol, tetrachlorophenol	h, 2-methyl-1-propene, 4-methyl-3-penten-2-one, tetradecane, acetic acid, formic acid, hexadecane, butylated hydroxytoluene, biphenyl
9d	1032	3.92	c, g, ethyl chloride,	h, 4-methyl-3-penten-2-one, acetic acid, butylated hydroxy-toluene, dibutyl phthalate

Key:

a chlorobenzene
b dichlorobenzene
c trichlorobenzene
d tetrachlorobenzene
e pentachlorobenzene
f hexachlorobenzene
g lindane (hexachlorocyclohexane)
h hexane and/or cyclohexane

Table 5-4 (continued): Summary of conditions and products for 100% DE of methylene chloride

Run	Temperature (°C)	Residence time (secs)	Chlorinated organic products	Other Organic products
9k	1031	4.58	b, c, d, e, f, g, ethyl chloride, dichloro-naphthalene, trichlorophenol, tetrachlorophenol,	h, 1-butene, ethyl acetate, 4-methyl-3-penten-2-one, dodecane, tetradecane, acetic acid, hexadecane, biphenyl
9j	1021	3.91	c, d, e, ethyl chloride, trichlorophenol, pentachlorobiphenyl, hexachlorobiphenyl	h, ethyl acetate, 4-methyl-3-penten-2-one, tetradecane, acetic acid, hexadecane, butylated hydroxy-toluene
9l	1020	4.33	c, d, e, f, ethyl chloride, trichloro-phenol, trichloro-naphthalene, hexachlorobiphenyl	h, 2-methyl-1-propene, ethyl ether, 4-methyl-3-penten-2-one, dodecane, tetradecane, acetic acid, hexadecane, 10-methyl-eicosane, butylated hyroxytoluene,
9g	1016	3.60	c, d, e, ethyl chloride, hydrochloric acid	h, acetaldehyde, tetradecane, acetic acid, hexadecane,
6d	946	2.06	a, b, c	h, benzene
9f	854	3.63	c, d, e, g, ethyl chloride, hydrochloric acid, pentachlorobiphenyl	h, 4-methyl-3-penten-2-one, butylated hydroxytoluene, tetradecane

Key:

a	chlorobenzene
b	dichlorobenzene
c	trichlorobenzene
d	tetrachlorobenzene
e	pentachlorobenzene
f	hexachlorobenzene
g	lindane (hexachlorocyclohexane)
h	hexane and/or cyclohexane

Chlorinated benzenes were formed as expected, however, tetra-, penta- and hexa-chlorobenzenes were also present. Figures 5-3 and 5-4 show the chlorinated benzene product distribution at

different temperatures, for two residence time ranges. Tetra- and penta-chlorobenzene production is reported in terms of GC peak area of product over GC peak area of solvent per mole of reactant. This gives a fair reflection of the relative quantities of the products produced

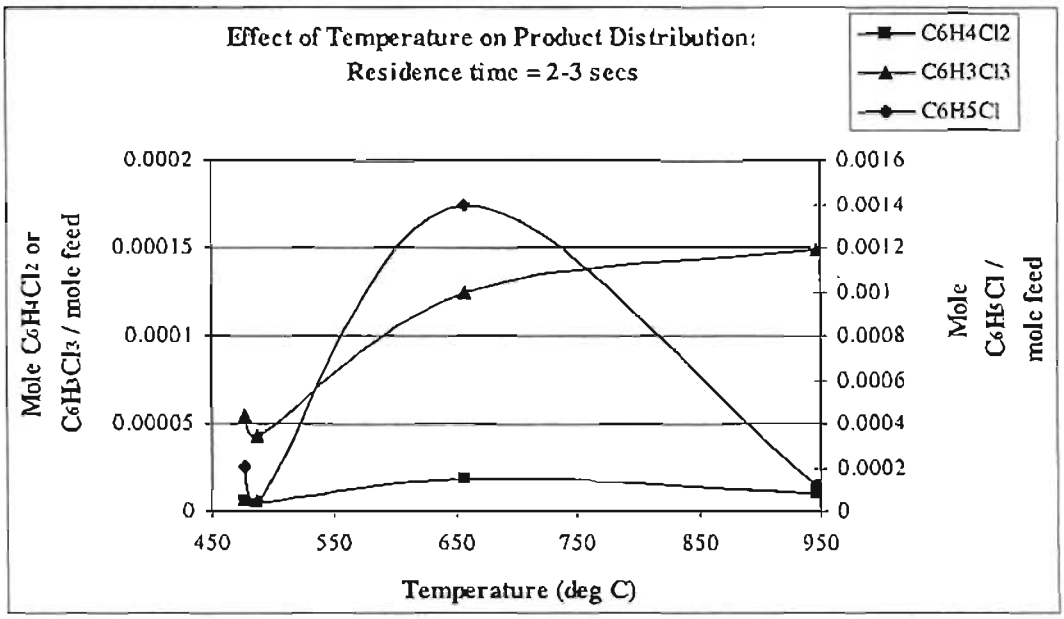


Figure 5-3: Product distribution for methylene chloride pyrolysis: residence time of 2-3 seconds

The mechanisms of formation of these and other PAH have been discussed earlier in this chapter, as well as in chapter 2. The formation of higher chlorinated benzenes (tetra-, penta-, and hexa-) during these runs could be as a result of longer residence times. During longer periods of reaction time, more intermediates can decompose into active chloride radicals, favouring molecular growth and propagation of longer chains such as eicosane and tetradecane.

It was observed that conversion from methylene chloride to trichlorobenzene was similar for both residence time ranges.

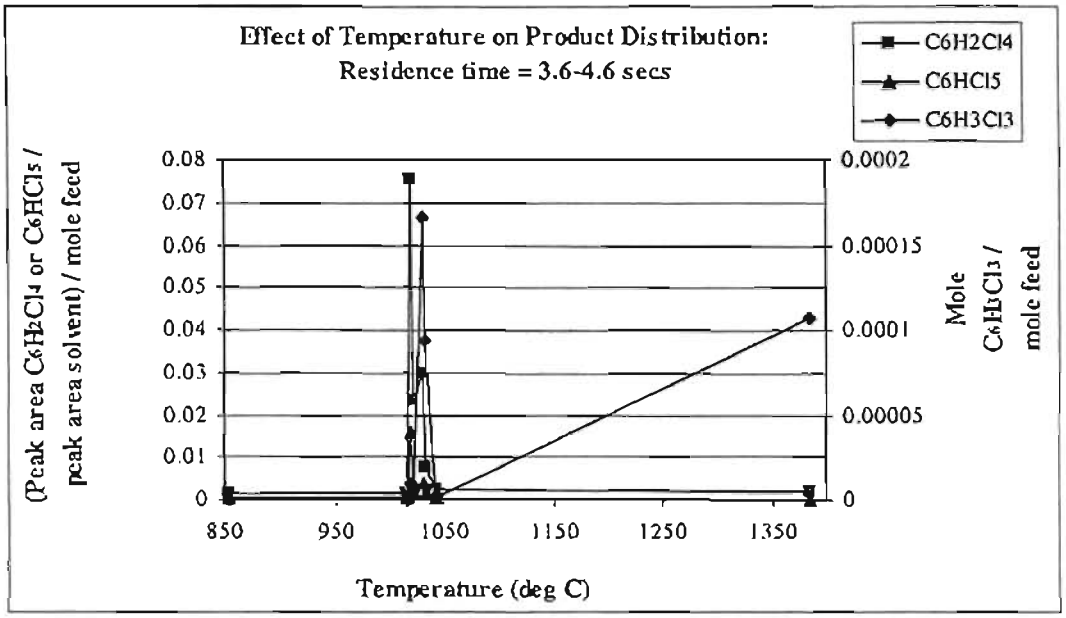


Figure 5-4: Product distribution for methylene chloride pyrolysis: residence time of 3.6 – 4.6 seconds

From Figure 5-3, it can be seen that at 658 °C a peak exists for conversion to chloro- and dichlorobenzene as illustrated. A similar peak is observed in Figure 5-4 at 1020 °C for tri-, tetra- and penta-chlorobenzene. At 1020 °C and 3.6 – 4.6 seconds' residence time, conversion of methylene chloride to trichlorobenzene peaks at 1.66×10^{-4} moles/mole feed. In general, conversion to chlorinated benzenes is lower at higher temperatures and longer residence times. Higher weight (4 –6 chlorine atoms) chlorinated benzenes are present only at higher temperatures, while chloro- and dichloro-benzene are only present below 946 °C.

A number of chromatogram peaks were identified as siloxy compounds. The source of this contamination is the sealing grease used on the heads of the dreshel bottles. This can be said with certainty, as no siloxy compounds were identified in the products when the boiling vessel was used to vapourise the feed.

A number of oxygenated compounds were identified in runs 9b-l, and appear to a far greater extent than for the previous set of methylene chloride runs. This can be attributed to the fact that these runs were the last to be carried out in the reactor. The reactor tube had not been replaced since the start of the experiments as no visible failure had been detected on inspections. However, it is likely that the small quantities of oxygen caused the graphite tube to oxidise, causing an increase in the

porosity of the tube. This in turn allows more oxygen to be leaked into the reaction zone. As mentioned earlier, the seal around the thermocouple inserted in the shell had become loose. As a result, oxygen leakage into the reactor could have occurred before the broken seal was detected. At the end of the experimentation, small pieces of ceramic were found collected in the bottom flange. The ceramic pipe insulation on which the graphite tube rested had begun to fail. This pipe was intact on the last inspection carried out before experiments 9b-l were performed, and must have failed during the course of these runs. During carbon removal downstream of the reactor, the reactor is exposed to air that could have been sucked into the spaces where the ceramic had failed. Similar oxygenated compound formation is reported by Van der Westhuisen [1994] for lindane pyrolysis.

Only three chlorinated oxygen-containing compounds were indentified: tri- and tetra-chlorophenol and butylated hydroxytoluene. Both were identified as trace quantities. This suggests that cleavage of all C-Cl bonds took place before any radical recombination with oxygen occurred. It would thus be suitable to have an excess of hydrogen atoms available to combine with chloride radicals to form hydrogen chloride rather than for chloride radicals to combine with oxygen radicals to produce peroxides, ethers, alcohols and corboxylic acids.

Chlorinated naphthalenes and biphenyls were also detected. It is likely that the formation of these compounds could be prevented by introducing hydrogen to increase the H:Cl ratio in the reactor. This should prevent chlorination of naphthalenes and biphenyls as well as inhibit soot formation.

5.3.2.2 Chlorine recovery

The GC/MS was calibrated for chlorinated products as listed in section 5.2. The acquisition of GC calibration standards of chlorinated biphenyls, naphthalenes, and phenols, as well as being expensive and in some instances, impossible, is also a time consuming process. Also, the peak areas for these compounds were small enough for their presence to be considered as trace quantities. Thus, the percentage chlorine recovered as organic products accounts only for the compounds calibrated for. The experimental set discussed above (runs 9b-l) was used for the purposes of chlorine mass balances. 100% destruction efficiencies were obtained for all runs tabulated below.

Table 5-5: Chlorine recovery and scrubber conditions

Run	Temperature (deg C)	% Cl in product	% Cl in scrubber	Scrubber set-up
9b	1222	0.02	10.2	1 scrubber, vacuum
9d	1032	1.21	37.1	1 scrubber, vacuum, increased liquid level
9e	1385	0.02	49.5	1 scrubber, vacuum, increased liquid level
9f	854	1.42	12.0	1 scrubber, vacuum, increased liquid level
9g	1016	0.31×10^{-3}	0.36	1 scrubber, sintered disc on inlet, vacuum
9h	1033	0.02	0.15	1 scrubber, nozzle on inlet, stirrer bar, vacuum
9i	1042	0.48×10^{-3}	35.7	2 scrubbers, sintered inlet in first scrubber, vacuum
9j	1021	0.23×10^{-3}	40.7	2 scrubbers, recirculating NaOH in first scrubber, smaller vacuum
9k	1031	0.66	57.7	2 scrubbers, recirculating NaOH in first scrubber, vacuum, increased liquid level
9l	1020	1.88×10^{-3}	86.2	2 scrubbers, recirculating NaOH in first scrubber, vacuum, increased liquid level

The chlorine recovery of 10.2% for run 9b was unacceptably low. Rather than being a case of low reactant conversion to hydrogen chloride, it was suspected that there was a mass transfer problem between the hydrogen chloride gas and the caustic soda liquid. Thus most of the hydrogen chloride gas produced was being discharged to drain. For the next run, it was decided to increase the liquid level in the scrubber, thus allowing the gas bubble to have a longer residence time in the liquid phase. This change saw immediate results, with the chlorine recovery increasing to 37.1%. The new scrubber set-up was used again, this time with the liquid level slightly increased. The chlorine recovery increased once again to 49.5% for run 9e.

The liquid-level was once again increased for run 9f, however chlorine recovery from the scrubber was only 12%. Referring to Table 5-4, large amounts of hydrochloric acid were detected in both the hexane solvent and the carbon residue by GC/MS. The pressure drop through the increased scrubber liquid level was too high, and the water ejector pump was not strong enough to provide enough driving force for the gas bubble to move through the scrubber.

During the previous runs, it was observed that the gas bubble travelling through the liquid phase was very large. Aside from increasing the bubble residence time to improve mass transfer, the

distribution of the gas phase could be improved. This was attempted by placing a sintered glass disc on the gas inlet into the scrubber liquid. This method also provided smaller bubbles that were better distributed in the caustic soda. However, the 0.15% chlorine recovery (run 9g) was disappointing. Similar to the previous run, the glass sinter caused the pressure drop to increase such that the driving force for the gas flow through the scrubber was too low. Again, hydrochloric acid was detected in samples analysed by GC/MS.

Run 9h was attempted with a different set-up. A magnetic stirrer bar was introduced into the scrubber to aid mixing and to distribute the gas phase more evenly in the liquid. The sintered disc was replaced with a plastic nozzle. The chlorine recovery was again disappointing at 0.36%. It was observed that although the nozzle decreased the gas bubble size, the sudden contraction caused the bubble velocity to increase, thus its residence time in the liquid decreased. Hydrochloric acid was again detected by GC/MS analysis of the samples.

An improved, but not yet acceptable 35.7% recovery was obtained for run 9I, using two scrubbers in series, both with high liquid levels and with no changes or adjustments to the 6 mm polyflow tubing inlet.

Two changes were made for run 9j. The first scrubber was replaced by a plastic bucket with a lid which was modified to recirculate caustic soda. This was effected by using a small fish tank pump submerged in the liquid. The pump outlet was modified to spray the caustic soda in from the top of the bucket. This was achieved by making a plastic device similar to a showerhead. Unreacted hydrogen chloride then passed through the second scrubber, and then to drain. To decrease the speed of the gas bubble through the liquid, a lower vacuum was used. The result was a 40.7% chlorine recovery. No hydrogen chloride was found in the samples, and had thus escaped to drain.

The same set-up was used for run 9k, with the liquid level in both scrubbers increased and the vacuum higher. The chlorine recovery improved to 57.7%, despite a leak found at the thermocouple insertion in the shell. The leak was repaired, and run 9l carried out using the same scrubber set-up. Chlorine recovery from the scrubber was a satisfactory 86.2%.

Reproducible chlorine recoveries were found for runs 10a (71.8%) and 10b (84.1%) where trichlorobenzene was pyrolysed and the scrubber assembly in run 9l was used. Detailed results can be found in section 5.4.

5.3.3 Scanning electron micrographs of carbon black

A scanning electron microscope was used to examine the carbon black produced in runs 1-3a. The carbon used for this part of the analysis had already been washed with acetone and hexane, and then dried in an oven. Micrographs can be found in Appendix I. It became clear from the magnification and resolution of the micrographs that the carbon particles were in the order of nanometers, if not smaller. Agglomeration of carbon was observed. It was noticed that a large amount of glass fibres from the wool used in the filter pot were present in the carbon sample. Agglomeration tended to occur around these strands of fibre. Due to the small range of temperatures (1018 - 1414 °C) at which the analysed carbon was produced, no structural or other differences with reaction temperature could be observed.

The carbon analysed from run 1a exhibits a fairly porous surface, suggesting the possibility of conversion to activated carbon. However, more thorough investigations into this avenue are necessary.

This first set of SEMs did not provide any information pertinent to the project and was thus discontinued.

5.4 Pyrolysis of 1,2,4-trichlorobenzene

The boiling vessel described in Chapter 4 was used to vapourise the trichlorobenzene feed. Reactant masses for the seven runs carried out ranged from 112.6 - 367.7g. Heating of the boiling vessel begun only once all the feed had been added and the vessel was sealed. This method of vapourisation did not allow for accurate measurement of residence time. Figure 5-5 shows the temperature variance of the reactor tube, reaction products and boiling vessel content with time. The feed time for trichlorobenzene into the reactor was estimated as the time period over which the reactant was at its boiling point of 213°C. In the case below, a feed time of 720 seconds was used.

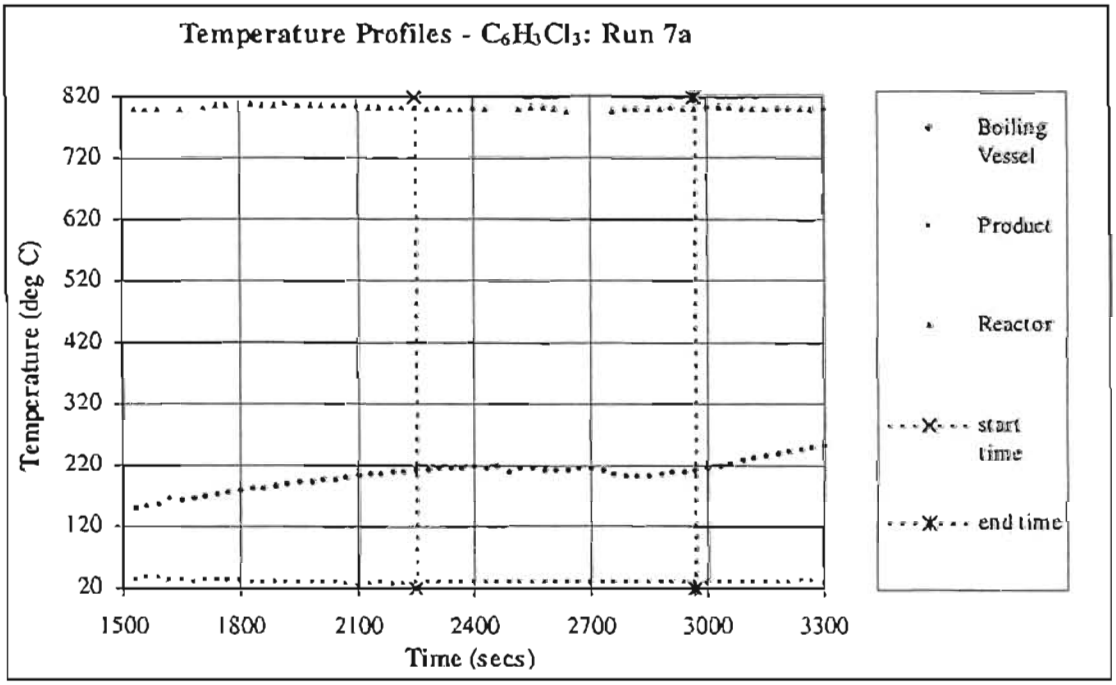


Figure 5-5: Temperature profiles for run

5.4.1 Products

Pyrolysis of trichlorobenzene was carried out over 635 - 1060°C, with residence times ranging from 1.3 - 2.6 seconds. Table 5-6 summarises experimental conditions and products obtained.

Only products identified with over 80% certainty by the GC/MS database are reported.
Hydrogen chloride production is not listed above but was present for all runs.

Table 5-6: Products and DE of trichlorobenzene pyrolysis at different temperatures and residence times

Run	Temperature (°C)	Residence time (secs)	DE (%)	Chlorinated organic products	Other Organic products
10b	1060	2.28	99.98	b, c, d, e, ethyl chloride, chlorobiphenyl, dichlorobiphenyl, trichlorobiphenyl, dichloronaphthalene, trichlorophenol	h, ethyl ether, 4-methyl-3-penten-2-one, acetic acid, naphthalene, butylated hydroxytoluene, biphenyl,
10a	1050	2.34	99.98	c, d, e, f, ethyl chloride, trichloronaphthalene	h, 2-methyl-1-propene, ethyl ether, ethylene oxide, 4-methly-4-penten-2-one, 4-methyl-3-penten-2-one, tetradecane, hexadecane, octadecane, acetic acid, formic acid, butylated hydroxytoluene
7e	950	2.57	99.96	a, b, c	benzene
7d	821	1.64	99.98	a, b, c	h, acetone, benzene,
7a	800	1.29	99.99	a, b, c	h, benzene, pentaethylene glycol, formic acid ethyl ester
7b	644	1.43	99.96	a, b, c, d, trichlorobiphenyl, tetrachlorobiphenyl, pentachlorobiphenyl, trichloronaphthalene, tetrachloronaphthalene,	h, benzene, 4-methyl-3-penten-2-one, acetic acid, triethylene glycol, pentaethylene glycol,
7c	635	1.88	99.98	a, b, c	h, heptane, benzene,

Key:

a chlorobenzene
b dichlorobenzene
c trichlorobenzene
d tetrachlorobenzene
e pentachlorobenzene
f hexachlorobenzene
g lindane (hexachlorocyclohexane)
h hexane and/or cyclohexane

Four nines (or 99.99%) destruction efficiency was achieved at 800°C and 1.29 seconds' residence time. Destruction efficiencies of 99.98% were obtained for runs 10a-b, 7d and 7c. There seems to be no visible trend for these for runs, as DE remained the same as reaction temperature and residence time were simultaneously decreased. Similar comparisons can be made between runs 7e and 7b, where lowering the reaction temperature and residence time by 306°C and 1.14 seconds respectively had no effect on the DE of 99.96%. These results could be attributed to the inaccuracy in the residence time calculation as discussed earlier. The range of destruction efficiencies obtained, 99.96-99.99%, is small.

Chloro- and dichloro-benzenes can be considered products of simple dechlorination reactions, (products of incomplete pyrolysis), while tetra-, penta- and hexa-chlorobenzenes result from chlorination reactions. Formation of compounds containing more chlorine substituents than the starting material was observed only at the two high temperatures of 1050 and 1060°C, while traces of tetrachlorobenzene were found at 644°C. Since no other source of chlorine is added to the reaction, it can be deduced that the chloride radical or HCl produced in the reaction is sufficiently reactive. At lower temperatures (runs 7a-e), benzene was a major product, and again can be considered a product of incomplete pyrolysis. Long chained, high molecular weight hydrocarbons such as tetra- and hexa-decane were not observed at these temperatures.

Traces of oxygenated compounds (formic acid ethyl ester and pentaethylene glycol) were detected in the sample of run 7a. Oxygen could have entered the system from the boiling vessel, which is only half-filled with reactant, leaving space for oxygen to be present. The presence of acetone detected in run 7d can be explained by traces present on glassware washed with acetone.

Although runs 10a and 10b occurred at similar temperatures and residence times and yielded identical destruction efficiencies, the nature of the products formed differ widely. Hexa-, octa- and tetra-decane were detected in run 10a, while no long chained hydrocarbons were present for run 10b. It is possible that these compounds, which were extracted from recovered carbon, were in fact formed in the previous set of methylene chloride runs.

Biphenyl with up to three chlorine substituents was detected in run 10b, however none was found for run 10a. Chlorinated naphthalenes were, however, found for both runs. In general, PCBs did not form at lower temperatures, except during run 7b at 644°C. As discussed in Chapter 2, the formation of chlorinated biphenyls can be explained by the attack of phenyl radicals on chlorinated

benzene molecules [Louw *et al*, 1973]. Dimerization (combination)of chlorine substituted phenyl radicals can also lead to PCB formation.

The detection of trichlorophenol (10b) and butylated hydroxytoluene (10a and 10b) as well as traces of methyl pentenones, ether and other oxygenated compounds is again a cause for concern. It was noted that butylated hydroxytoluene formed only at higher temperatures. A similar pattern was observed for methylene chloride pyrolysis, in which butylated hydroxytoluene formed at temperatures of 854 - 1385°C.

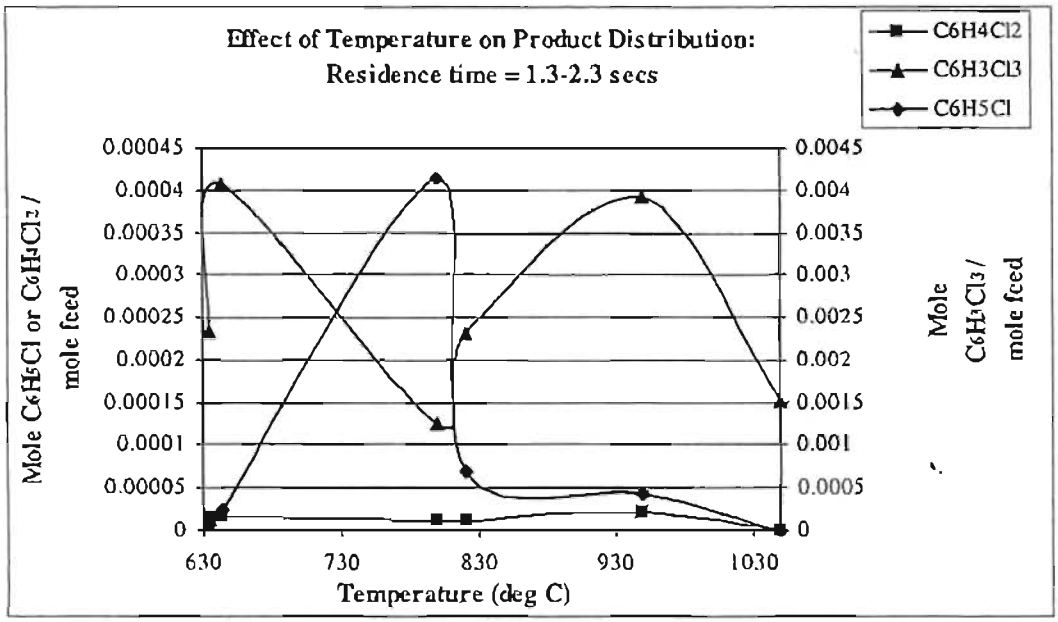


Figure 5-6: Product distribution for trichlorobenzene pyrolysis: residence time of 1.3 – 2.3 seconds and DE range of 99.96-99.99%

Figure 5-6 shows the distribution of chloro- and dichloro-benzene formation with temperature. Also represented is the distribution of the starting material, trichlorobenzene. The two trichlorobenzene peaks occur when the lowest DE is obtained, at and 644 and 950°C, and at these points, the formation of chloro- and dichlor-benzene products are at their lowest, as expected. Chlorobenzene product formation peaks at 800°C, where trichlorobenzene destruction peaks at 99.99%.

5.4.2 Chlorine recovery

A chlorine recovery of 17.3% from the scrubber was obtained for run 7e, with a collection set-up of just one scrubber. The series of methylene chloride runs carried out to improve the scrubber efficiency were then carried out, followed by the last two trichlorobenzene runs, 10a and 10b. The chlorine recovery for these two runs was satisfactory at 71.8% and 84.1% respectively. The recovery set-up consisted of one scrubber with recirculating caustic soda in series with another scrubber followed by a water ejector vacuum pump.

5.5 Pyrolysis of lindane

Two hexachlorocyclohexane (lindane) runs were attempted at temperatures of 1068 and 1017 °C, respectively. The boiling vessel used during the trichlorobenzene runs in the previous set of experiments was again used to vapourise the lindane. The destruction efficiencies are summarised in the table below.

Table 5-7: Results of lindane pyrolysis

Run	Temperature (°C)	DE (%)	Major chlorinated products (% (mol) of feed)
8a	1068	100	trichlorobenzene (56.3%)
8b	1017	81.54	lindane (18.5%)

Traces of mono- and di-chlorobenzene products were found for both runs, while 0.5g trichlorobenzene was found in the product of run 8b. The reaction products for both runs included benzene, with the benzene peak area for run 8a being 17 times larger than that for run 8b.

Although the conversion result from run 8a looked promising, a large amount of condensed lindane was found on inspection of the inlet tube of the reactor after the second run. On attempting a third run, the tube between the boiling vessel and the reactor blocked at the inlet to the reactor, causing a back pressure through the argon rotameter. The pressure was relieved through one of the safety manometers installed specifically for such a case. It was clear that the temperature at the inlet end of the reactor was below 323 °C, causing the lindane to condense and cake along the insides of the tube, causing the blockage. It was thus impossible to know the actual quantity of lindane reacted, and the destruction efficiencies calculated are thus not representative of actual conditions.

Investigations into heating the tube between the boiling vessel to well above the boiling point of lindane were carried out, as this could possibly prevent the condensation problem. However, due to the small diameter (6 mm) and short length (less than 500 mm) of the tube and the high temperature required, a variac and nichrome heating wire could not be used. More sophisticated methods, such as cartridge heating were suggested, but were rejected due to time constraints. It was also not certain that this improvement would solve the problem. For these reasons, it was decided to abort reactions using lindane and to concentrate on improving the scrubber efficiency and thus the collection of hydrogen chloride gas produced in the reactions.

5.6 Energy Balance and Efficiency

The distribution of energy supplied to the process is illustrated in Figure 5-7.

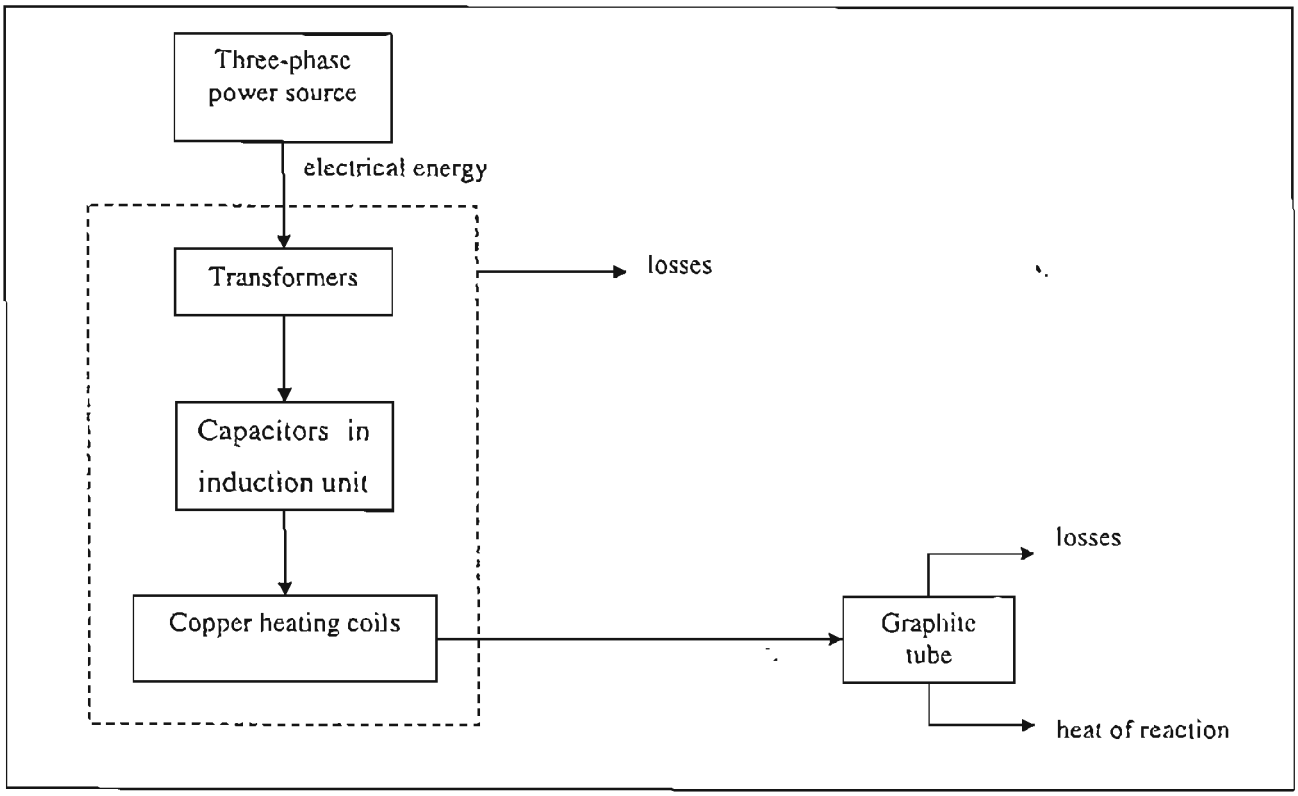


Figure 5-7: Schematic diagram showing energy flow in the pyrolysis process

The power supplied from the three-phase source was determined by measurement and is discussed later. Heat absorbed by the graphite tube was also calculated. An overall heat transfer coefficient for heat loss from the reactor tube to the atmosphere was determined experimentally. Together,

these values were used to evaluate the combined heat loss over the transformer, induction unit and copper heating coils, and thus to evaluate the efficiency of induction heating. The efficiency of the insulation material used was also evaluated.

5.6.1 Power output of three-phase supply to induction unit

The three-phase power output was determined as follows. The voltage (V), current (I) and phase angle (ϕ), were measured with the use of an oscilloscope, voltmeter and ammeter. Appendix D contains specifications of the oscilloscope and meters used. The waveforms generated by the three-phase voltage and current can also be found in this appendix, along with the relevant calculations.

The power is calculated using the following equation:

$$P = V A \cos \phi \qquad (5\text{-}1)$$

The power output for one phase was found to be 12.06 kW. Usually, this value is multiplied by 3 to give the total power output of a three-phase source. However, due to the nature of the waveforms, a multiplication factor of $3^{0.5}$ was used [Munnik, 2001]. The end result is summarised in Table 5-8.

Table 5-8: Parameter summary for three-phase power supply

	Symbol	Value
Voltage per phase	V	369 V
Current per phase	I	76 A
Phase angle	ϕ	64.8°
Power per phase	P	12 kW
Total power output	P_t	20 kW

The maximum rated power output of the Pillar induction unit was 67 kW. For all runs, induction heating was carried out at 30% of the rated maximum output and was thus expected to be running at 20.1 kW. The measurement of the three-phase supply confirmed this value to be correct.

5.6.2 Efficiency of induction heating

The reactor tube was heated from 295 – 372 K by 6.7 kW (10% of rated maximum) of energy supplied by the induction unit. The supply power was then increased to 20 kW (30% of rated maximum). The resultant temperature versus time graph (Figure 5-8) was used to calculate the amount of energy transferred to the tube. During the heating of the tube, 0.60 dm^3/min of argon was allowed to flow through the tube and all other conditions, such as cooling water flow and operation of extraction fans, were similar as for when reactions took place.

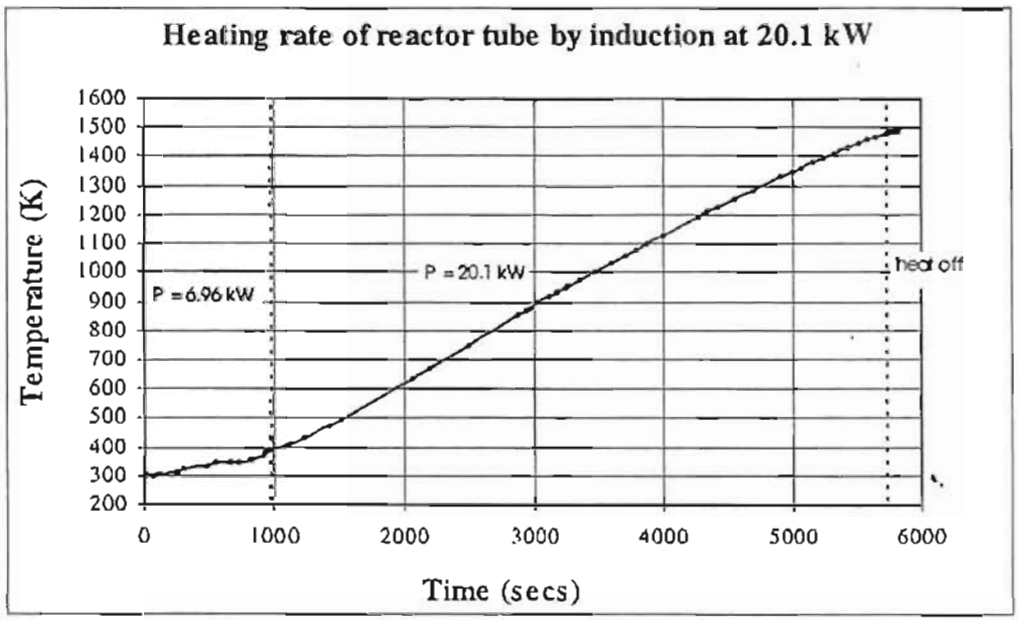


Figure 5-8: Heating rate of reactor tube

It was observed that a time difference of 230 seconds existed between the switching off of the induction unit and the maximum temperature of the reactor tube being reached. Induction heating is known to exhibit this type of heating pattern. For this reason, the power output of the induction unit and the power transferred to the reactor tube were based on different times. The results are summarised in Table 5-9.

Table 5-9: Results of power calculations

Total power supplied by induction unit	18.6 kW
Total power transferred to reactor tube	18.4 kW
Efficiency of power transfer	98.9 %
Percentage power loss from unit	1.1 %

These results prove that the method of induction heating is, as expected, highly efficient. The losses translate into 0.2 kW. However, on carrying out an energy balance over the induction unit and the reactor tube, the energy transferred to the reactor tube was found to be higher than that supplied by the induction unit (Table 5.10). This error can be attributed to the inaccuracy of the thermocouple measuring the temperature of the tube. This inaccuracy is likely to increase with temperature, thus accounting for the error in the calculated energy value.

Table 5-10: Results of energy transfer calculations

Energy output from induction unit	106209 kJ
Energy change in reactor tube	109500 kJ

5.6.3 Heat losses from reactor

To comment on the effectiveness of the insulation of the reactor, a value for the heat losses from the reactor tube to the atmosphere had to be found. This was done by applying a simple energy balance equation:

$$\frac{d}{dt}(m_t Cp_t T) = -UA(T - T_a) \qquad (5\text{-}2)$$

where

m_t	=	mass of graphite tube	[kg]
Cp_t	=	specific heat of graphite tube	[kJ/kg.K]
T	=	temperature of graphite tube	[K]
T_a	=	ambient air temperature	[K]
U	=	overall heat transfer coefficient	[W/m^2.K]
A	=	heat transfer area	[m^2]
t	=	time	[secs]

This equation can be expanded and re-arranged (see Appendix E) to give:

$$\frac{dT}{dt} = \frac{-UA(T - T_a)}{m_t(T\frac{\partial Cp_t}{\partial T} + Cp_t)} \qquad (5\text{-}3)$$

The values of interest, the overall heat transfer co-efficient from the reactor tube to the surroundings, U, and the overall heat transfer area, A, were evaluated as a single constant over the temperature range 980 – 1210 K. The value for dT/dt was found by heating the reactor to 1210 K and recording the temperature change with time. This was carried out twice – once with a small argon flow of 0.60 dm^3/min, and once without. The resulting cooling curves can be found in Appendix E (Figure E-1), and show that argon is indeed transparent to thermal radiation. That is, the heat capacity for argon gas is very low (20.8 J/mol.K at all temperatures, as reported by Perry *et al*, 2001). Conditions such as cooling water flow and extraction fans were again kept consistent with conditions under which reactions are carried out.

dT/dt was evaluated from measurements taken when argon flowed through the reactor as this is most consistent with reactor conditions.

The average value of (UA), measured under conditions of no reaction, over the temperature range 982 – 1216 K was found to be 3.6W/K, with values for (UA) ranging from 2.9 – 4.3 W/K. Again, the values found could be inaccurate due to the inaccuracies of temperature measurement. Heat is radiated inwards into the reaction zone from the reactor tube. Essentially, it is the temperature change within the reaction zone rather than that of the tube that is of interest. However, the thermocouple is positioned to measure the temperature on the outside surface of the reactor tube. Thus the calculated values for (UA), based on the temperature change on the outside surface of the reactor tube, should differ from the true values.

5.6.4 Heat losses under reaction conditions

To test the applicability of the calculated (UA) value under reaction conditions, heat loss to the atmosphere was evaluated using experimental data and theoretical heats of reaction for three

methylene chloride and three trichlorobenzene runs. These values were then compared to the expected heat loss predicted by using the (UA) value obtained under conditions of no reaction. Appropriate equations and data can be found in Appendix F. An overall heat balance on the reactor can be simplified to solve for heat loss to the atmosphere:

$$\frac{UA(T_1 - T_a)}{\Delta t} = m_t(Cp_{t1}T_1 - Cp_{t2}T_2) + H_R - m_o(Cp_{to}T_1 - Cp_{ino}T_{in}) \qquad (5\text{-}4)$$

where subscripts

t	=	reactor tube
o	=	organic feed
1	=	initial reactor condition
2	=	final reactor condition
in	=	initial condition of organic feed
H_R	=	heat of reaction [kJ]

and all other symbols are as explained earlier.

The heat of reaction value was calculated from thermodynamic data found in Appendix A. The results are summarised in Table 5.11.

Table 5.11: Comparison of predicted and calculated heat loss

Run	6d	9g	9i	7e	10a	10b
Feed material	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2	$C_6H_3Cl_3$	$C_6H_3Cl_3$	$C_6H_3Cl_3$
Feed method	boiling vessel	dreschel bottles	dreschel bottles	boiling vessel	boiling vessel	boiling vessel
Predicted heat loss (kJ) [a]	41326	47910	71049	30815	14871	15165
Actual calculated heat loss (kJ) [b]	34276	41569	45404	24545	15422	15472
% difference	-20.6	-15.3	-56.5	-25.5	3.6	2.0

[a] using UA ($T-T_n$)
[b] using equation (5-3) to evaluate UA ($T-T_a$)

In four of the six cases, the predicted heat losses were between 20 and 57 % higher than the actual calculated value. At high temperatures, the accuracy of the temperature measurement by thermocouple is questionable. In addition, the shortcomings of the values obtained for the

combined overall heat transfer coefficient and heat transfer area, (UA) have been discussed in the previous section. Errors in heat loss predictions can be attributed to these errors.

A second source of error exists in the measurement of the mass of organic reactant fed into the reactor. In the case of feed via dreschel bottles, the bottles are weighed before and after the experiment. During the time that the bottles are transferred to and from the water bath, it is likely that some of the gas evaporates. Methylene chloride, especially, is very volatile. This could result in the measured mass of the reactant being higher than the actual mass fed into the reactor. Consequently, the calculated absolute value for heat of reaction will also be higher than the actual heat used for the pyrolysis reaction. Since the reactions are endothermic, the heat of reaction value, H_R, is negative and it can be seen from equation (3) above that if the absolute H_R value is higher than the actual value, the calculated heat loss will lower.

The flowrate of argon used during the experiment to determine UA was 0.60 dm^3/min. This argon flowrate was maintained in runs 6d, 7e, 10a and 10b. Argon flowrates of 0.94 dm^3/min and 1.15 dm^3/min were used for runs 10a and 10b respectively, to achieve the desired residence times in the reaction zone. The change in flowrates could have an effect on the distribution of the heat in the reaction zone. A higher flow is likely to increase mixing in the reaction zone, thereby creating a more uniform heat distribution within the reaction zone. This condition will not be reflected in the measured data due to the positioning of the thermocouple, as discussed earlier, and will contribute to the difference in the calculated and predicted heat losses.

6. COST ANALYSIS

Costs for the pyrolysis process as presented and discussed below are based on data from the destruction of methylene chloride (run 9g) at 1016°C with a residence time of 3.6 seconds. An operating time of 8000 hours per year was assumed, and this translated into a process capacity of 4.73 tpa.

Fixed capital costs were estimated using the order-of-magnitude or ratio estimate as described by Peters and Timmerhaus [1991]. This method is based on similar previous cost data and has an accuracy of estimate over approximately 30%.

A water absorption column was costed for the recovery of hydrogen chloride produced in the process, yielding 30,7% (wt) hydrochloric acid.

During preliminary costing, it was observed that the inert gas, argon, was the major operating cost. As discussed in Chapter 4, argon was used as it is transparent to thermal radiation, and would thus prevent a high temperature product stream that would have to be cooled further. It also offered the advantage of being an atomic (rather than molecular) gas that would not form radicals and react with the chlorinated hydrocarbons. Results showed that the temperature of the product stream did not exceed 48°C, thus justifying the use of argon. However, argon is approximately 3,7 times more expensive than nitrogen. Medjoub *et al* [1998] pyrolysed 1.07 % (mole) hexachlorobenzene in nitrogen at temperatures between 900-1200°C and no nitrogenous products were reported, showing that nitrogen can be used as the inert gas in this temperature range. Product temperatures were not available from their study. It is expected that product temperatures will be higher when nitrogen is used as the inert gas. This hot product gas stream could be used to preheat the reactor feed material when process integration is considered, making it unnecessary for further cooling water use.

It was thus decided to use nitrogen as the inert gas due to its lower cost, and only make-up gas usage was estimated, assuming that the inert gas would be recovered and recycled in the process. A single cyclone was costed for separation and collection of the carbon black. A gas chromatograph was included in the purchased equipment costs for on-line product analyses.

Details of costs and sources can be found in Appendix J. Marshall and Swift cost indices were used to update costs from previous years. Table 6-1 shows purchased equipment and fixed capital costs, based on a 4.73 tpa capacity.

Table 6-1: Capital cost summary

Cost	R
Purchased equipment	301 432
Total fixed capital investment	913 429

Fixed capital costs were available for the catalytic extraction process (CEP), plasma arc technology and incineration [Arnold, 2000] for plant capacities of 7440 tpa. The 'two-thirds' scale up factor,

$$\text{cost capacity a} = \text{cost capacity b} \left(\text{capacity a} / \text{capacity b}\right)^{2/3}$$

could not be used to generate a fixed cost comparison between these process and the 4.73 tpa pyrolysis process because of the large capacity difference.

The two products of the pyrolysis process are carbon black and 30.7 % (wt) hydrochloric acid. The grade and properties of the carbon black are yet to be investigated, and the market for hydrochloric acid is presently saturated. For these reasons, sales revenue from the process was omitted.

The pyrolysis process is envisaged to attach onto the end of an already established process as a waste destruction unit, rather than as a stand-alone plant. For this reason, consumption of raw materials and utilities were calculated on a quantity per ton of waste basis, and compared to similar consumption figures for other destruction processes. These comparisons can be found in Table 6-2.

Table 6-2: Raw material & utility consumption per ton of waste

	unit / t	CEP [a]	Plasma arc [a]	Incineration [a]	Pyrolysis
Raw materials					
Oxygen	t	0.5			
Caustic soda	t		0.005		
HCl	t		0.001		
Process chemicals	t			2	
Utilities					
Process water	m^3			94	2
Cooling water	m^3		230		187
Electricity	MWh	0.5	1.55	0.23	16
Nitrogen	m^3		510		10
Natural gas	t	0.23	1.77	2.84	
Steam	t	0.91			

a Arnold [2000]

Based on run data, it was calculated that the induction unit had to run for 1 minute every 9 minutes to maintain the reactor temperature within 10°C of the desired operating temperature. Cooling water is used to cool down the induction unit and the induction coils, and thus only has to flow when the induction unit is running.

It is clear from Table 6-2 that cooling water and inert gas consumption for pyrolysis is much lower than that for plasma arc destruction. Pyrolysis does, however, use approximately ten times more electrical power than the plasma arc process.

7. CONCLUSIONS AND RECOMMENDATIONS

The reactor assembly for the pyrolysis of chlorinated hydrocarbons proved to be successful for the destruction of both methylene chloride (100%) and trichlorobenzene (99.99%), meeting the United States Conservation and Recovery Act stipulation of a destruction and removal efficiency of 99.99% for halogenated waste. These destruction efficiencies compare favourably (see Table 3-1) with those for incineration (≥99.99%), the catalytic extraction process (≥99.99%) and the plasma arc process (≥99.9999%), bearing in mind that only two compounds have been pyrolysed in the pilot-plant scale reactor used in this project.

Pyrolysis of industrial lindane was unsuccessful due to limitations of the vapourisation and feed inlet system, as discussed in Chapter 5. Future work includes the development of a feed system able to handle wastes with high boiling points.

The experiments carried out were to determine the effect of reaction temperature and residence time on the destruction efficiency and the product spectra. The formation of soot molecules such as naphthalenes can be inhibited by increasing the hydrogen : chlorine ratio. The reactants used in this project had hydrogen : chlorine ratios of 1. The formation of biphenyls, chlorinated biphenyls and high molecular weight aromatic chlorinated and non-chlorinated compounds such as benzene and pentachlorobenzene are in agreement with previous work as discussed in Chapter 5. It is recommended that attention be given to the design of the reactor exit and cooling system in future, so as to minimise the formation of these unwanted compounds in the post hot zone section of the reactor.

The detection of high weight molecular hydrocarbons such as decane and tetradecane in the product spectrum is an interesting result. Such products have not been reported in reviewed literature and pose a challenge for further work.

The graphite reactor tube did not fail during the course of the project, although it is possible that oxygen leaked into the system could have caused an increase in the porosity of the tube by oxidising the graphite. In time, this could lead to failure of the graphite tube and highlights the importance of an air-tight system. As mentioned earlier, blockage of the reactor tube posed a major problem in the past. This problem was not encountered with the reactor assembly used for this

project and seems to have been overcome firstly by using a larger diameter tube orientated in the vertical position and secondly by ensuring minimal carbon formation on the tube wall by blanketing it with argon.

The ceramic insulation pipe on which the reactor tube rested began to crack after approximately 20 runs and was likely to be caused by exposure to high temperatures rather than by chemical attack. In future, the investigation into the use of a more durable (i.e. high thermal shock and chemical resistance) material such as silica can be undertaken.

Carbon collection proved difficult and it is recommended that the reactor assembly either be moved or raised to allow for the exit pipe to be vertically orientated so that the product stream enters the filter system from the top rather than from the side. This change will require a small modification to the exit flange of the reactor and will facilitate a more efficient recovery system. The product temperature did not exceed 50°C for any of the runs, thus invalidating the need for a long exit pipe. Carbon collection by, for example, an online bag-filter, will ensure that the reactor is not opened up and exposed to oxygen each time the filter requires cleaning.

The ceramic reactor shell remained cool to the touch during experimentation, showing that the relatively cheap carbon black and alumina wool insulation were indeed effective.

Residence times below 1.3 seconds could not be achieved due to the nature of the dreschel bottle feed system for methylene chloride. Also, residence times calculated for trichlorobenzene (fed from boiling vessel) cannot be considered accurate. The development of a well-controlled vapourisation and feed system will be important if work is to be continued.

Sample analysis turn-around time during the project was very slow and impeded fast progression of experimentation. On-line product gas analysis by GC/MS is recommended in future, as opposed to the solvent method used in this project. This will allow for almost instantaneous sample analysis, which will in turn permit planning of subsequent experimental conditions to progress at a much faster rate. This will be essential during the optimisation stages. Liquid samples were stored in refrigerators for up to four days before being analysed. The use of on-line gas sampling and analysis will eliminate inaccuracies and errors introduced by the present method. Dioxin monitoring is costly but will have to be implemented if the process is to be used commercially.

The South African limit for hydrogen chloride emission is 10 mg/m^3 and should be easily met on installation of a hydrogen chloride absorption column. Facilities for the monitoring of the effluent gas stream for volatile organic compounds would be advantageous.

It can be concluded that induction heating is a very efficient method of heating for the purposes of pyrolysis. Not only is energy transfer from the three-phase power source to the reactor tube highly efficient (98.9%), but the method is far neater and easier to maintain than, for example, locating a heating element within the reaction zone or embedding an element in the graphite tube. Heat losses translated into 0.2 kW.

In assessing the data obtained in the energy evaluations, it must be born in mind that the pyrolysis reactor and associated instrumentation were not constructed for numerous accurate measurements to be carried out, as would be done for an intensive kinetic study. The equipment set-up of this project was limited by budget constraints, and intensive energy modeling was not part of the scope of this project. However, the results obtained from the energy calculations indicate that there is scope for further work of a more intensive nature, with the addition of high quality instrumentation and control. The thermocouple accuracy at high temperatures is questionable and the use of an optical pyrometer should be considered for more accurate data collection and where precise measurements are essential for progression to modeling and kinetic studies.

Raw material and utility consumption for pyrolysis compares favourably with values for incineration, plasma arc and the catalytic extraction process destruction methods on a per ton of waste destroyed basis (see Table 6-2). Although the pyrolysis process uses approximately 10 and 70 times the amount of electrical power than the plasma arc and incineration processes respectively, it must be noted that both these processes make additional use of natural gas, which requires extra costs, as well as additional hazard and safety considerations.

The reactor assembly used and the method of induction heating have proved to be both effective and successful, however the claims to the success of the process on a wide scale are limited by the fact that only two compounds were destroyed. Of the objectives set out at the start of the project (see Section 1.5), only one - the successful destruction of industrial lindane - was not met. This failure was linked to a secondary objective of destroying solid waste. However, the results presented from this project show that there is definitely scope for more research to be carried out on the pyrolysis process, including

- improvements to up and down stream processing,
- destruction of mixtures of compounds to simulate actual waste conditions,
- optimisation of the process (reaction time and temperature) for specific wastes,
- investigating the feasibility of using nitrogen as the inert gas to reduce operating costs,
- implementation of inert gas recycling,
- kinetic studies (subject to changes as discussed above) and
- process integration once the pyrolysis reactor is to be added as a waste destruction unit at the end of an existing process.

It can be concluded that the technology for the destruction of chlorinated compounds, which was used for the first time at a pilot plant scale, shows promise and justifies further research. The experimental set-up described in this project can be considered as the first step in an ongoing series of improvements and modifications.

8. REFERENCES

8.1 References

Agarwal, K.B. (1992). Pyrolysis process and apparatus. Patent number 5129995, United States, General Motors Corp.

Arnold, D.R. (2000). Personal communication.

Ballschmiter, K., Kirschmer, P., *et al.* (1986). 'Experiments in High-temperature Chemistry of Organohalogens.' *Chemosphere* **15** (9-12): 1369-1372.

Ballschmiter, K., Braunmiller, I., *et al.* (1988). 'Reaction pathways for the formation of polychlorodibenzodioxins (PCDD) and --dibenzofirans (PCDF) in combustion processes: II. Chlorobenzenes and chlorophenols as precursers in the formation of polychloro-dibenzodioxins and --dibenzofurans in flame chemistry.' *Chemosphere* **17** (5): 995-1005.

Barton, D.H.R. and Howlett, K.E. (1951). 'The kinetics of the dehydrochlorination of substituted hydrocarbons. Part VII: The mechanism of the thermal decompositions of 1:1:2:2- and 1:1:1:2-tetrachloroethane.' *J. Amer. Chem. Soc.*: 2033-2038.

Benson, S.W. (1960). The Foundations of Chemical Kinetics. McGraw-Hill, New York.

Benson, S.W. and Vaisman, M.A. (1991). Conversion of halogenated toxic substances. Patent number 4982039, United States, University of Southern California.

Boon, R. (2001). 'Pesticides to Pontypool.' *African Wildlife* **53**: 18-21.

Chagger, H.K., Jones, J.M., *et al.* (2000). 'The formation of VOC, PAH and dioxins during incineration.' *Trans IchemE* **78B**: 53-59.

Chittick, D.E. (1986). Fuel gas-producing pyrolysis reactors. Patent number 4584947, United States.

Dickson, L.C. and Karasek, F.W. (1987). 'Mechanisms of formation of polychlorinated dibenzo-p-dioxins produced on municipal incinerator flyash from reactions of chlorinated phenols.' *J. Chromatography* **389**: 127-137.

EQUILIB-Web (1999). www.crct.polymtl.ca/fact/web/equiweb/htm, access date: June 2000

Fairley, P. and Chynoweth, E. (1994). 'Hazwaste firms struggle to survive market doldrums.' *Chemical Week*: 26-35.

Frenklach, M. and Warnatz, J. (1987). 'Detailed modeling of PAH profiles in a sooting low-pressure acetylene flame.' *Combust. Sci. & Tech.* **51**: 265-283.

Holland, K.M. (1995). Apparatus for waste pyrolysis. Patent number 5387321, United States.

Kern, R.D., Xie, K., et al. (1992). 'A shock tube study of chlorobenzene pyrolysis.' *Combust. Sci. & Tech* .**5**: 77-86.

Kloster, G. and Reisinger, K. (1990). 'Laboratory scale pyrolysis experiments using halogenated benzenes.' *J. Anal. & Appl. Pyrolysis* **17**: 357-369.

Lee, C.S. and Huffman, G.L. (1989). 'Innovative thermal destruction technologies.' *Environ. Progress* **8** (3): 190-199.

Lenoir, D., Wehrmeier, K. et al. (1998). 'Thermal formation of polychlorinated dibenoz-p-dioxins and –furans: Investigations on relevant pathways.' *Environ. Eng. Sci.* **15** (1): 37-47.

Louw, R., Rothuizen, J.W. et al. (1973). 'Vapouir phase chemistry of arenes, Part II.' *J.C.S. Perkin* **II**: 1635-1640.

Marr, J., Allison, D.M. et al. (1992). 'The effect of chlorine on PAH, soot and tar yields from a jet stirred / plug flow reactor system.' *Combust. Sci. & Tech* **85**: 66-76.

Matovich E. (1977). High temperature chemical reaction processes utilizing fluid-wall reactors. Patent number 4057396, United States, Thagard Technology Co.

McKinnon, J.T. and Howrad, J.b. (1990). 'Application of soot formation model: Effects of chlorine.' *Combust. Sci. & Tech.* **74**: 175-197.

Mejdoub, N., Sonizi, A., *et al.* (1998). ''Experimental and numerical study of the thermal destruction of hexachlorobenzene.' *J. Anal. & Appl. Pyrolysis* **47**: 77-94.

Munnik, T. (2001). Personal communication. School of Electronic and Electrical Engineering, University of Natal, Durban.

Perry, R.H. and Green, D.W. (1984). 'Perry's Chemical Engineers' Handbook.' 6th edition, McGraw-Hill, Singapore.

Peters, M.S. and Timmerhaus, K.D. (1991). 'Plant design and economics for chemical engineers.' McGraw-Hill, Singapore.

Reid, R.C., Prausnitz, J.M. and Polling, B.E. (1997). 'The properties of Gases and Liquids.' 4th edition, McGraw-Hill, Singapore.

Rey de Castro, B. (1989). 'Six burn technologies roll onto site.' *Waste Age*: 128-136.

Rice, F.O. and Herzfeld, K.F. (1934). *J. American Chem. Soc.* **56**: 284-298.

Ritter, E.R. and Bozelli, J.W. (1990). 'Kinetic study on thermal decomposition of chlorobenzene diluted in H_2.' *J. Phys. Chem.* **94**: 2493-2504.

Saito, N. and Fuwa, A. (2000). 'Prediction for thermodynamic function of dioxins for gas phase using semi-emphiracal molecular orbital method with PM3 Hamiltonian.' *Chemosphere* **40**: 131-145.

Savage, P. (2000). 'Mechanisms and kinetic models for hydrocarbon pyrolysis.' *J. Anal. & Appl. Pyrolysis* **54**: 109-126.

Schraam, D.E. (1987). Perforatred reactor tube for a fluid wall reactor and a method of forming a fluid wall. Patent number 4671944, United States, J.M. Huber Corp.

Smith, J.M., Van Ness, H.C., et al. (1996). Introduction to Chemical Engineering Thermodynamics. McGraw-Hill, Singapore.

Taylor, P.H. and Dellinger, B. (1988). 'Thermal degradation characteristics of chloromethane mixtures.' *Environ. Sci. & Tech.* **22**: 438-447.

Taylor, P.H., Tirey, D.A., et al. (1994). 'Detailed modeling of the pyrolysis of trioethene: Formation of chlorinated aromatic species.' *Combust. Sci. & Tech.* **101**: 75-102.

Taylor, P.H., Tirey, D.A., et al. (1996). 'A detailed kinetic model of the high-temperature pyrolysis of tetrachloroethene.' *Combust. & Flame* **104**: 260-271.

Taylor, P.H. and Dellinger, B. (1999). 'Pyrolysis and molecular growth of chlorinated hydrocarbons.' *J. Anal. & Appl. Pyrolysis* **49**: 9-29.

Tirey, D.A, Taylor, P.H., et al. (1990). 'Gas phase formation of chlorinated aromatic compounds from the pyrolysis of tetrachloroethylene.' *Combust. Sci. & Tech.* **74**: 137-157.

UNEP Chemicals (1995). www.chem.unep.ch/pops, access date: June 2000

UNEP Chemicals (1999). Dioxin and Furan Inventories. Switzerland.

Van der Westhuizen, E. (1994). The Destruction of Chlorinated Hydrocarbons by Means of Reductive Pyrolysis. University of Stellenbosch, Stellenbosch.

Wang, C.S. (1997). Ultra-pyrolysis reactor for hazardous waste destruction. Patent number 5614156, United States.

Weast, R.C. (1983-1984). Handbook of Chemistry and Physics. 64th edition, CRC Press Inc., United States.

Weber, R. and Hagenmaier, H. (1999). 'PCDD / PCDF formation in fluidized bed incineration.' *Chemosphere* **38** (11): 2643-2654.

Welgemoed, C.J. (1996). Hydrogen Cyanide Gas Production. Patent number 96/0126, South Africa, Quadro Chemicals Engineering (Pty) Ltd. and Eskom.

Wu, A.C. and Chen, S.C. (1995). Thermal conversion pyrolysis reactor system. Patent number 5411714, United States.

8.2 Bibliography

Environmental Health Criteria 2 : Polychlorinated Biphenyls and Terphenyls. World Health Organisation. (1976).

Proposed plasma conversion of toxic waste at Halfontein. *Chemical World*: 24-25. (1998).

Ackerman, D. G., Scinto L. L, *et al.* (1983). 'Destruction and disposal of PCB by thermal and non-thermal methods.' Noyes Data Corporation.

Beckwith, T. G., Buck, N. L. *et al.* (1982). Mechanical Instruments. Addison-Wesley, Philoppines.

Blazso, M. (1997). 'Formation of chlorinated phenols under pyrolysis from a phenolic antioxidant used as plastics additive.' *Journal of Analytical and Applied Pyrolysis* **40-41**: 69-78.

Bonnet, J., El Mejdoub, N. *et al.* (1997). 'Study of the gas phase combustion of hexachlorobenzene, influence of the oxygen concentration, Attempt at a global kinetic formulation.' *Journal of Analytical and Applied Pyrolysis* **44**: 1-11.

Brouwer, J., Longwell, J. P. *et al.* (1992). 'Chloro-Carbon Induced Incomplete Combustion In A Jet-Stirred Reactor.' *Combustion Science & Technology* **85**: 87-100.

Chaala, A., Darmstadt, H. *et al.* (1997). 'Vacuum pyrolysis of electric cable wastes.' *Journal of Analytical and Applied Pyrolysis* **39**: 79-96.

Chen, Y. and Tschuikow-Roux E. (1993). 'Mechanism of Hydrogen Abstraction Reactions by Free Radicals: Simple Metathesis or Involving Intermediate Complex?' *Journal of Physical Chemistry* **97**: 3742-3749.

Christmann, A. (1988). Waste pyrolysis and method. United States, Deutsche Babcock Anlagen Aktiengesellschaft.

Collet, C. V. and. Hope A. D. (1974). Engineering Measurements. Pitman Publishing, Bath, UK.

Cui, J. P., He Y. Z., *et al.* (1989). 'Rate Constants for Hydrogen Atom Attack on Some Chlorinated Benzene at High Temperatures.' *Journal of Physical Chemistry* **93**: 724-727.

De Souza, K. (1994). Ways to rid South Africa of toxic matter. *Engineering News*.

Fiedler, H. (1998). 'Thermal Formation of PCDD/PCDF: A Survey.' *Environmental Engineering Science* **15** (1): 49-58.

Font, R., Marcilla A., *et al.* (1995). 'Comparison between the pyrolysis products obtained from different organic wastes at high temperatures.' *Journal of Analytical and Applied Pyrolyis* **32**: 41-49.

Fortuna, F., Cornacchia G., *et al.* (1997). 'Pilot-scale experimental pyrolysis plant: mechanical and operational aspects.' *Journal of Analytical and Applied Pyrolysis* **40-41**: 403-417.

Franz, J. A., Camaioni D. M., *et al.* (2000). 'Measurement of select radical processes in hydrocarbon pyrolysis.' *Journal of Analytical and Applied Pyrolysis* **54**: 37-64.

Fribance, A. E. (1962). Industrial Instrumentation Fundamentals. McGraw-Hill, U.S.A.

Graham, J. L., Hall D., *et al.* (1996). 'Laboratory Investigation of Thermal Degradation of a mixture of Hazardous Organic Compounds.' *Environ. Sci. Technol.* **20**: 703-710.

Gullet, B. K., Sarofim A. F., *et al.* (2000). 'The Role of Chlorine in Dioxin Formation.' *Trans IChemE* **78(B)**: 47 - 52.

Harvey, W. S., Davidson J. H., *et al.* (1998). 'Thermolysis of Hydrogen Sulfide in the Temperature Range 1350-1600 K.' *Ind. Eng. Chem. Res.* **37**: 2323-2332.

Hatakeda, K., Ikushima Y., *et al.* (1999). 'Supercritical water oxidation of polychlorinated biphenyls using hydrogen peroxide.' *Chemical Engineering Science* **54**: 3079-3084.

Kaune, A., Schramm K. W., *et al.* (1999). 'Polychlorinated dibenzodioxins and dibenzofurans in the aluminum recycling process.' *Journal of Analytical and Applied Pyrolysis* **49**: 191-198.

Koshland, C. P., Fisher E. M., *et al.* (1992). 'Thermal Destruction of Some Chlorinated C_1 and C_2 Hydrocarbons.' *Combustion Science & Technology* **82**: 49-65.

Liodakis, S., Gakis D., *et al.* (1997). 'Electrochemical methods for monitoring the volatile pyrolysis products of Pinus halepensis pine-needle.' *Journal of Analytical and Applied Pyrolysis* **43**: 139-144.

Nasato, L. V., Karan K., *et al.* (1994). 'Modeling Reaction Quench Times in the Waste Heat Boiler of a Claus Plant.' *Ind. Eng. Chem. Res.* **33**: 7-13.

Pant, K. K. and Kunzru D. (1996). 'Pyrolysis of n-heptane: kinetics and modeling.' *Journal of Analytical and Applied Pyrolysis* **36**: 103-120.

Pilling, M. J. (1992). 'The kinetics and thermodynamics of free radical reactions.' *Pure and Applied Chemistry* **64** (10): 1473-1480.

Pont, G., Cadou C. P., *et al.* (1998). 'Emissions Reduction and Pyrolysis Gas Destruction in an Acoustically Driven Dump Combustor.' *Combustion and Flame* **113**: 249-257.

Poutsma, M. L. (2000). 'Fundamental reactions of free radicals relevant to pyrolysis reactions.' *Journal of Analytical and Applied Pyrolysis* **54**: 5-35.

Robertson, R. W. J. and Hanesian D. (1975). 'An Optimization Study of the Pyrolysis of Ethane in a Tubular Reactor.' *Industrial Engineering Chemistry, Process Design and Development* **14** (3): 216-221.

Rotman, D. and Begeley R. (1994). Hazardous Waste. *Chemical Week*: 24-25.

Simon, C. M., Kaminsky W., *et al.* (1996). 'Pyrolysis of polyolefins with steam to yield olefins.' *Journal of Analytical and Applied Pyrolysis* **38**: 75-87.

Tsang, W. (1990). 'Mechanisms for the Formation and Destruction of Chlorinated Organic Products of Incomplete Combustion.' *Combustion Science and Technology* **74**: 99-116.

Wenpin, H., Qing-Rui Y., *et al.* (1992). 'Kinetic Study on Pyrolysis and Oxidation of CH_3Cl in $Ar/H_2/O_2$ Mixtures.' *Combustion Science and Technology* **85**: 23-63.

Williams, P. T. and Besler S. (1992). 'The Pyrolysis of Municipal Solid Waste.' *J. of the Institute of Energy* **65**: 192-200.

Williams, P. T. and Besler S. (1994). 'Polycyclic aromatics hydrocarbons in waste derived pyrolytic oils.' *Journal of Analytical and Applied Pyrolysis* **30**: 17-33.

APPENDIX A - Thermodynamic Data and Equations

The following thermodynamic equations taken from Smith *et al* [1996] were used to calculate the standatd heat of reaction (ΔH°) and the Gibbs free energy change (ΔG°) respectively, for the pyrolysis reactions investigated:

$$\Delta H_T^\circ = \Delta H_0^\circ + R\int_{T_0}^{T} \frac{\Delta Cp_0}{R} dT \tag{1}$$

$$\frac{\Delta G_T^\circ}{RT} = \frac{\Delta G_0^\circ - \Delta H_0^\circ}{RT} + \frac{\Delta H_0^\circ}{RT} + \frac{1}{RT}\int_{T_0}^{T} \Delta Cp_0 dT - \frac{1}{R}\int_{T_0}^{T} \frac{\Delta Cp_0}{T} dT \tag{2}$$

The temperature dependent equation for specific heat capacity takes the form:

$$Cp_0 = A + BT + CT^2 + DT^3 + \frac{E}{T^2} \tag{3}$$

where Cp has the units J/mol.K and the reference temperature, T_0, is 298 K.

The constants, A, B, C, D and E, as well as values for the standard heat of reaction and standard Gibbs free energy are tabulated below with the relevant sources.

	CH_2Cl_2 [a]	1,2,4-$C_6H_3Cl_3$ [b]	HCl [a]	C	Units
A	12.95	163.43	30.67	17.2 [c]	J/mol
B	1.623e-1	81.27e-3	-7.201e-3	4.27e-3 [c]	J/mol
C	-1.302e-4	-16.059e-6	1.246e-5	0	J/mol
D	4.208e-8	0	-3.898e-9	0	J/mol
E	0	-63.41e-5	0	-8.79e5 [c]	J/mol
ΔH°_0	-95.46	19.8	-92.36	0 [d]	kJ/mol
ΔG°_0	-68.91	-	-95.33	0 [d]	kJ/mol
ΔS°_0	-	0.366	-	-	kJ/mol

[a] Reid, R.C., Prausnitz, J.M., Poling, B.E., The Properties of Gases and Liquids, 4th edition, McGraw-Hill.

[b] Saito, N., Fuwa, A., *Prediction for the thermodynamic function of dioxins for gas phase using semi-empirical molecular orbital method with PM3 Hamiltonian*, Chemosphere, 40 (2000).

[c] Weast, R.C *et al*, CRC Handbook of Chemistry and Physics, 64th edition, CRC Press Inc., 1983

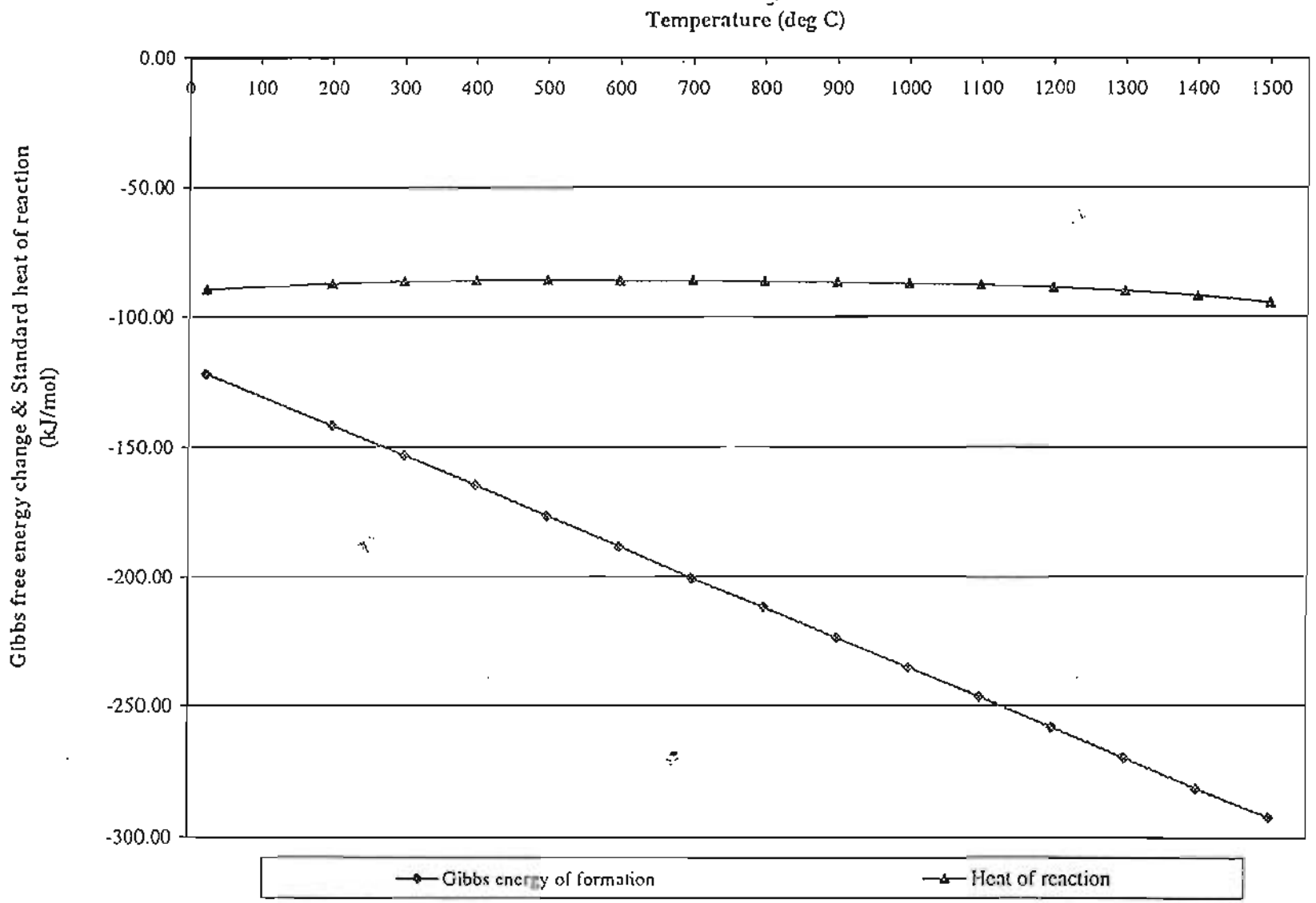
[d] Smith, J.M., Van Ness, H.C., Abbott, M.M., Introduction to Chemical Engineering Thermodynamics, 5th edition, McGraw-Hill, 1996.

ΔG°_0 for 1,2,4-trichlorobenzene was evaluated from the equation

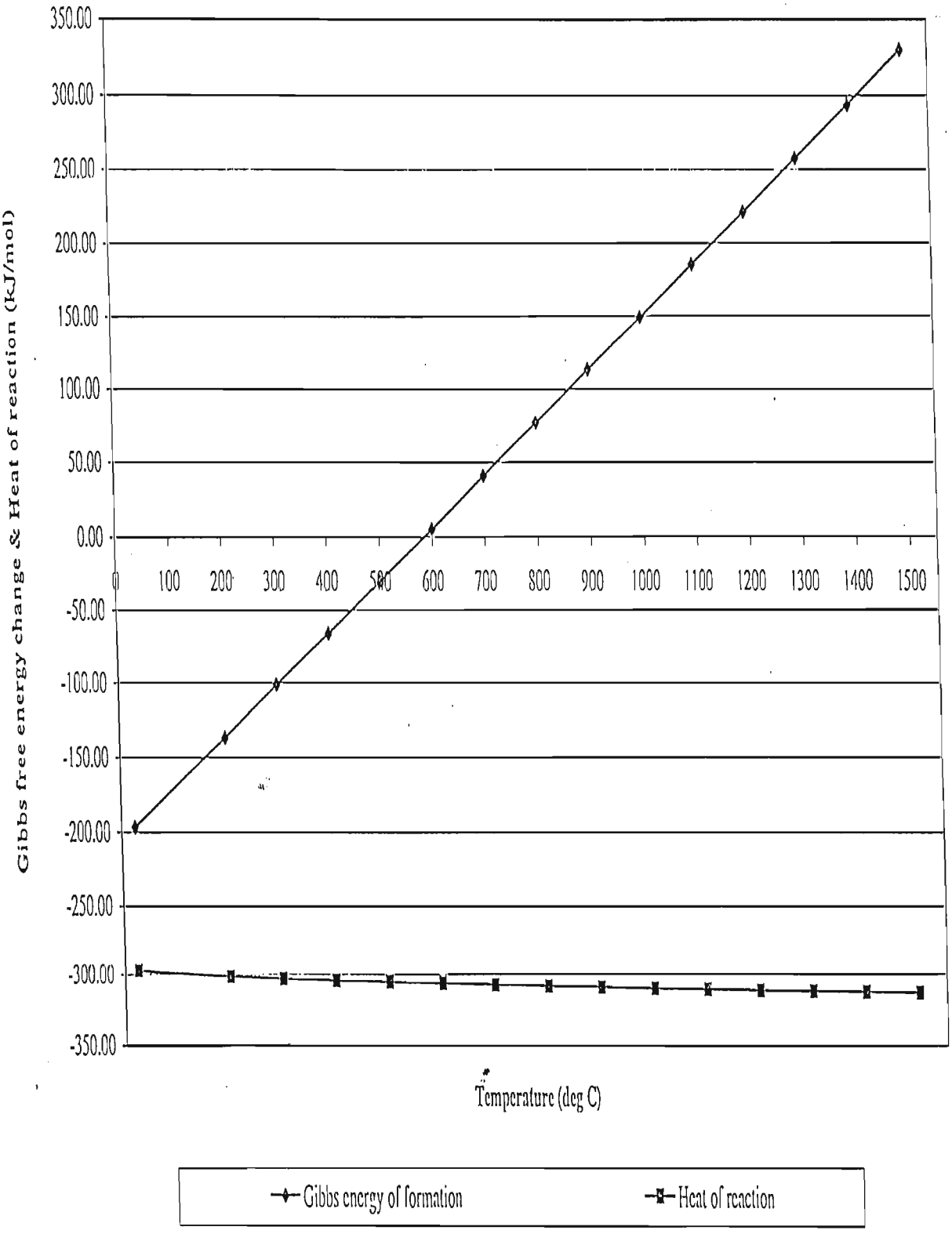
$$\Delta G_0^{\circ} = \Delta H_0^{\circ} - T\Delta S_0^{\circ} \qquad (4)$$

It was expected that the Gibbs free energy change would decrease with increasing temperature, however, this was not observed from the parameters calculated for trichlorobenzene pyrolysis. Thermodynamic data for trichlorobenzene is not as easily available as that for methylene chloride, and the data used (reference b above) could be inaccurate.

Gibbs free energy & Heat of reaction for thermal degradation of CH_2Cl_2 to HCl and C



Gibbs free energy & Heat of reaction for thermal degradation of $C_6H_3Cl_3$ to HCl and C



Team: J. Duzzard
D. Arnold
D. Ramjugernath
B. Ravno
K. Jack
P. Devnarain
V. Avidi
K. Pillay

Date: 18 September 2000

FOR LINE / UNIT REFERENCE, SEE FLOWSHEET INCLUDED

LINE / UNIT REFERENCE	OPERATING DEVIATION	ACTION NOTES AND QUERIES	ACTION BY	FOLLOW-UP REVIEW COMMENTS
A	T increase, P build up, bottle explodes	Have loose fitting cap on bottle top	DA, KP	It was decided to use a carburetor feed system with Ar as carrier gas. This eliminates the dosing pump as well as the possibility of air flow into the reactor.
1	No flow - Vessel A empty	Run Ar into vessel A, prevent air flow into reactor		
			BR	If CH_2Cl_2 flow increases, Air Exclusion Seal system (see diagram included) will be considered.
2	Heat input too low	Line now needs heat to prevent condensation of organic vapour		No longer necessary for CH_2Cl_2 vapourisation, but feed line to reactor will still have to be heated to prevent condensation of CH_2Cl_2.
	No flow	Switch off H_2, leave Ar running		Action accepted.
11 & 3	More pressure - regulator fails	Install manometers in lines 3 & 11, vent to hood if fan motor is H_2 proof	KJ, KP KP	Fan motor not hydrogen proof, therefore vent out through window.

LINE / UNIT REFERENCE	OPERATING DEVIATION	ACTION NOTES AND QUERIES	ACTION BY	FOLLOW-UP REVIEW COMMENTS
6 & 7	Reverse pressure - $P_{tube} > P_{shell}$ causing feed flow into shell	Install separate manometers on each line	KJ, KP	Action accepted.
R	More heat from induction unit	Limit output from induction unit	Quaddro	Action accepted.
		Inductor cut out at set reactor temperature	Quaddro	Action accepted.
		Install extra thermocouple	KP	Action accepted.
		Monitor temperature on two thermocouples	KP	Action accepted.
8	More pressure	Lock valve V7 open (unnecessary valve)	KJ	Action accepted.
9	Less flow - carbon blockage in E	Install manometer and monitor DP across E	KJ	Action accepted.
		Pressure relief valve discharging into scrubber		
10	Less flow - ejector pump fails - No water supply	Check viability of separate water tank on roof to run ejector pump	KP	Water pressure from tank on roof insufficient to run pump (see calculations included).
				Set up air ejector pump in parallel.

ADDITIONAL NOTES:

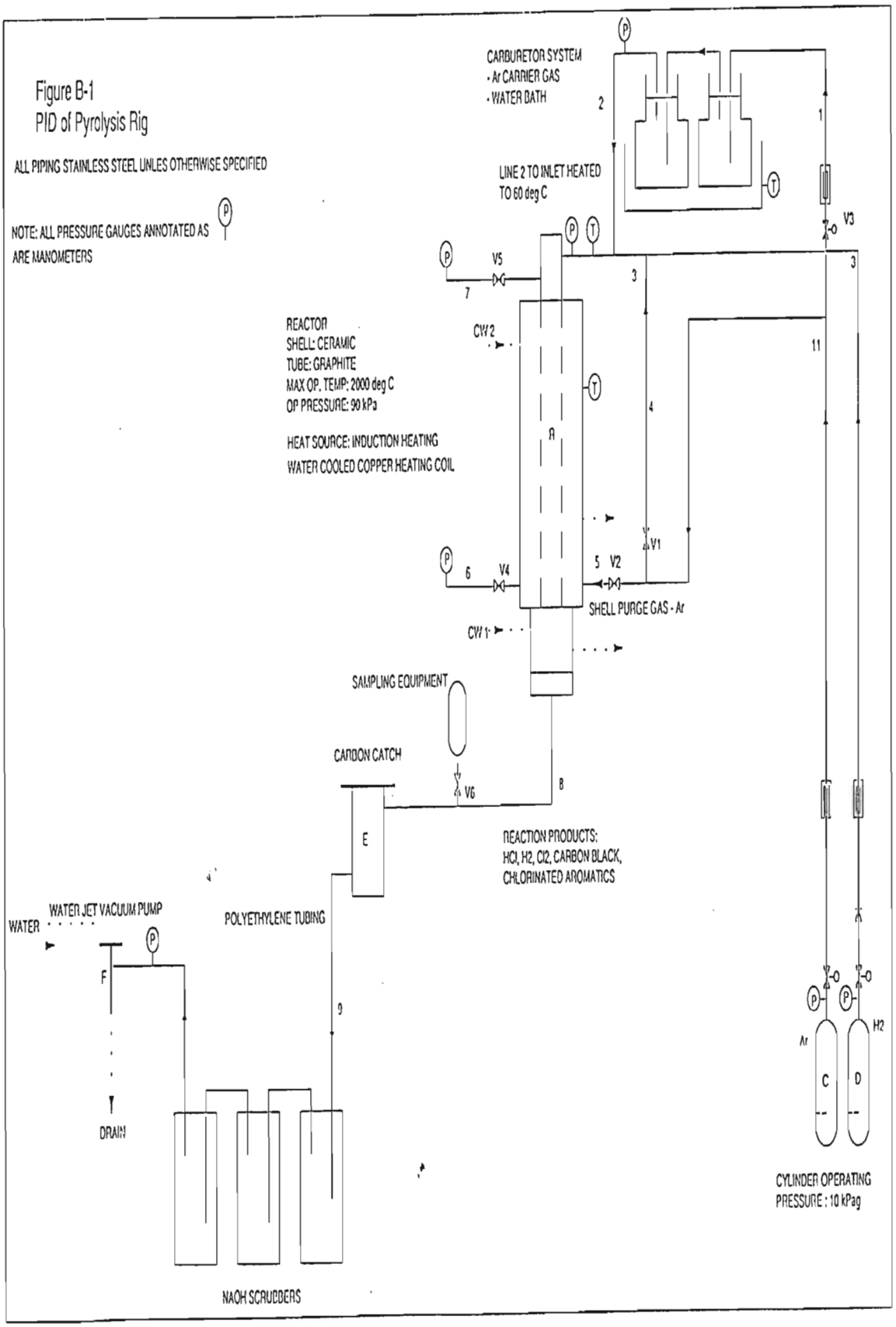
Safety data sheets for CH_2Cl_2 and H_2 included

Fire fighting measures for hydrogen fires are included.

ABBREVIATIONS:

T	Temperature
P	Pressure
DP	Pressure change
CH_2Cl_2	Methylene chloride
Ar	Argon
H_2	Hydrogen

Figure B-1
PID of Pyrolysis Rig



Sigma Chemical Co.
P.O. Box 14508
St. Louis, MO 63178
Phone: 314-771-5765

Aldrich Chemical Co., Inc.
1001 West St. Paul
Milwaukee, WI 53233
Phone: 414-273-3850

Fluka Chemical Corp.
1001 West St. Paul
Milwaukee, WI 53233
Phone: 414-273-3850

SECTION 1. - - - - - - - - - CHEMICAL IDENTIFICATION- - - - - - - - -
CATALOG #: 173
NAME: METHYLENE CHLORIDE
SECTION 2. - - - - - COMPOSITION/INFORMATION ON INGREDIENTS - - - - - -
CAS #: 75-09-2
MF: CH2CL2
EC NO: 200-838-9
SYNONYMS
AEROTHENE MM * CHLORURE DE METHYLENE (FRENCH) * DICHLOROMETHANE (DOT: OSHA) * METHANE DICHLORIDE * METHYLENE BICHLORIDE * METHYLENE CHLORIDE (ACGIH:DOT:OSHA) * METHYLENE DICHLORIDE * METYLENU CHLOREK (POLISH) * NARKOTIL * NCI-C50102 * R 30 * R30 (REFRIGERANT) * RCRA WASTE NUMBER U080 * SOLAESTHIN * SOLMETHINE * UN1593 (DOT) *
SECTION 3. - - - - - - - - - - HAZARDS IDENTIFICATION - - - - - - - - -
LABEL PRECAUTIONARY STATEMENTS
TOXIC (USA)
HARMFUL (EU)
HARMFUL BY INHALATION, IN CONTACT WITH SKIN AND IF SWALLOWED.
IRRITATING TO EYES, RESPIRATORY SYSTEM AND SKIN.
POSSIBLE RISK OF IRREVERSIBLE EFFECTS.
CALIF. PROP. 65 CARCINOGEN.
POSSIBLE CARCINOGEN.
POSSIBLE MUTAGEN.
NEUROLOGICAL HAZARD.
READILY ABSORBED THROUGH SKIN.
TARGET ORGAN(S):
LIVER
PANCREAS
IN CASE OF CONTACT WITH EYES, RINSE IMMEDIATELY WITH PLENTY OF WATER AND SEEK MEDICAL ADVICE.
DO NOT BREATHE VAPOR.
WEAR SUITABLE PROTECTIVE CLOTHING.
SECTION 4. - - - - - - - - - - FIRST-AID MEASURES- - - - - - - - - - -
IN CASE OF CONTACT, IMMEDIATELY WASH SKIN WITH SOAP AND COPIOUS AMOUNTS OF WATER.
CONTAMINATION OF THE EYES SHOULD BE TREATED BY IMMEDIATE AND PROLONGED IRRIGATION WITH COPIOUS AMOUNTS OF WATER.
ASSURE ADEQUATE FLUSHING OF THE EYES BY SEPARATING THE EYELIDS WITH FINGERS.
IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.
IF SWALLOWED, WASH OUT MOUTH WITH WATER PROVIDED PERSON IS CONSCIOUS.
CALL A PHYSICIAN.
WASH CONTAMINATED CLOTHING BEFORE REUSE.
SECTION 5. - - - - - - - - - FIRE FIGHTING MEASURES - - - - - - - - - -
EXTINGUISHING MEDIA
NONCOMBUSTIBLE.
USE EXTINGUISHING MEDIA APPROPRIATE TO SURROUNDING FIRE CONDITIONS.

SPECIAL FIREFIGHTING PROCEDURES
WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO PREVENT CONTACT WITH SKIN AND EYES.
UNUSUAL FIRE AND EXPLOSIONS HAZARDS
EMITS TOXIC FUMES UNDER FIRE CONDITIONS.
SECTION 6. - - - - - - - - ACCIDENTAL RELEASE MEASURES- - - - - - - - -
EVACUATE AREA.
WEAR SELF-CONTAINED BREATHING APPARATUS, RUBBER BOOTS AND HEAVY RUBBER GLOVES.
ABSORB ON SAND OR VERMICULITE AND PLACE IN CLOSED CONTAINERS FOR DISPOSAL.
VENTILATE AREA AND WASH SPILL SITE AFTER MATERIAL PICKUP IS COMPLETE.
SECTION 7. - - - - - - - - - - HANDLING AND STORAGE- - - - - - - - - -
REFER TO SECTION 8.
SECTION 8. - - - - - - EXPOSURE CONTROLS/PERSONAL PROTECTION- - - - - -
WEAR APPROPRIATE NIOSH/MSHA-APPROVED RESPIRATOR, CHEMICAL-RESISTANT GLOVES, SAFETY GOGGLES, OTHER PROTECTIVE CLOTHING.
USE ONLY IN A CHEMICAL FUME HOOD.
SAFETY SHOWER AND EYE BATH.
DO NOT BREATHE VAPOR.
AVOID CONTACT WITH EYES, SKIN AND CLOTHING.
AVOID PROLONGED OR REPEATED EXPOSURE.
READILY ABSORBED THROUGH SKIN.
WASH THOROUGHLY AFTER HANDLING.
TOXIC.
POSSIBLE CARCINOGEN.
IRRITANT.
NEUROLOGICAL HAZARD.
POSSIBLE MUTAGEN.
KEEP TIGHTLY CLOSED.
KEEP AWAY FROM HEAT AND OPEN FLAME.
STORE IN A COOL DRY PLACE.
SECTION 9. - - - - - - - PHYSICAL AND CHEMICAL PROPERTIES - - - - - - -
APPEARANCE AND ODOR
COLORLESS LIQUID
PHYSICAL PROPERTIES
BOILING POINT: 39.8 C TO 40 C
MELTING POINT: -97 C
FLASHPOINT NONE
EXPLOSION LIMITS IN AIR:
UPPER 22%
LOWER 14%
AUTOIGNITION TEMPERATURE: 1223 F 661C
VAPOR PRESSURE: 6.83PSI 20 C 24.48PSI 55 C
SPECIFIC GRAVITY: 1.325
VAPOR DENSITY: 2.9
SECTION 10. - - - - - - - - -STABILITY AND REACTIVITY - - - - - - - - -
INCOMPATIBILITIES
ALKALI METALS
ALUMINUM
HEAT
HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS
CARBON MONOXIDE, CARBON DIOXIDE
HYDROGEN CHLORIDE GAS
PHOSGENE GAS
SECTION 11. - - - - - - - - - TOXICOLOGICAL INFORMATION - - - - - - - -

ACUTE EFFECTS
HARMFUL IF SWALLOWED, INHALED, OR ABSORBED THROUGH SKIN.
VAPOR OR MIST IS IRRITATING TO THE EYES, MUCOUS MEMBRANES AND UPPER RESPIRATORY TRACT.
CAUSES SKIN IRRITATION.
DICHLOROMETHANE IS METABOLIZED IN THE BODY PRODUCING CARBON MONOXIDE WHICH INCREASES AND SUSTAINS CARBOXYHEMOGLOBIN LEVELS IN THE BLOOD, REDUCING THE OXYGEN-CARRYING CAPACITY OF THE BLOOD.
EXPOSURE CAN CAUSE:
NAUSEA, DIZZINESS AND HEADACHE
MAY CAUSE NERVOUS SYSTEM DISTURBANCES.
CHRONIC EFFECTS
POSSIBLE CARCINOGEN.
LABORATORY EXPERIMENTS HAVE SHOWN MUTAGENIC EFFECTS.
TARGET ORGAN(S):
LIVER
PANCREAS
NERVES
CARDIOVASCULAR SYSTEM
TO THE BEST OF OUR KNOWLEDGE, THE CHEMICAL, PHYSICAL, AND TOXICOLOGICAL PROPERTIES HAVE NOT BEEN THOROUGHLY INVESTIGATED.
RTECS #: PA8050000
METHANE, DICHLORO-
IRRITATION DATA

SKN-RBT 810 MG/24H SEV	EJTXAZ 9,171,76
SKN-RBT 100 MG/24H MOD	85JCAE -,88,86
EYE-RBT 162 MG MOD	EJTXAZ 9,171,76
EYE-RBT 10 MG MLD	TXCYAC 6,173,76
EYE-RBT 500 MG/24H MLD	85JCAE -,88,86

TOXICITY DATA

ORL-HMN LDLO:357 MG/KG	34ZIAG -,390,69
ORL-RAT LD50:1600 MG/KG	FAONAU 48A,94,70
IHL-RAT LC50:52 GM/M3	TPKVAL 15,64,79
IPR-RAT LD50:916 MG/KG	ENVRAL 40,411,86
UNR-RAT LD50:5350 MG/KG	GISAAA 53(6),78,88
IHL-MUS LC50:14400 PPM/7H	NIHBAZ 191,1,49
IPR-MUS LD50:437 MG/KG	AGGHAR 18,109,60
SCU-MUS LD50:6460 MG/KG	TXAPA9 4,354,62
UNR-MUS LD50:4770 MG/KG	ESKGA2 28,P31,82
UNR-RBT LD50:1225 MG/KG	GISAAA 53(6),78,88

TARGET ORGAN DATA
PERIPHERAL NERVE AND SENSATION (PARESTHESIA)
BEHAVIORAL (ALTERED SLEEP TIME)
BEHAVIORAL (EUPHORIA)
BEHAVIORAL (SOMNOLENCE)
BEHAVIORAL (CONVULSIONS OR EFFECT ON SEIZURE THRESHOLD)
BEHAVIORAL (ATAXIA)
CARDIAC (CHANGE IN RATE)
LUNGS, THORAX OR RESPIRATION (CHANGE IN TRACHEA OR BRONCHI)
LUNGS, THORAX OR RESPIRATION (ACUTE PULMONARY EDEMA)
LUNGS, THORAX OR RESPIRATION (TUMORS)
LIVER (LIVER FUNCTION TESTS IMPAIRED)
SPECIFIC DEVELOPMENTAL ABNORMALITIES (MUSCULOSKELETAL SYSTEM)
SPECIFIC DEVELOPMENTAL ABNORMALITIES (UROGENITAL SYSTEM)
TUMORIGENIC (CARCINOGENIC BY RTECS CRITERIA)
ONLY SELECTED REGISTRY OF TOXIC EFFECTS OF CHEMICAL SUBSTANCES

(RTECS) DATA IS PRESENTED HERE. SEE ACTUAL ENTRY IN RTECS FOR COMPLETE INFORMATION.

SECTION 12. - - - - - - - - - ECOLOGICAL INFORMATION - - - - - - - - - -

DATA NOT YET AVAILABLE.

SECTION 13. - - - - - - - - - DISPOSAL CONSIDERATIONS - - - - - - - - -

DISSOLVE OR MIX THE MATERIAL WITH A COMBUSTIBLE SOLVENT AND BURN IN A CHEMICAL INCINERATOR EQUIPPED WITH AN AFTERBURNER AND SCRUBBER. OBSERVE ALL FEDERAL, STATE AND LOCAL ENVIRONMENTAL REGULATIONS.

SECTION 14. - - - - - - - - - - TRANSPORT INFORMATION - - - - - - - - -

CONTACT SIGMA CHEMICAL COMPANY FOR TRANSPORTATION INFORMATION.

SECTION 15. - - - - - - - - - REGULATORY INFORMATION - - - - - - - - - -

EUROPEAN INFORMATION

EC INDEX NO: 602-004-00-3

HARMFUL

R 40

POSSIBLE RISK OF IRREVERSIBLE EFFECTS.

S 23

DO NOT BREATHE VAPOR.

S 24/25

AVOID CONTACT WITH SKIN AND EYES.

S 36/37

WEAR SUITABLE PROTECTIVE CLOTHING AND GLOVES.

REVIEWS, STANDARDS, AND REGULATIONS

OEL=MAK

ACGIH TLV-ANIMAL CARCINOGEN DTLVS* TLV/BEI,96

ACGIH TLV-TWA 174 MG/M3 (50 PPM) DTLVS* TLV/BEI,96

IARC CANCER REVIEW:ANIMAL SUFFICIENT EVIDENCE IMEMDT 41,43,86

IARC CANCER REVIEW:HUMAN INADEQUATE EVIDENCE IMEMDT 41,43,86

IARC CANCER REVIEW:GROUP 2B IMSUDL 7,194,87

EPA FIFRA 1988 PESTICIDE SUBJECT TO REGISTRATION OR RE-REGISTRATION FEREAC 54,7740,89

MSHA STANDARD-AIR:TWA 500 PPM (1750 MG/M3) DTLVS* 3,171,71

OSHA PEL (GEN INDU):8H TWA 500 PPM;CL 1000 PPM;PK 2000 PPM/5M/2H CFRGBR 29,1910.1000,94

OSHA PEL (CONSTRUC):SEE 56 FR 57036 CFRGBR 29,1926.55,94

OSHA PEL (SHIPYARD):8H TWA 500 PPM (1740 MG/M3 CFRGBR 29,1915.1000,93

OSHA PEL (FED CONT):8H TWA 500 PPM (1740 MG/M3) CFRGBR 41,50-204.50,94

OEL-AUSTRALIA:TWA 100 PPM (350 MG/M3);CARCINOGEN JAN93

OEL-AUSTRIA:TWA 100 PPM (360 MG/M3) JAN93

OEL-BELGIUM:TWA 50 PPM (174 MG/M3);CARCINOGEN JAN93

OEL-DENMARK:TWA 50 PPM (175 MG/M3);SKIN;CARCINOGEN JAN93

OEL-FINLAND:TWA 100 PPM (350 MG/M3);STEL 250 PPM (870 MG/M3) JAN93

OEL-FRANCE:TWA 100 PPM (360 MG/M3);STEL 500 PPM (1800 MG/M3) JAN93

OEL-GERMANY:TWA 100 PPM (360 MG/M3);CARCINOGEN JAN93

OEL-HUNGARY:STEL 10 MG/M3;CARCINOGEN JAN93

OEL-JAPAN:TWA 100 PPM (350 MG/M3) JAN93

OEL-THE NETHERLANDS:TWA 100 PPM (350 MG/M3);STEL 500 PPM JAN93

OEL-THE PHILIPINES:TWA 500 PPM (1740 MG/M3) JAN93

OEL-POLAND:TWA 50 MG/M3 JAN93

OEL-RUSSIA:TWA 100 PPM;STEL 50 MG/M3 JAN93

OEL-SWEDEN:TWA 35 PPM (120 MG/M3);STEL 70 PPM (250 MG/M3);SKIN JAN93

OEL-SWITZERLAND:TWA 100 PPM (360 MG/M3);STEL 500 PPM JAN93

OEL-THAILAND:TWA 500 MG/M3;STEL 1000 MG/M3 JAN93
OEL-TURKEY:TWA 500 PPM (1740 MG/M3) JAN93
OEL-UNITED KINGDOM:TWA 100 PPM (350 MG/M3);STEL 250 PPM JAN93
OEL IN BULGARIA, COLOMBIA, JORDAN, KOREA CHECK ACGIH TLV
OEL IN NEW ZEALAND, SINGAPORE, VIETNAM CHECK ACGIH TLV
NIOSH REL TO METHYLENE CHLORIDE-AIR:CA LOWEST FEASIBLE CONCENTRATION
NIOSH* DHHS #92-100,92
NOHS 1974: HZD 47270; NIS 374; TNF 89025; NOS 192; TNE 975696
NOES 1983: HZD 47270; NIS 363; TNF 87086; NOS 212; TNE 1438196; TFE 352536
ATSDR TOXICOLOGY PROFILE (NTIS** PB/89/194468/AS)
EPA GENETOX PROGRAM 1988, POSITIVE: CELL TRANSFORM.-RLV F344 RAT EMBRYO
EPA GENETOX PROGRAM 1988, POSITIVE: HISTIDINE REVERSION-AMES TEST
EPA GENETOX PROGRAM 1988, POSITIVE: S CEREVISIAE GENE CONVERSION; S CEREVISIAE-HOMOZYGOSIS
EPA GENETOX PROGRAM 1988, POSITIVE: S CEREVISIAE-REVERSION
EPA GENETOX PROGRAM 1988, NEGATIVE: D MELANOGASTER SEX-LINKED LETHAL
EPA TSCA SECTION 8(B) CHEMICAL INVENTORY
EPA TSCA 8(A) PRELIMINARY ASSESSMENT INFORMATION, FINAL RULE FEREAC 47,26992,82
EPA TSCA SECTION 8(D) UNPUBLISHED HEALTH/SAFETY STUDIES
ON EPA IRIS DATABASE
EPA TSCA TEST SUBMISSION (TSCATS) DATA BASE, APRIL 1997
NIOSH CURRENT INTELLIGENCE BULLETIN 46, 1986
NIOSH ANALYTICAL METHOD, 1994: METHYLENE CHLORIDE, 1005
NTP CARCINOGENESIS STUDIES (INHALATION);CLEAR EVIDENCE:MOUSE,RAT NTPTR* NTP-TR-306,86
NTP 7TH ANNUAL REPORT ON CARCINOGENS, 1992 : ANTICIPATED TO BE CARCINOGEN
OSHA ANALYTICAL METHOD #ID-59

U.S. INFORMATION

THIS PRODUCT IS SUBJECT TO SARA SECTION 313 REPORTING REQUIREMENTS.
CALIFORNIA PROPOSITION 65:
THIS PRODUCT IS OR CONTAINS CHEMICAL(S) KNOWN TO THE STATE OF CALIFORNIA TO CAUSE CANCER.

SECTION 16. - - - - - - - - - - OTHER INFORMATION- - - - - - - - - - -

THE ABOVE INFORMATION IS BELIEVED TO BE CORRECT BUT DOES NOT PURPORT TO BE ALL INCLUSIVE AND SHALL BE USED ONLY AS A GUIDE. SIGMA, ALDRICH, FLUKA SHALL NOT BE HELD LIABLE FOR ANY DAMAGE RESULTING FROM HANDLING OR FROM CONTACT WITH THE ABOVE PRODUCT. SEE REVERSE SIDE OF INVOICE OR PACKING SLIP FOR ADDITIONAL TERMS AND CONDITIONS OF SALE.

Sigma Chemical Co.
P.O. Box 14508
St. Louis, MO 63178
Phone: 314-771-5765

Aldrich Chemical Co., Inc.
1001 West St. Paul
Milwaukee, WI 53233
Phone: 414-273-3850

Fluka Chemical Corp.
1001 West St. Paul
Milwaukee, WI 53233
Phone: 414-273-3850

SECTION 1. - - - - - - - - - CHEMICAL IDENTIFICATION- - - - - - - - -
CATALOG #: 295396
NAME: HYDROGEN, 99.99+%
SECTION 2. - - - - - COMPOSITION/INFORMATION ON INGREDIENTS - - - - - -
CAS #: 1333-74-0
MF: H2
EC NO: 215-605-7
SYNONYMS
HYDROGEN (ACGIH:OSHA) * HYDROGEN, COMPRESSED (UN1049) (DOT) *
HYDROGEN, REFRIGERATED LIQUID (CRYOGENIC LIQUID) (UN1966) (DOT) *
UN1049 (DOT) * UN1966 (DOT) *
SECTION 3. - - - - - - - - - - HAZARDS IDENTIFICATION - - - - - - - - -
LABEL PRECAUTIONARY STATEMENTS
FLAMMABLE (USA)
EXTREMELY FLAMMABLE (EU)
DANGER: FLAMMABLE HIGH-PRESSURE GAS.
KEEP AWAY FROM SOURCES OF IGNITION - NO SMOKING.
TAKE PRECAUTIONARY MEASURES AGAINST STATIC DISCHARGES.
IN CASE OF INSUFFICIENT VENTILATION, WEAR SUITABLE
RESPIRATORY EQUIPMENT.
WEAR SUITABLE PROTECTIVE CLOTHING.
CYLINDER TEMPERATURE SHOULD NOT EXCEED 125 F(52 C).
DO NOT PUNCTURE OR INCINERATE THIS CYLINDER.
SECTION 4. - - - - - - - - - - FIRST-AID MEASURES- - - - - - - - - -
IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL
RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.
IF SWALLOWED, WASH OUT MOUTH WITH WATER PROVIDED PERSON IS CONSCIOUS.
CALL A PHYSICIAN.
SECTION 5. - - - - - - - - - FIRE FIGHTING MEASURES - - - - - - - - - -
EXTINGUISHING MEDIA
DO NOT EXTINGUISH BURNING GAS IF FLOW CANNOT BE SHUT OFF IMMEDIATELY.
USE WATER SPRAY OR FOG NOZZLE TO KEEP CYLINDER COOL. MOVE CYLINDER
AWAY FROM FIRE IF THERE IS NO RISK.
SPECIAL FIREFIGHTING PROCEDURES
WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO
PREVENT CONTACT WITH SKIN AND EYES.
DANGER: FLAMMABLE HIGH-PRESSURE GAS.
UNUSUAL FIRE AND EXPLOSIONS HAZARDS
FORMS EXPLOSIVE MIXTURES IN AIR.
SECTION 6. - - - - - - - - ACCIDENTAL RELEASE MEASURES- - - - - - - - -
EVACUATE AREA AND KEEP PERSONNEL UPWIND.
WEAR SELF-CONTAINED BREATHING APPARATUS, RUBBER BOOTS AND HEAVY
RUBBER GLOVES.
SHUT OFF LEAK IF THERE IS NO RISK.
VENTILATE AREA AND WASH SPILL SITE AFTER MATERIAL PICKUP IS COMPLETE.
SECTION 7. - - - - - - - - - - HANDLING AND STORAGE- - - - - - - - - -
REFER TO SECTION 8.
ADDITIONAL INFORMATION

LITHIUM, CALCIUM, BARIUM AND STRONTIUM REACT READILY IN HYDROGEN AT TEMPERATURES ABOVE 300 C, SOMETIMES RESULTING IN IGNITION. SODIUM AND POTASSIUM REACT MORE SLOWLY TO FORM THEIR CORRESPONDING HYDRIDES. HYDROGEN MAY IGNITE OR EXPLODE ON CONTACT WITH: FLUORINE, CHLORINE, BROMINE, BROMINE FLUORIDE, BROMINE TRIFLUORIDE, IODINE HEPTAFLUORIDE, XENON HEXAFLUORIDE, DIFLUORODIAZENE, CHLORINE DIOXIDE, NITROGEN OXIDE, DICHLORINE OXIDE, DINITROGEN OXIDE AND DINITROGEN TETROXIDE. HEATING A MIXTURE OF POWDERED MAGNESIUM AND CALCIUM CARBONATE IN A STREAM OF HYDROGEN CAUSED A VIOLENT EXPLOSION. MIXTURES OF HYDROGEN AND ORGANIC VAPORS CAN IGNITE OR EXPLODE ON CONTACT WITH FINELY DIVIDED RANEY NICKEL, PALLADIUM, PLATINUM IN THE PRESENT OF OXYGEN.

SECTION 8. - - - - - - EXPOSURE CONTROLS/PERSONAL PROTECTION- - - - -

CHEMICAL SAFETY GOGGLES.
COMPATIBLE CHEMICAL-RESISTANT GLOVES.
NIOSH/MSHA-APPROVED RESPIRATOR IN NONVENTILATED AREAS AND/OR FOR EXPOSURE ABOVE THE ACGIH TLV.
MECHANICAL EXHAUST REQUIRED.
SAFETY SHOWER AND EYE BATH.
USE NONSPARKING TOOLS.
DO NOT BREATHE GAS.
DO NOT GET IN EYES, ON SKIN, ON CLOTHING.
AVOID PROLONGED OR REPEATED EXPOSURE.
WASH THOROUGHLY AFTER HANDLING.
KEEP TIGHTLY CLOSED.
CYLINDER TEMPERATURE SHOULD NOT EXCEED 125 F(52 C).
KEEP AWAY FROM HEAT, SPARKS, AND OPEN FLAME.
CONTENTS UNDER PRESSURE.
WARNING: SUCK-BACK INTO CYLINDER MAY CAUSE RUPTURE.
USE BACK-FLOW-PREVENTIVE DEVICE IN PIPING.
USE WITH EQUIPMENT RATED FOR CYLINDER PRESSURE, AND OF COMPATIBLE MATERIALS OF CONSTRUCTION. CLOSE VALVE WHEN NOT IN USE AND WHEN EMPTY.
MAKE SURE CYLINDER IS PROPERLY SECURED WHEN IN USE OR STORED.

SECTION 9. - - - - - - - PHYSICAL AND CHEMICAL PROPERTIES - - - - - - -

APPEARANCE AND ODOR
COLORLESS GAS
PHYSICAL PROPERTIES
BOILING POINT: -252.8 C
MELTING POINT: -259.2 C
EXPLOSION LIMITS IN AIR:
UPPER 74.2%
LOWER 4%
AUTOIGNITION TEMPERATURE: 1060 F 570C
VAPOR DENSITY: .07 @ 21 C

SECTION 10. - - - - - - - - -STABILITY AND REACTIVITY - - - - - - - - -

INCOMPATIBILITIES
STORE AWAY FROM HEAT AND DIRECT SUNLIGHT.
OXIDIZING AGENTS

SECTION 11. - - - - - - - - - TOXICOLOGICAL INFORMATION - - - - - - - -

ACUTE EFFECTS
MAY BE HARMFUL.
EXPOSURE CAN CAUSE:
NAUSEA, DIZZINESS AND HEADACHE
ADDITIONAL INFORMATION
AT HIGH CONCENTRATIONS HYDROGEN FUNCTIONS AS A SIMPLE ASPHYXIANT BY DISPLACING AIR. SYMPTOMS OF EXPOSURE MAY INCLUDE HEADACHE, FATIGUE, INCREASED BREATHING RATE, DIZZINESS, MUSCULAR INCOORDINATION, NAUSEA,

VOMITING AND LOSS OF CONSCIOUSNESS.
RTECS #: MW8900000
HYDROGEN
ONLY SELECTED REGISTRY OF TOXIC EFFECTS OF CHEMICAL SUBSTANCES (RTECS) DATA IS PRESENTED HERE. SEE ACTUAL ENTRY IN RTECS FOR COMPLETE INFORMATION.
SECTION 12. - - - - - - - - - ECOLOGICAL INFORMATION - - - - - - - - - -
DATA NOT YET AVAILABLE.
SECTION 13. - - - - - - - - - DISPOSAL CONSIDERATIONS - - - - - - - - -
CAUTION: NO-RETURN CYLINDER. DO NOT REUSE. EMPTY CYLINDER WILL CONTAIN HAZARDOUS RESIDUE. FOLLOW PROPER DISPOSAL TECHNIQUES.
OBSERVE ALL FEDERAL, STATE AND LOCAL ENVIRONMENTAL REGULATIONS.
SECTION 14. - - - - - - - - - - TRANSPORT INFORMATION - - - - - - - - -
CONTACT ALDRICH CHEMICAL COMPANY FOR TRANSPORTATION INFORMATION.
SECTION 15. - - - - - - - - - REGULATORY INFORMATION - - - - - - - - - -
EUROPEAN INFORMATION
EC INDEX NO: 001-001-00-9
EXTREMELY FLAMMABLE
R 12
EXTREMELY FLAMMABLE.
S 9
KEEP CONTAINER IN A WELL-VENTILATED PLACE.
S 16
KEEP AWAY FROM SOURCES OF IGNITION - NO SMOKING.
S 33
TAKE PRECAUTIONARY MEASURES AGAINST STATIC DISCHARGES.
REVIEWS, STANDARDS, AND REGULATIONS
OEL=MAK
ACGIH TLV-SIMPLE ASPHYXIANT, NO TWA DTLVS* TLV/BEI,96
MSHA STANDARD:ASPHYXIANTS/GASES
DTLWS* 3,20,73
OSHA PEL (CONSTRUC): SIMPLE ASPHYXIANT-INERT GASES AND VAPORS
CFRGBR 29,1926.55,94
OSHA PEL (SHIPYARD):SIMPLE ASPHYXIANTS - INERT GASES AND VAPORS
CFRGBR 29,1915.1000,93
OEL-AUSTRALIA:ASPHYXIANT JAN93
OEL-BELGIUM:ASPHYXIANT JAN93
OEL-HUNGARY:ASPHYXIANT JAN93
OEL-THE NETHERLANDS:ASPHYXIANT JAN93
OEL-SWITZERLAND:ASPHYXIANT JAN93
OEL-UNITED KINGDOM:ASPHYXIANT JAN93
OEL IN BULGARIA, COLOMBIA, JORDAN, KOREA CHECK ACGIH TLV
OEL IN NEW ZEALAND, SINGAPORE, VIETNAM CHECK ACGIH TLV
NOHS 1974: HZD 38585; NIS 90; TNF 5607; NOS 68; TNE 49112
NOES 1983: HZD 38585; NIS 116; TNF 8936; NOS 87; TNE 149225; TFE 15985
EPA TSCA SECTION 8(B) CHEMICAL INVENTORY
EPA TSCA SECTION 8(D) UNPUBLISHED HEALTH/SAFETY STUDIES
EPA TSCA TEST SUBMISSION (TSCATS) DATA BASE, APRIL 1997
SECTION 16. - - - - - - - - - - OTHER INFORMATION- - - - - - - - - - - -
THE ABOVE INFORMATION IS BELIEVED TO BE CORRECT BUT DOES NOT PURPORT TO BE ALL INCLUSIVE AND SHALL BE USED ONLY AS A GUIDE. SIGMA, ALDRICH, FLUKA SHALL NOT BE HELD LIABLE FOR ANY DAMAGE RESULTING FROM HANDLING OR FROM CONTACT WITH THE ABOVE PRODUCT. SEE REVERSE SIDE OF INVOICE OR PACKING SLIP FOR ADDITIONAL TERMS AND CONDITIONS OF SALE.

Appendix C – Gas Chromatography Specifications and Method

Gas Chromatograph:	Agilent 68690
Detector:	Agilent 5973 EI
Column:	HP-Innowax polyethylene glycol, P/N 19091N-133
Length:	300mm
Diameter:	0.25mm
Film thickness:	0.25µm
Carrier gas:	Helium
Flowrate:	30 cm^3/sec

Temperature Program:

Injector:	250°C	
Column:	Initial temperature:	35°C
	Hold time:	5 min
	Temperature ramp rate:	10°C / min
	Final temperature:	250°C
	Hold time:	2 min

Figures C1 and C2 are examples of gas chromatograph spectra obtained for products of methylene chloride destruction at 1031°C with a residence time of 4.6 seconds. Figure C1 is a spectrum of the product gas dissolved in the hexane solvent, while Figure C2 shows products which formed residues on the solid carbon black product. Peak identification is included in Tables C1 and C2 respectively.

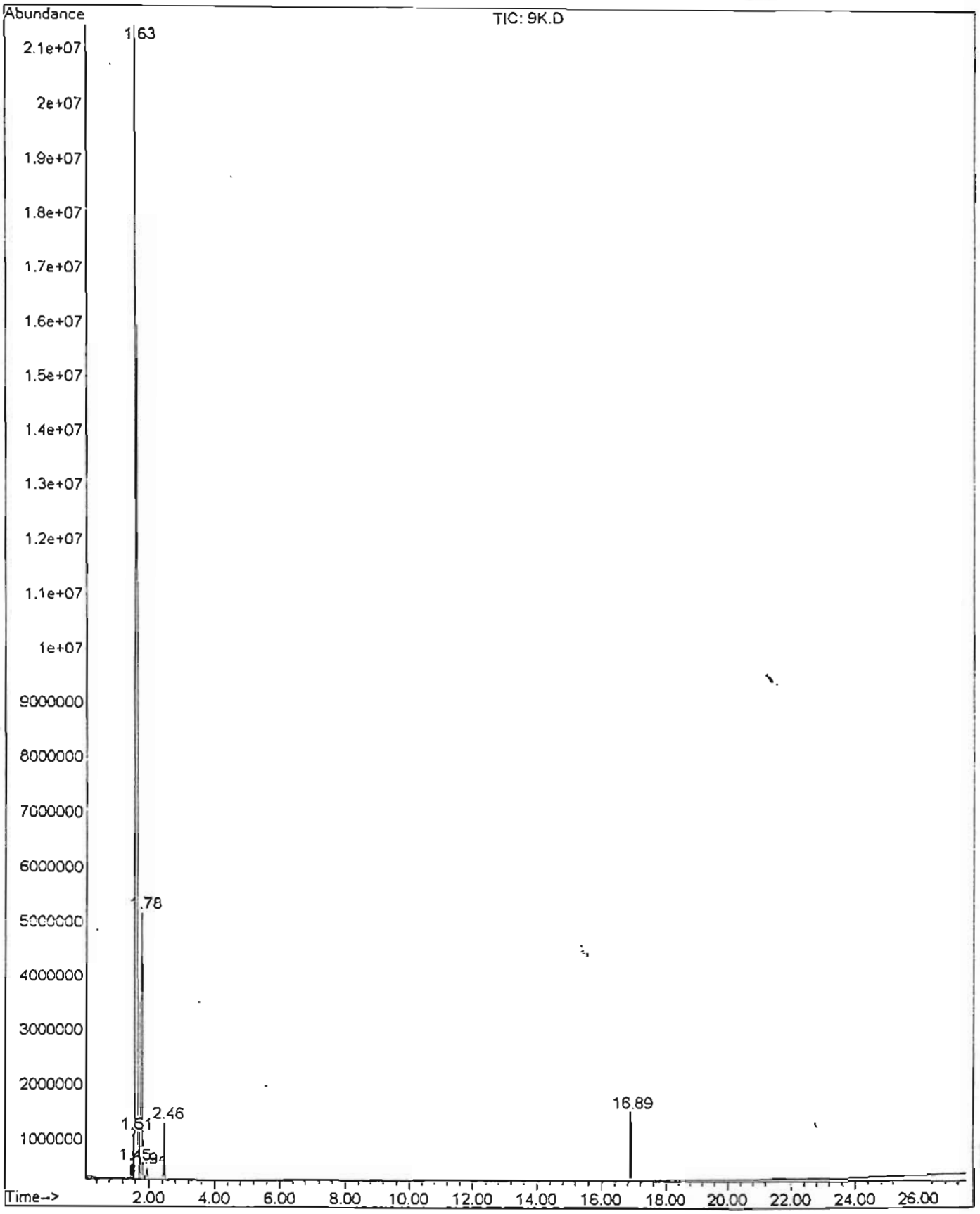


Figure C1: GC trace - dissolved product gases in hexane

Table C1: Peak identification for GC trace C1

Peak number	Retention time (mins)	Peak area (arbitrary units)	Compound identification	% certainty
1	1.46	3438738	Carbon dioxide	7
2	1.51	114471089	Pentane	90
3	1.63	660207329	Hexane	93
4	1.78	153452269	Methyl-cyclopentane	91
5	1.94	5468962	Cyclohexane	94
6	2.46	19907758	Acetone	86
7	16.9	23407429	1,3,5-trichlorobenzene	98

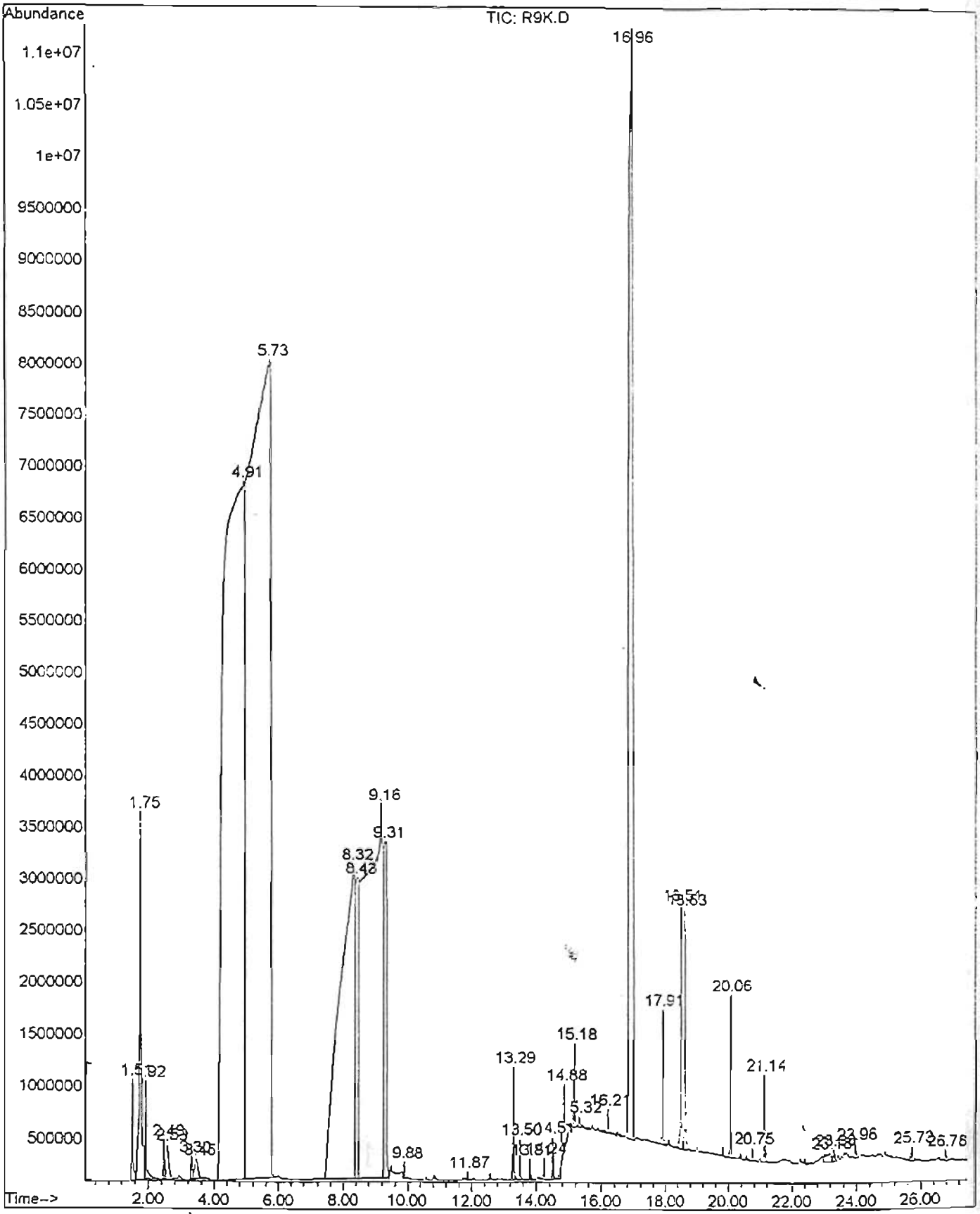


Figure C2: GC trace - residue on solid product

Table C2: Peak identification for GC trace C2

Peak number	Retention time (mins)	Peak area (arbitrary units)	Compound identification	% certainty
1	1.51	24911207	1-Butene	83
2	1.75	138256242	Ethyl Chloride	97
3	1.92	21612812	Cyclohexane	95
4	2.48	8392710	Acetone	86
5	2.59	18366175	Acetone	49
6	3.3	6794670	Ethyl Acetate	87
7	3.45	13619211	Ethyl Acetate	91
8	4.91	2857484253	Ethanol	91
9	5.72	3556794544	Hydroxy-acetic acid	9
10	8.32	977823809	Ammonia	2
11	8.43	210034690	Air with water and helium	4
12	9.16	1369182965	4-Methyl-3-penten-2-one	91
13	9.31	194575107	Ammonia	2
14	9.88	3549185	Dodecane	95
15	11.87	1587506	4-Hexen-2-one	43
16	13.29	23857284	Guanidine	43
17	13.5	6826117	Tetradecane	98
18	13.81	4237418	1,4-dichlorobenzene	97
19	14.24	4454292	1,4-dichlorobenzene	98
20	14.513	9717743	Acetic acid	91
21	14.88	31750826	Hydrochloric acid	53
22	15.18	16200832	1,3,5-trichlorobenzene	98
23	15.32	3002545	Formic acid	72
24	16.21	5146009	Hexadecane	98
25	16.96	854500673	1,2,3-trichlorobenzene	98
26	17.9	25729846	1,2,3-trichlorobenzene	98
27	18.51	51787645	1,2,5,4-tetrachlorobenzene	99
28	18.64	52056279	1,2,5,4-tetrachlorobenzene	99
29	20.07	32124597	1,2,5,4-tetrachlorobenzene	99
30	20.75	2842612	Biphenyl	93
31	21.13	17788503	Pentachlorobenzene	99
32	23.18	11009528	2,3-dichloronaphthalene	64
33	23.3	3899243	hexachlorobenzene	95
34	23.96	3226141	2,4,6-trichlorophenol	99
35	25.73	4463814	Lindane	91
36	26.79	3324964	2,3,4,6-tetrachlorophenol	94

Appendix D - Oscilloscope Specifications and Measurements for Three-phase Power Output

Oscilloscope: HP 54500 B

Measurement module: HP 54659 B

Measuring Instruments:

Current: Lemflex R 3330

Voltage: Gould Isolation Unit

Voltage measured white-to-red cables.

Current measured in white cable.

The three waveforms below show the voltage, current and power phase angle respectively.

Voltage was calculated from waveform D-1 as follows:

Peak to peak voltage on waveform			=	10.44V
Measurement device correction scaling			=	100
Actual peak to peak voltage			=	1044 V
RMS voltage	=	1044 V/ $(2 * 2^{0.5})$	=	369.11 V

Current was calculated in a similar manner from waveform D-2:

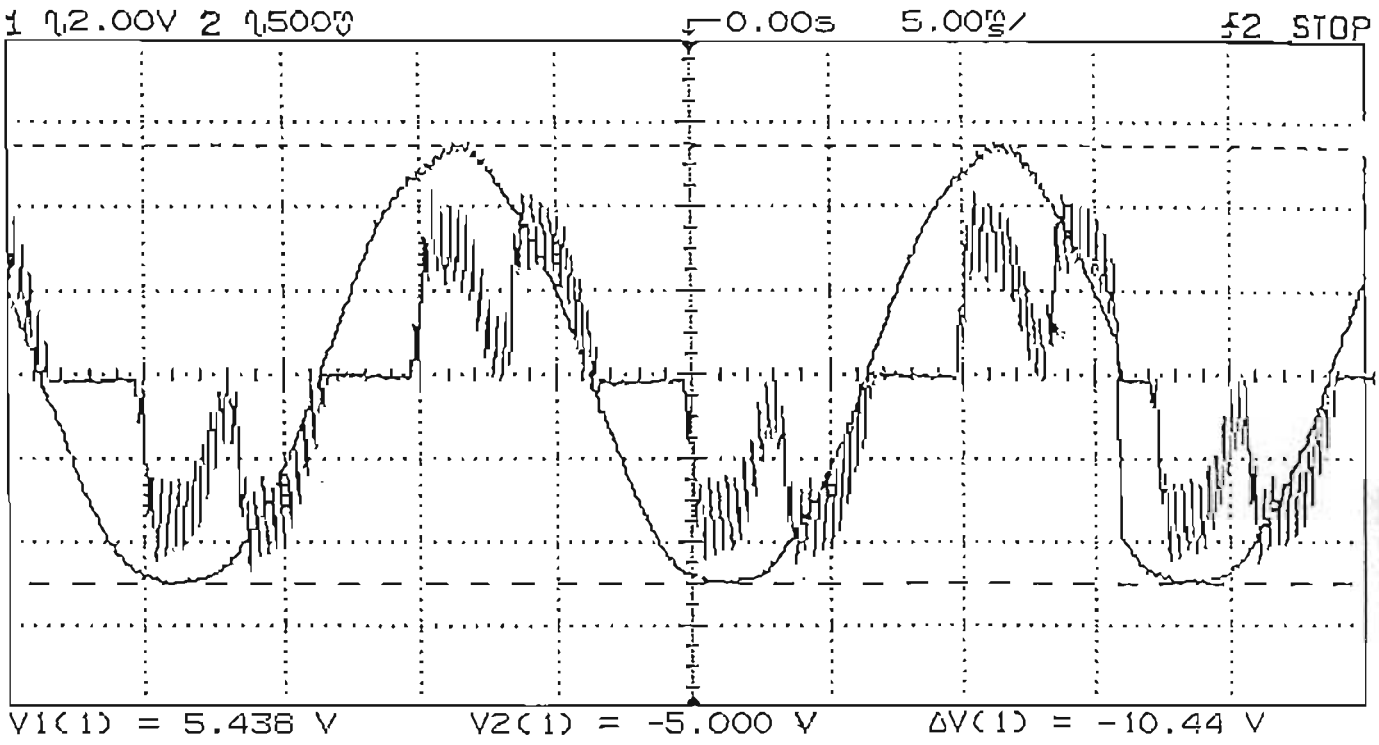
Peak to peak voltage on waveform			=	2.17V
Correction scaling			=	10 mV / A
Actual peak to peak current	=	2170 mV / 10 mV/A	=	217 A
RMS current	=	217/ $(2 * 2^{0.5})$	=	76.72 A

The phase angle, ϕ, (between the voltage and current) was obtained from waveform D-3:

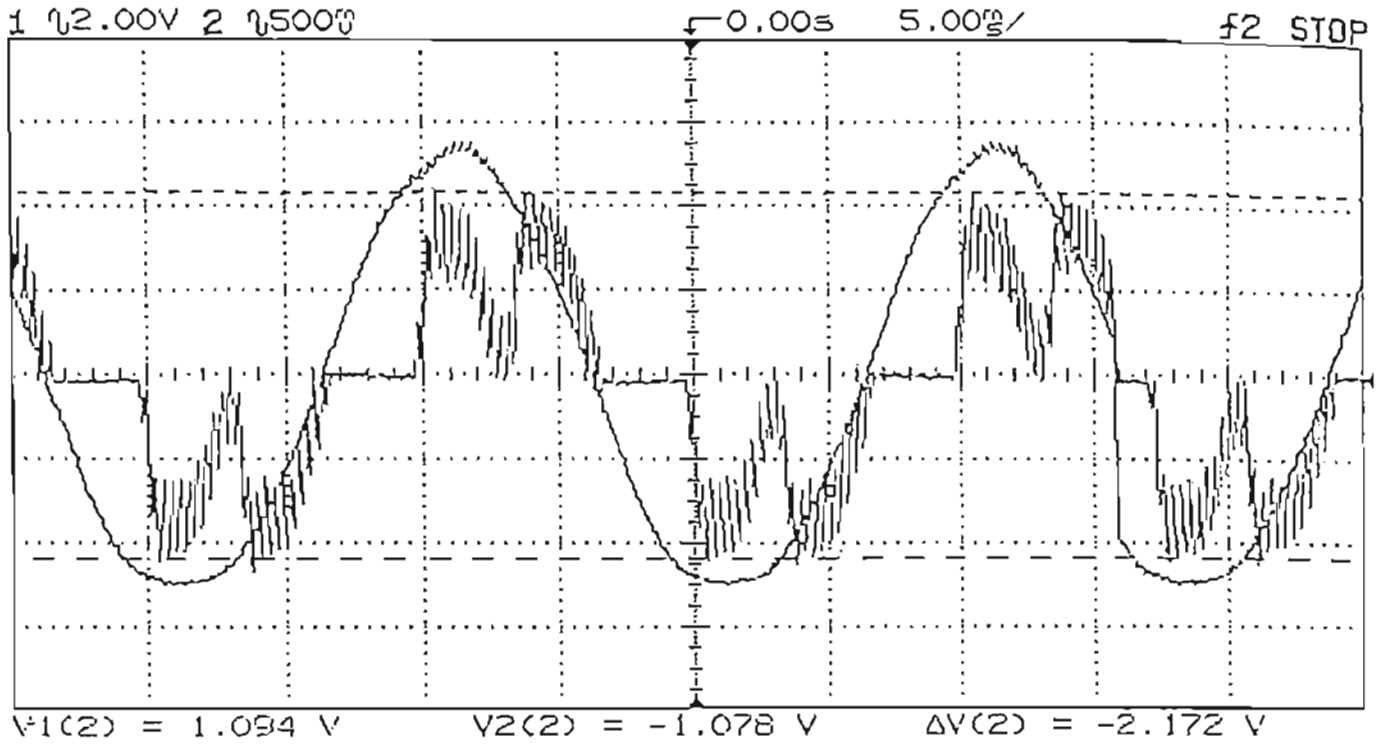
1 voltage or current cycle	=	50 Hz	=	20 ms	=	360°
ϕ (phase angle)	=	Δt	=	3.6 ms	=	64.8°

The power output, P, is calculated using the following equation:

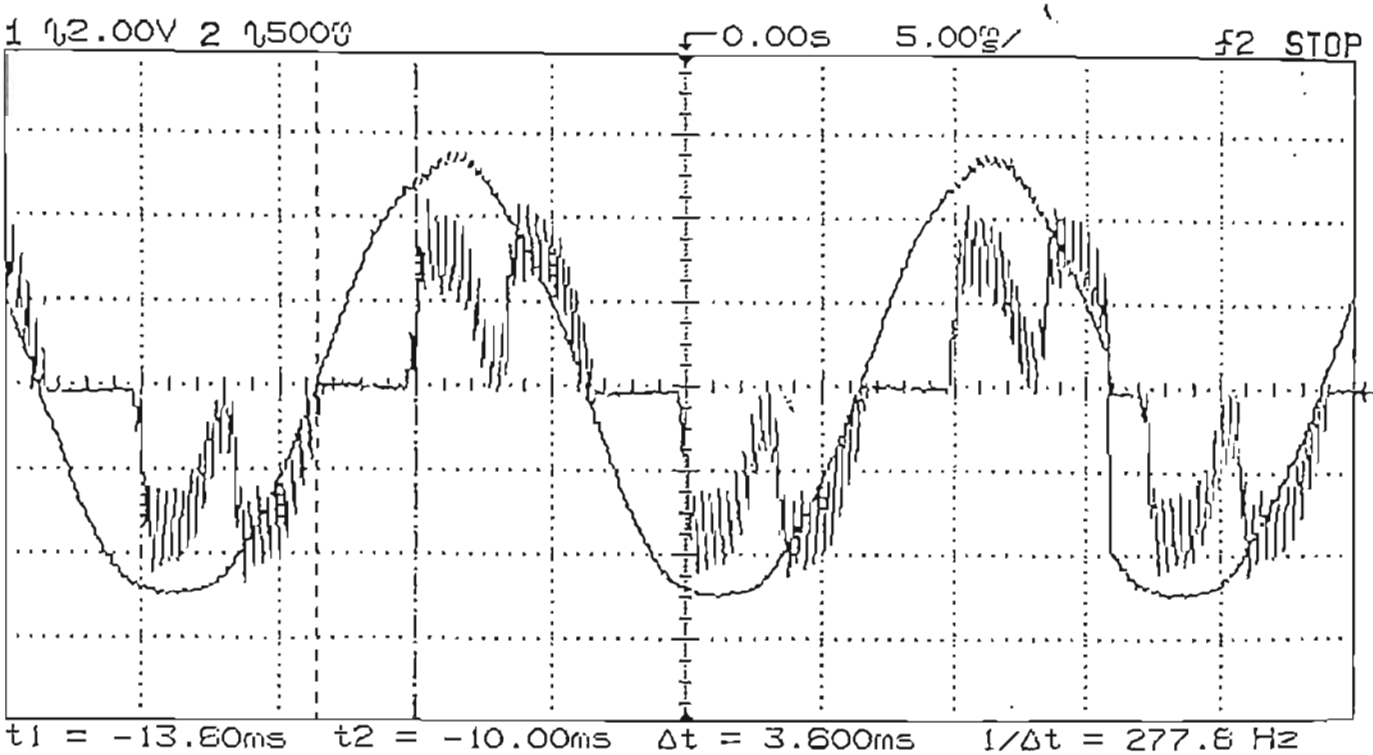
$$P = V A \cos\phi$$
$$= 369.11 * 76.72 * \cos(64.8°)$$
$$= 12.06 \text{ kW}$$



Waveform D-1: Peak-to-peak voltage



Waveform D-2: Peak-to-peak current



Waveform D-3: Phase shift

Appendix E - Energy Equations and Calculations

An unsteady state equation describing heat loss from the reactor when no reaction occurs can be written as follows:

$$\frac{d}{dt}(m_t Cp_t T) = -UA(T - T_a) \qquad (1)$$

where

m_t	=	mass of graphite tube	[kg]
Cp_t	=	specific heat of graphite tube	[kJ/kg.K]
T	=	temperature of graphite tube	[K]
T_a	=	ambient air temperature	[K]
U	=	overall heat transfer coefficient	[W/m^2.K]
A	=	heat transfer area	[m^2]
t	=	time	[secs]

This equation can be expanded to:

$$m_t(T\frac{\partial Cp_t}{\partial T}\frac{\partial T}{\partial t} + Cp_t\frac{dT}{dt}) = -UA(T - T_a) \qquad (2)$$

and can be rearranged to give:

$$\frac{dT}{dt} = \frac{-UA(T - T_a)}{m_t(T\frac{\partial Cp_t}{\partial T} + Cp_t)} \qquad (3)$$

The specific heat of graphite is related to temperature as shown below and was obtained from Perry *et al* [1984]:

$$Cp_t = 0.931986 + 9.1246 \times 10^{-4} T - 40759.33 T^{-2} \quad [kJ/kg.K]$$

The term UA in (3) can be reduced to one variable, α, which accounts for the heat transferred from the graphite tube, through the carbon black, alumina wool and ceramic shell to the atmosphere and accounts for the different thermal conductivities and heat transfer surface areas. This leads to equation (4):

$$\frac{dT}{dt} = \frac{-\alpha(T - T_o)}{m_t(T\frac{\partial Cp_t}{\partial T} + Cp_t)} \qquad (4)$$

dT / dt was evaluated by plotting a graph of reactor temperature with respect to time. Figure E-1 shows two reactor cooling curves when no reaction occurs. External conditions such as cooling water flow and extractor fans are the same in both cases, however argon flow was allowed through the reactor in one instance.

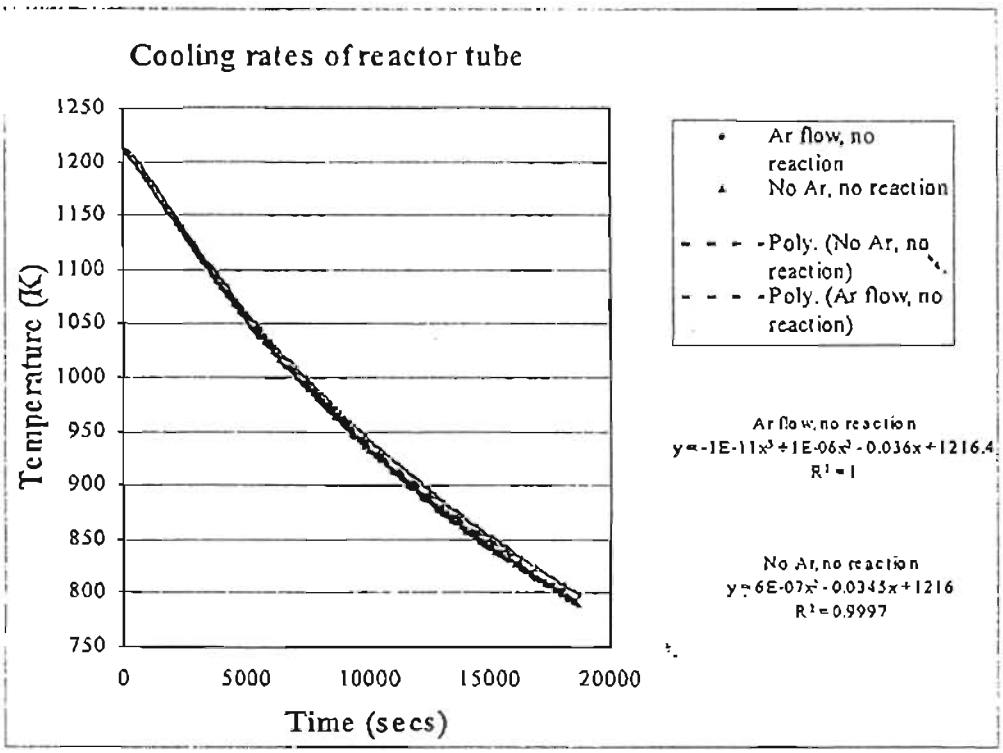


Figure E-1: Reactor cooling curves

The resulting graph shows that argon is indeed transparent to thermal radiation, as the curves are identical. Because argon flows during the reactions, it was decided to use the curve generated with argon flow to evaluate dT/dt. Curves were fitted to the experimental cooling data, and equations were generated which best described the data.

The average ambient temperature, T_a, during the cooling was measured as 292 K. α was evaluated at several temperatures. The average value of α over the temperature range 1216 – 982 K was evaluated as 3.6 W/K.

A graph of temperature versus α was generated to illustrate how little this value varied over the said temperature range. This can be seen in Figure E-2.

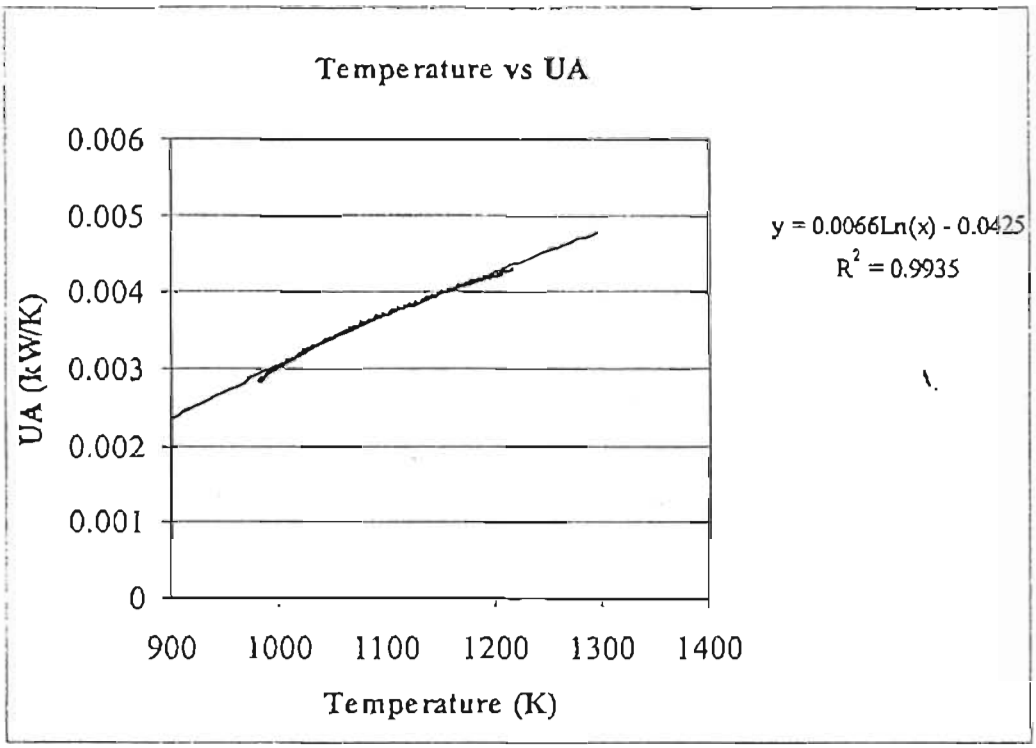


Figure E-2: Dependence of α (UA) on temperature.

Appendix F - Heat balances for calculation of heat loss from reactor under reaction conditions

A total heat balance over the reactor can be written as follows:

$$m_t Cp_{1t} T_1 + H_R + m_o Cp_{in_o} T_{in} = m_t Cp_{2t} T_2 + m_o Cp_{1o} T_1 + \frac{UA(T_1 - T_a)}{\Delta t} \qquad (1)$$

where

T	=	temperature	[K]
Cp	=	heat capacity	[kJ/kg.K]
m	=	mass	[kg]
H_R	=	heat of reaction	[kJ]
U	=	overall heat transfer coefficient	[W/m^2.K]
A	=	heat transfer area	[m^2]
t	=	time	[secs]

and subscripts

1	-	initial conditions of reactor tube
2	-	final conditions of reactor tube
t	-	tube condition
o	-	organic feed condition
in	-	organic feed condition pre-entry to reaction zone
a	-	ambient condition

The terms above account for heat loss from the reactor to

1) losses to the atmosphere
2) heat used for reaction
3) sensible heat to bring organic feed up to reaction temperature

Equation (1) can be rearranged to solve for the heat losses from the reactor:

$$\frac{UA(T_1 - T_a)}{\Delta t} = m_t(Cp_{1t} T_1 - Cp_{2t} T_2) + H_R - m_o(Cp_{1o} T_1 - Cp_{in_o} T_{in}) \qquad (2)$$

Heat of reaction, H_R, was calculated from thermodynamic data (see Appendix A). The change in temperature of the reactor tube with time was logged for each run. The logged data for the methylene chloride and trichlorobenzene runs can be seen in Figures F-1 and F-2 respectively.

Heat capacities of organic feed can be found in Appendix A, while that for the graphite tube is the same as used in Appendix E.

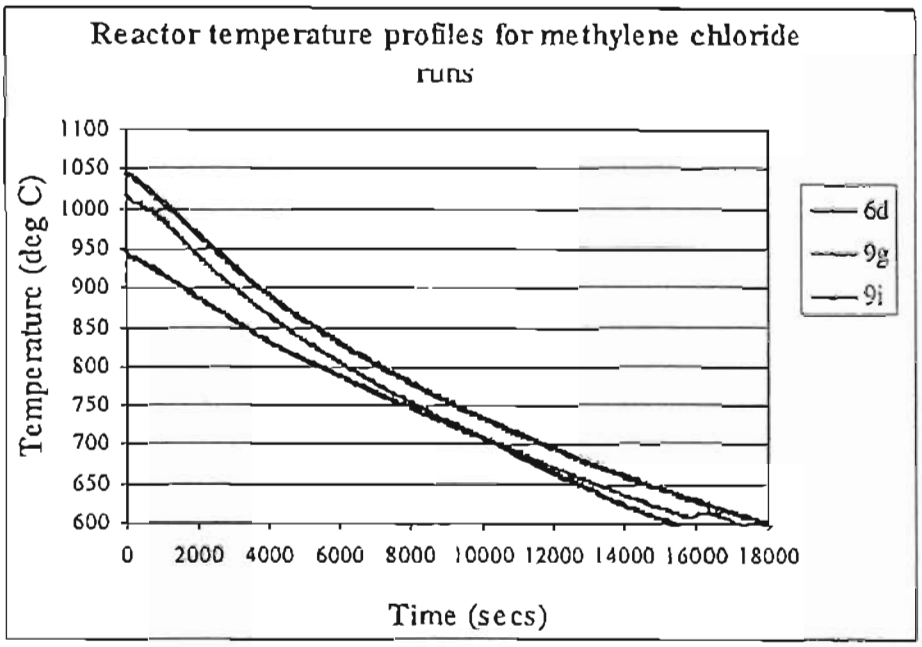


Figure F-1: Temperature profiles for methylene chloride runs

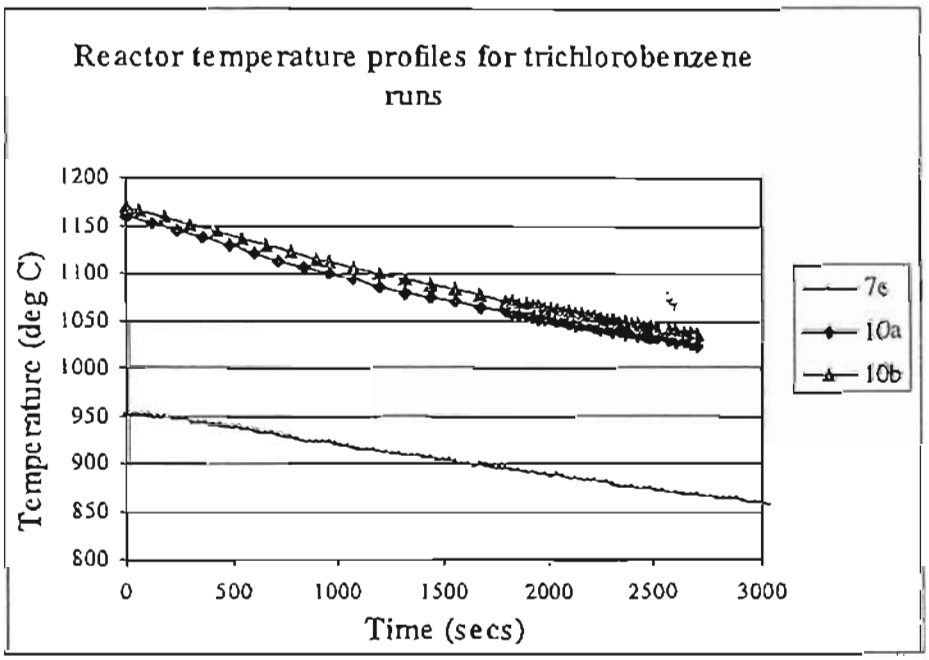


Figure F-2: Temperature profiles for trichlorobenzene runs

Appendix G – Reactants & Solvents

Table G-1: Chemical purity, contaminants and suppliers

Chemical	Supplier	Purity [a]	Impurities [a]		RI measured (24°C)	RI literature (20°C) [b]
ethanol	c	99.9%	aldehydes	0.001%	1.354	1.361
			furfuraldehydes	0.001%		
			higher alcohols	0.01%		
			methanol	0.05%		
			water	0.2%		
hexane	c	99%	aromatics	0.01%	1.367	1.375
			non-volatiles	0.01%		
methylene chloride	d	99.8%	water	0.05%	1.416	1.424
chlorobenzene	e	99.5%	acetic acid	0.03%	1.517	1.524
1,2-dichlorobenzene	f	99%	hydrochloric acid	0.001%	1.545	1.551
			chloride	0.00001%		
			water	0.01%		
1,2,4-trichlorobenzene	e	99%			1.565	1.572

Key:

RI refractive index

a As stated by supplier

b Weast, R.C. (1983-1984). Handbook of Chemistry and Physics. 64th edition, CRC Press Inc., United States.

c Saarchem (Pty) Ltd., Johannesburg.

d BDH Lab. Supplies, Poole, England.

e Fluka Chemie, Germany.

f RdH Laborchemikalien, Germany.

Appendix H - GC/MS calibration curves

Explanation of symbols used:

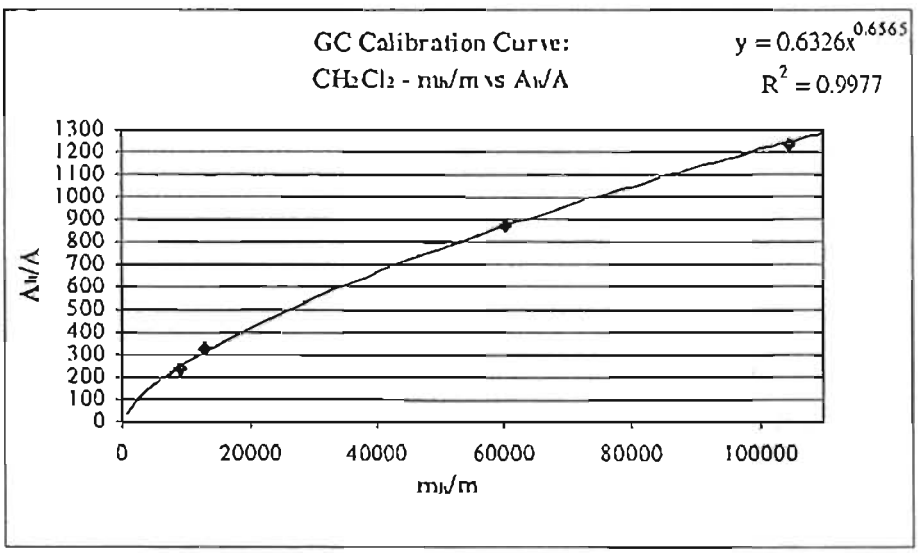
A	-	peak area	[arbitrary units]
m	-	mass	[g]

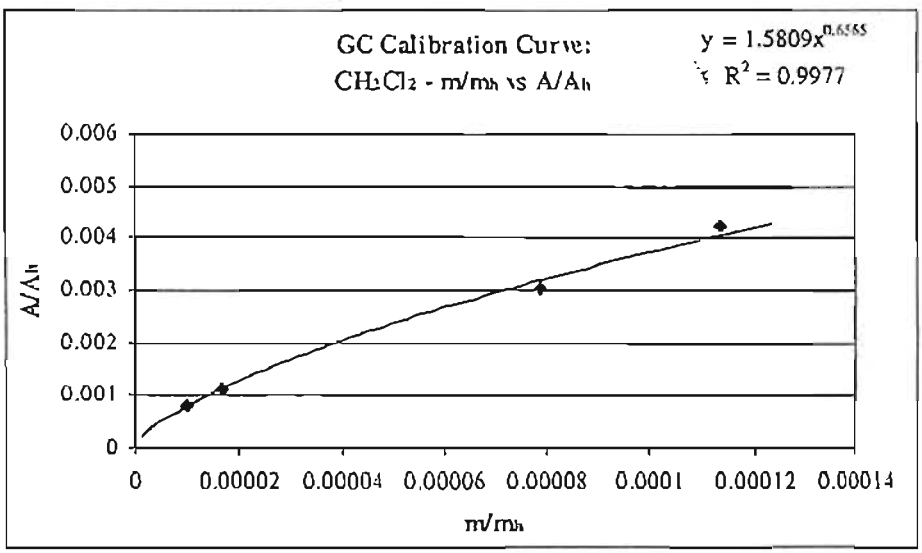
subscripts:

e	-	ethanol
h	-	n-hexane

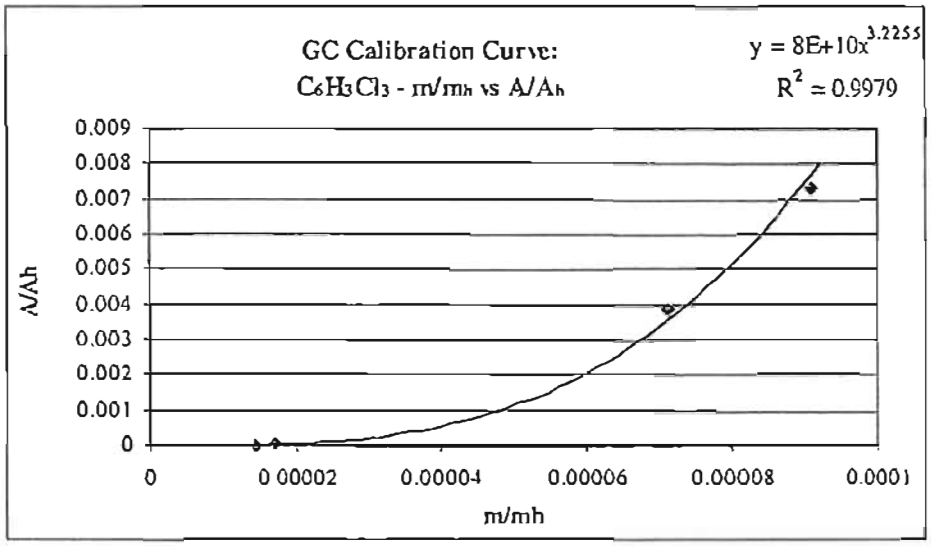
Symbols used without subscripts denote peak areas and masses of the compounds being calibrated for.

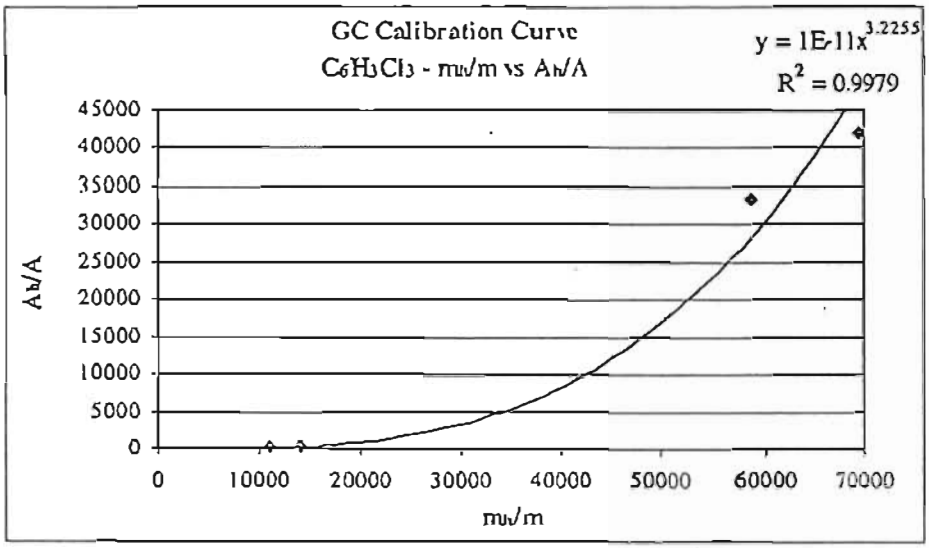
H.1 Methylene chloride in n-hexane:



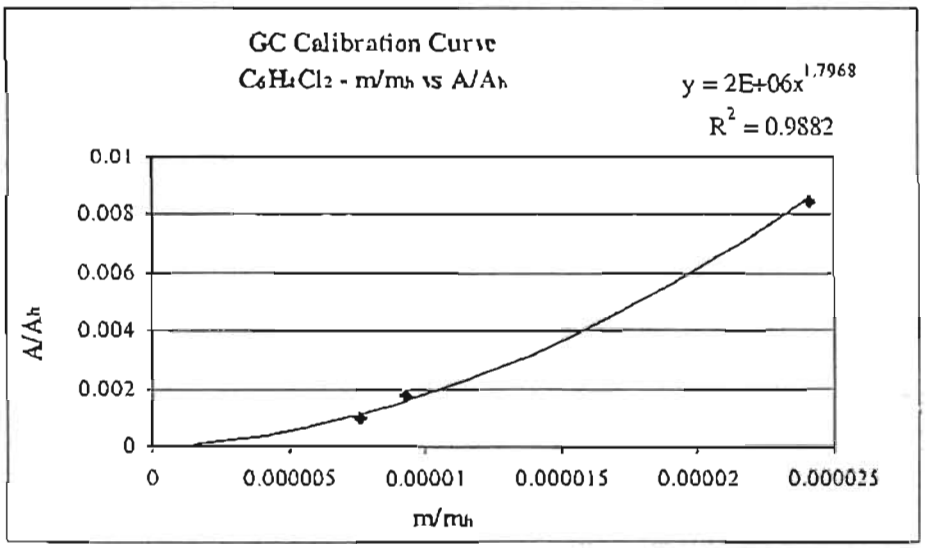


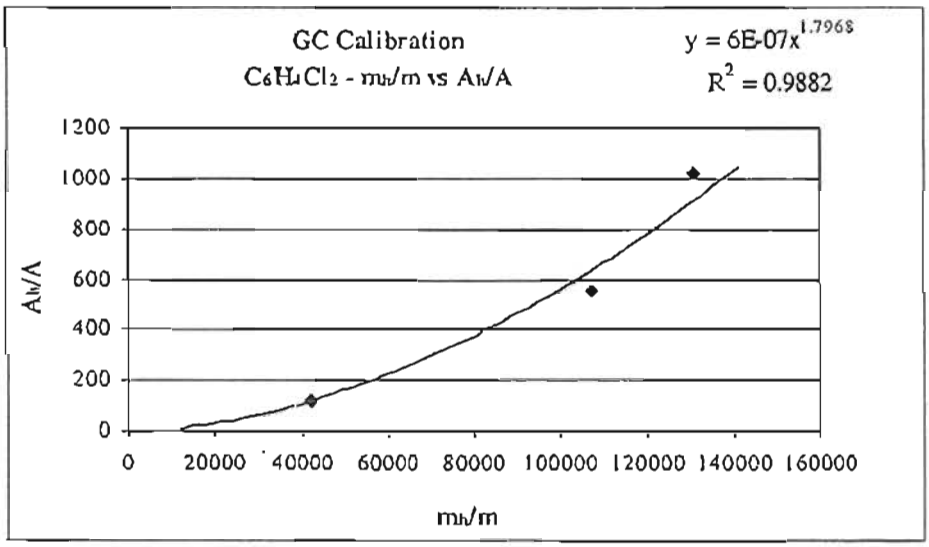
H.2 1,2,4-Trichlorobenzene in n-hexane



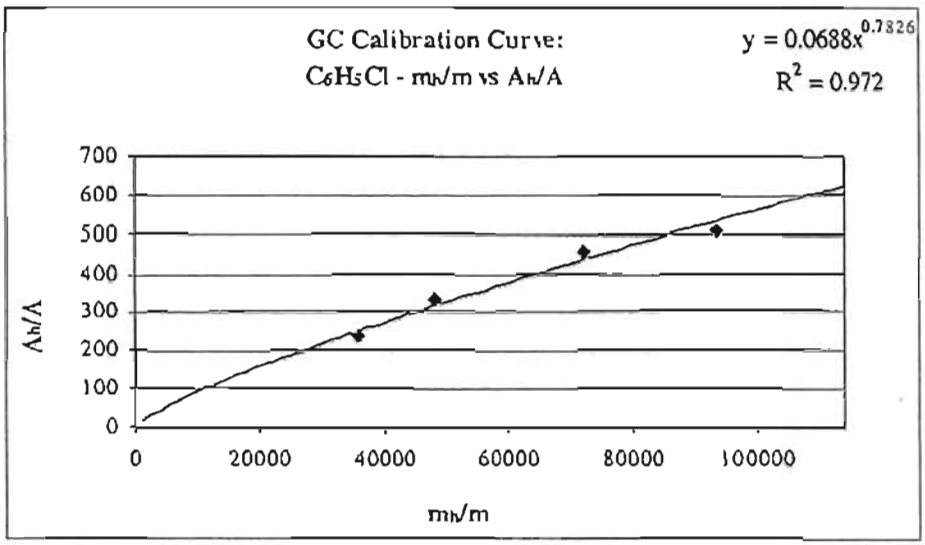


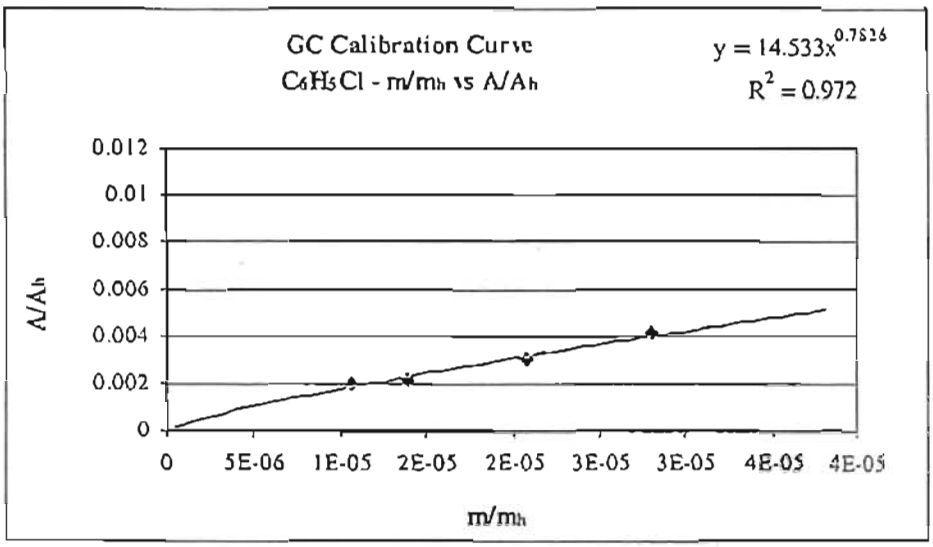
H.3 1,2-Dichlorobenzene in n-hexane



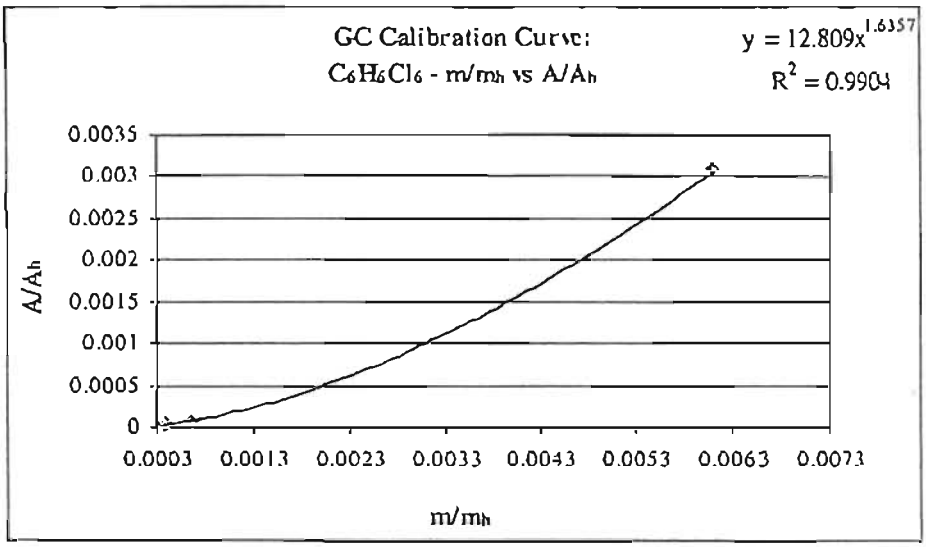


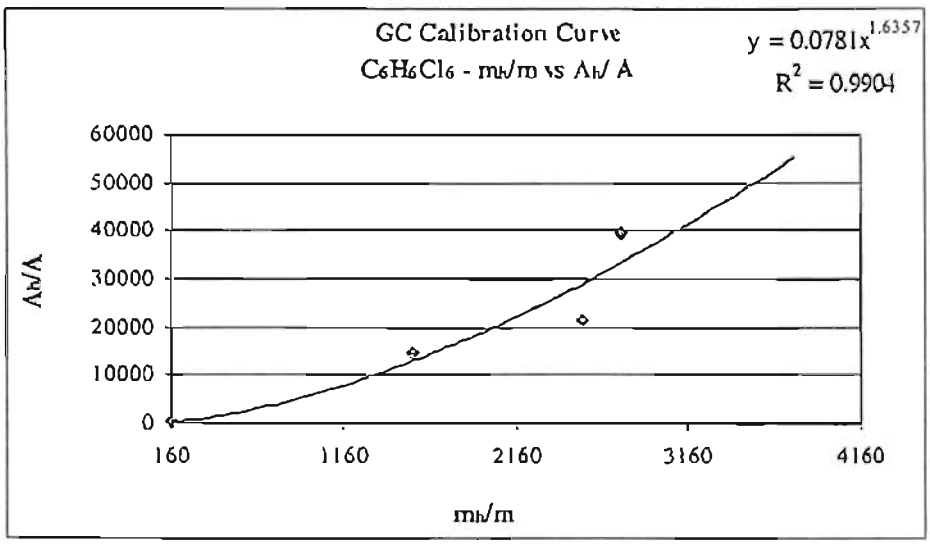
H.4 Chlorobenzene in n-hexane



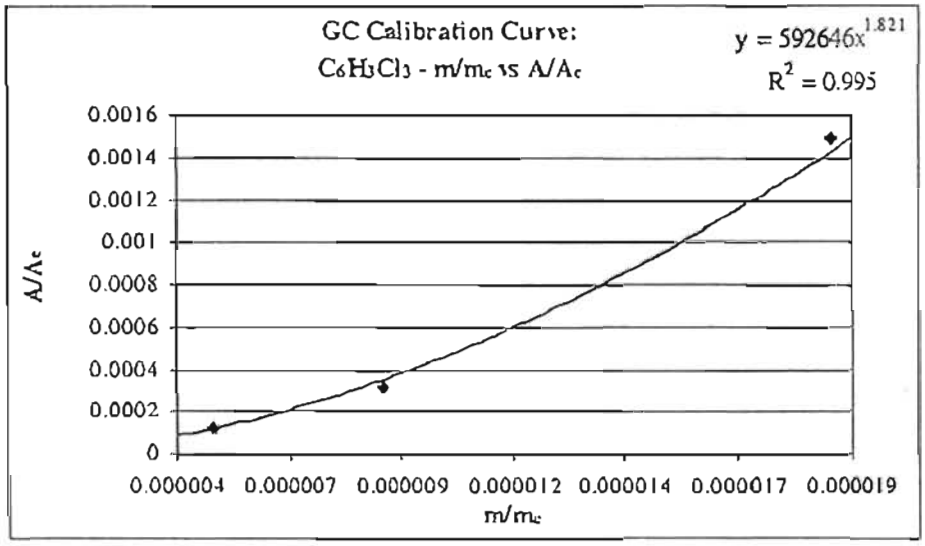


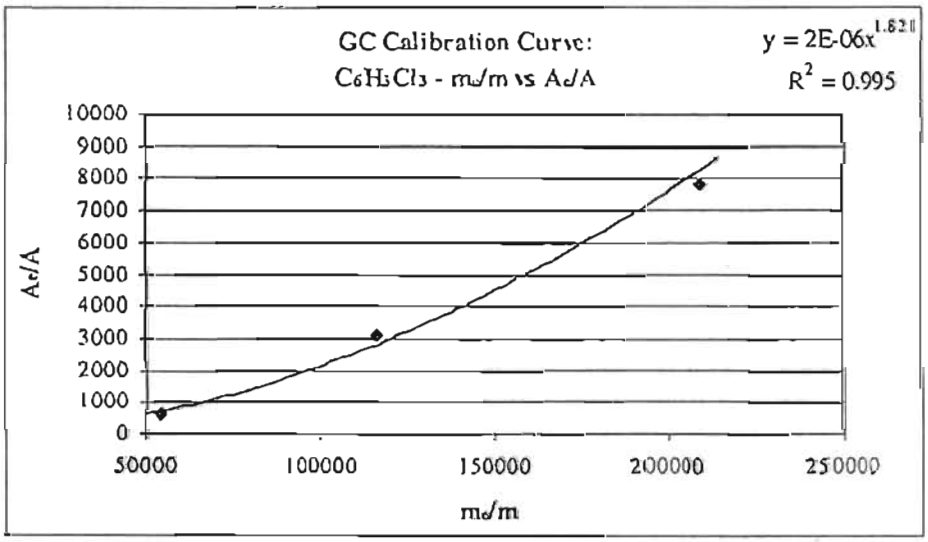
H.5 Industrial lindane in n-hexane





H.6 1,2,4-Trichlorobenzene in ethanol





Appendix I - Scanning electron micrographs

A scanning electron microscope was used to investigate the nature of the carbon formed for runs 1a-c, 2a-c and 3a. Reaction temperature and residence time is given in brackets.

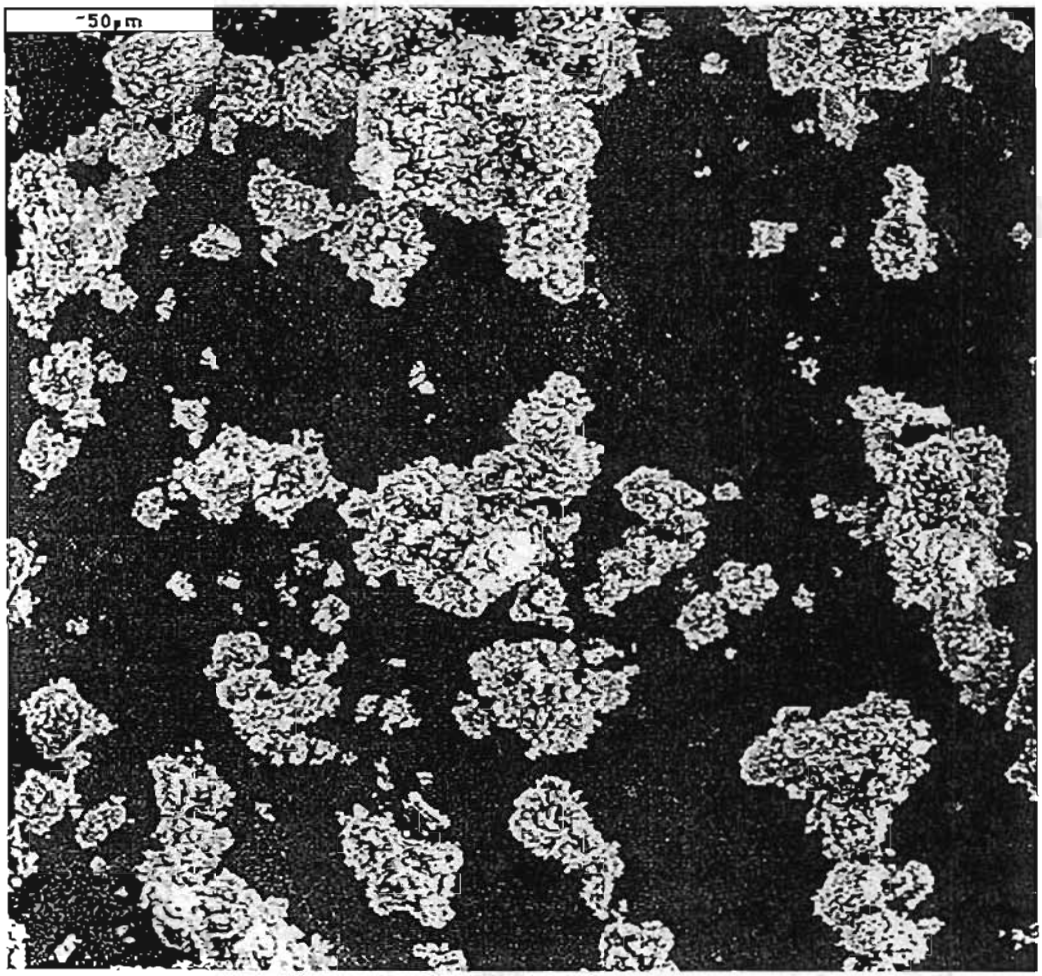


Figure I-1: Run 1a (1018°C, 2.96 secs)

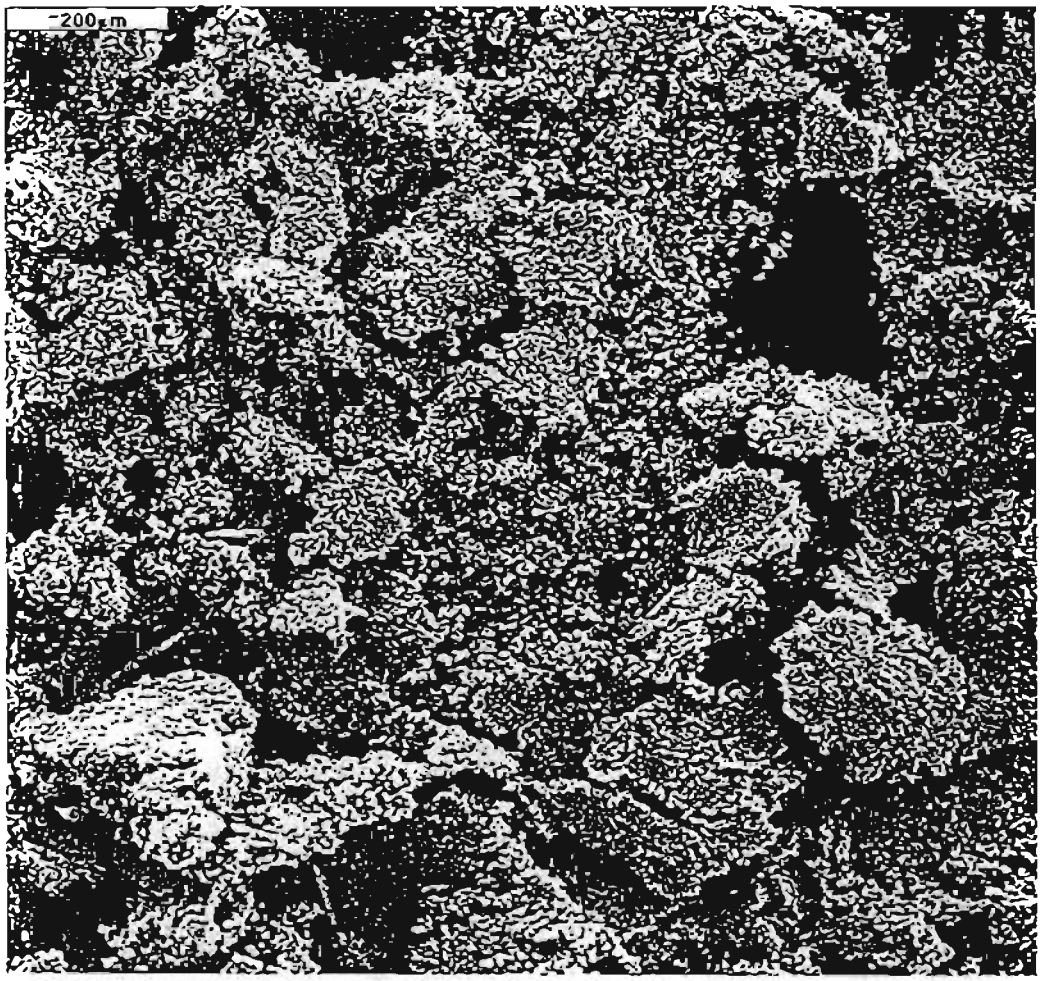


Figure E-2: Run 1b (1040°C, 2.12 secs)

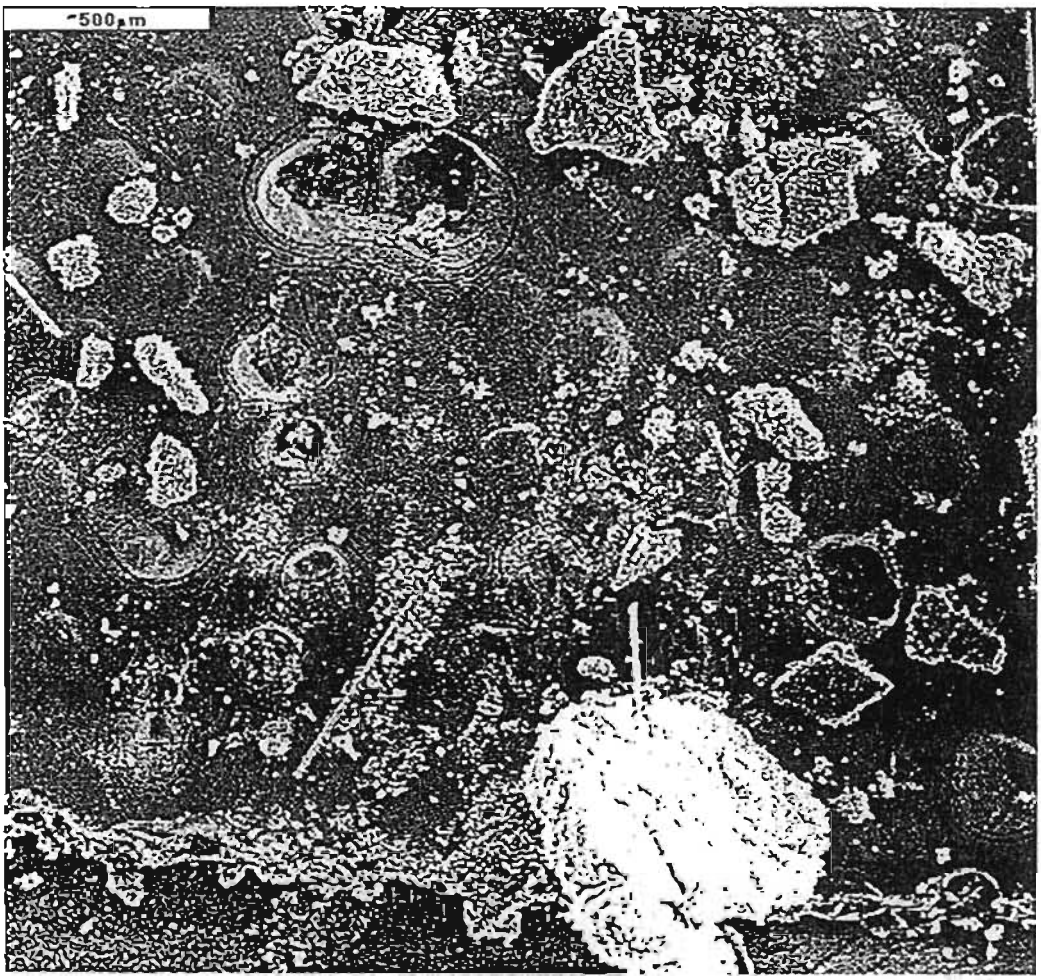


Figure I-3: Run 1c (1041°C, 4.75 secs)

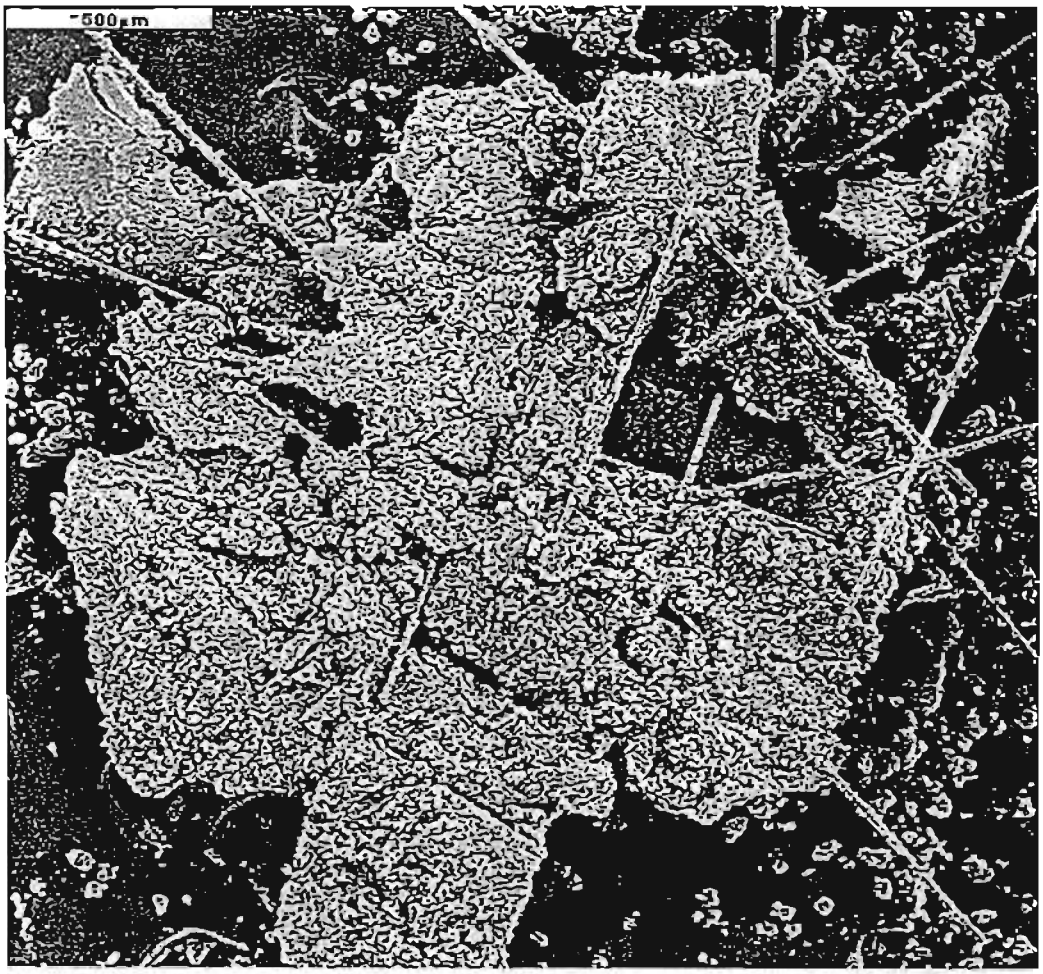


Figure I-4: Run 2a (1210°C, 2.58 secs)

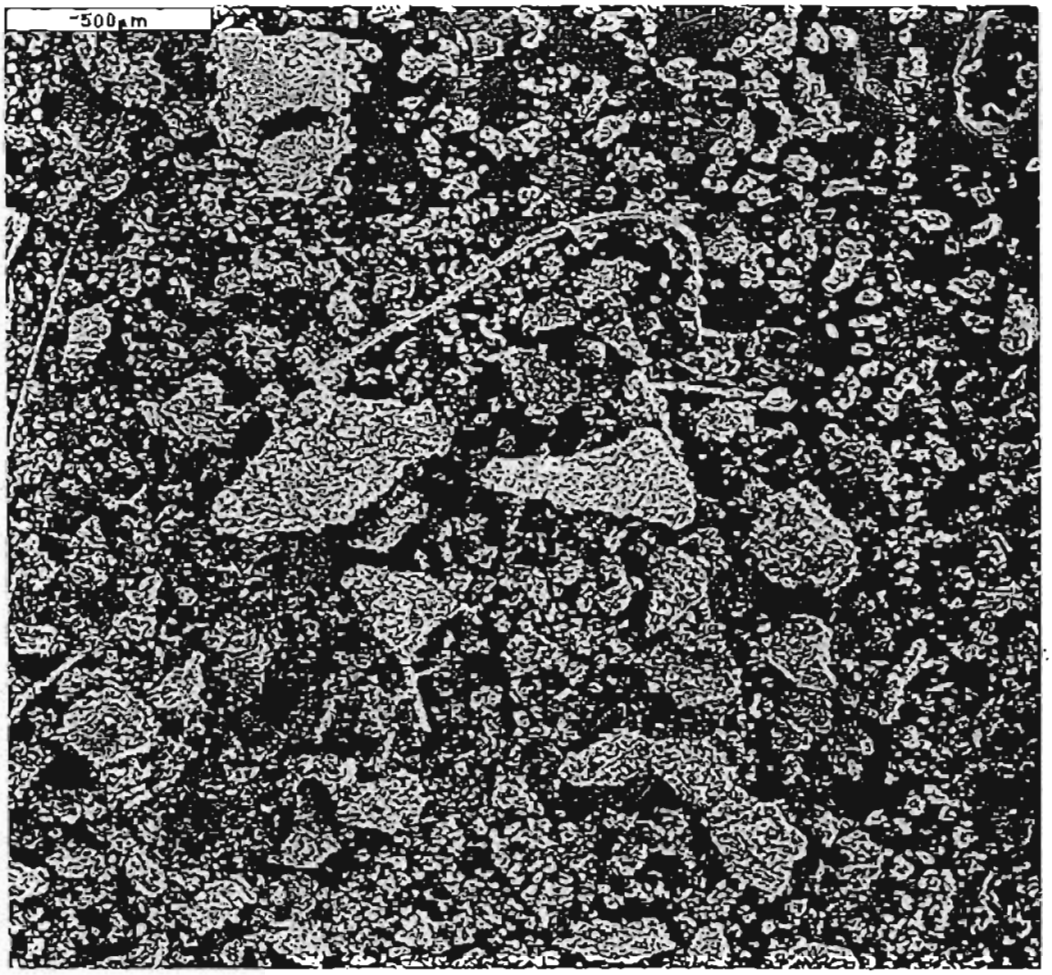


Figure I-5: Run 2b (1221°C, 3.78 secs)

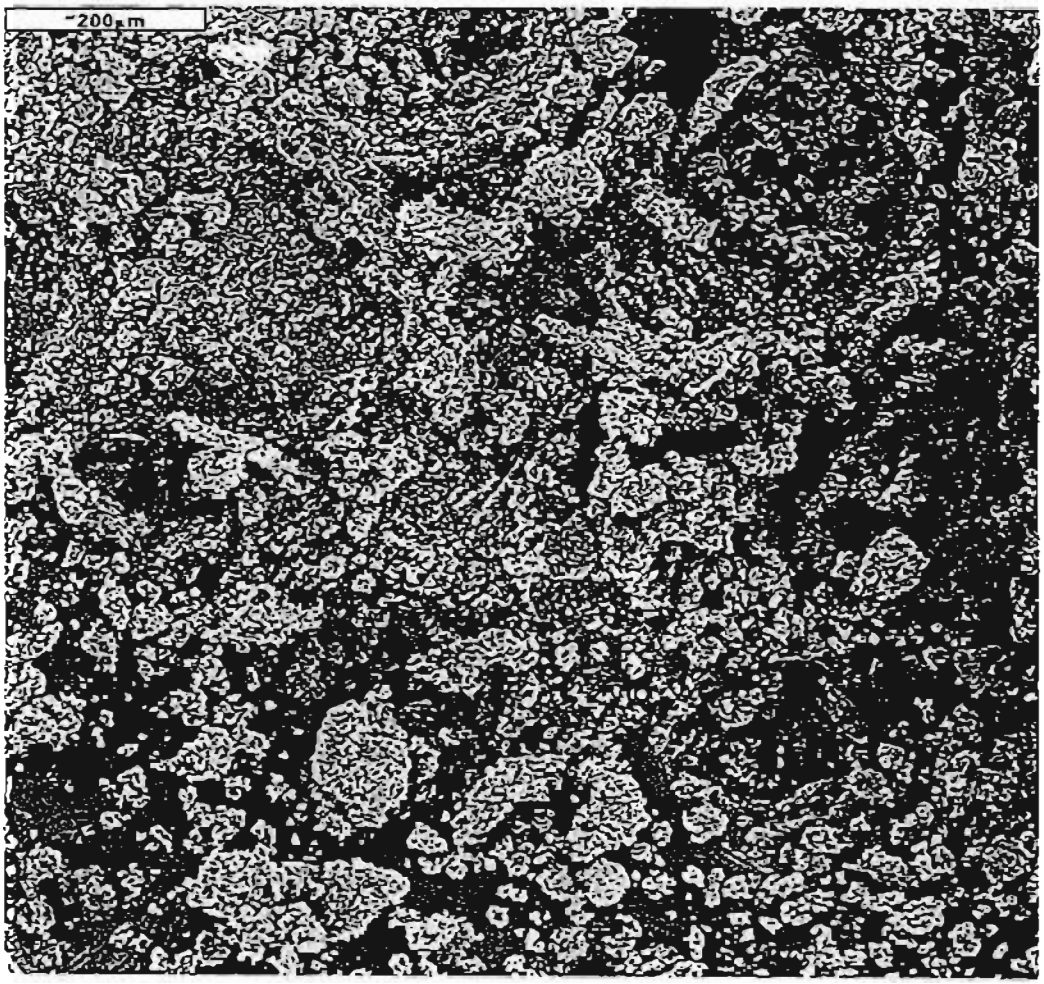


Figure I-6: Run 2c (1225°C, 1.25 secs)

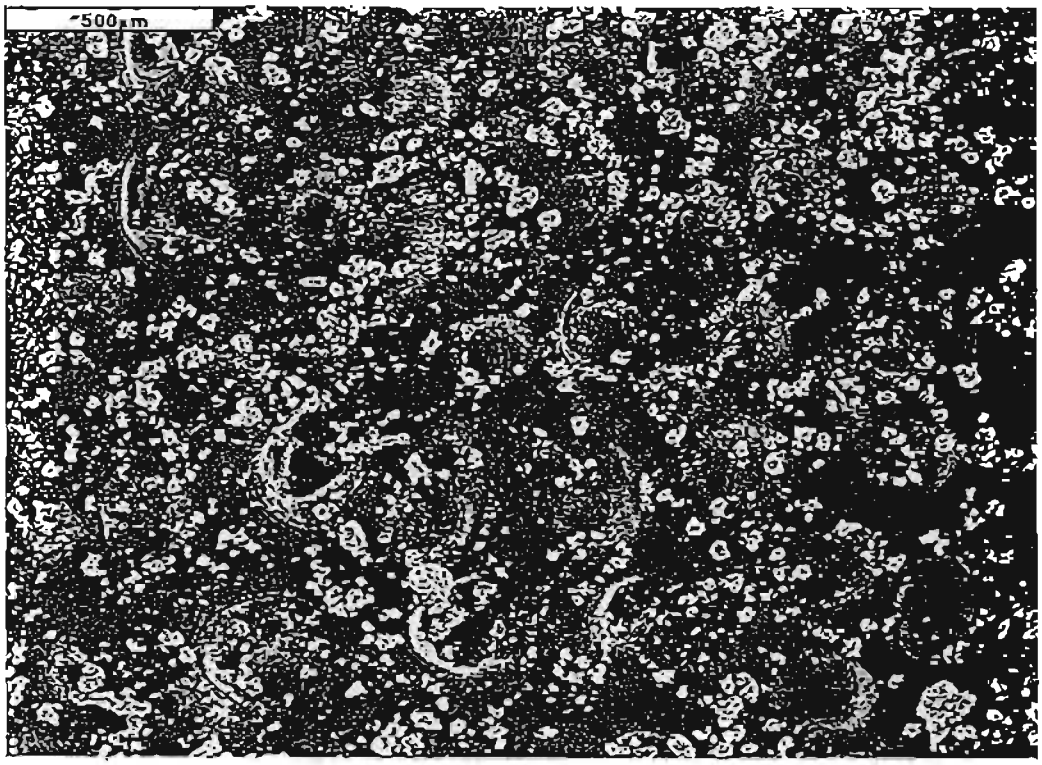


Figure I-7: Run 3a (1414°C, 3.34 secs)

Appendix J - Costing

J.1 References

(1) Peters, M.S., Timmerhaus, K.D., Plant design and economics for chemical engineers, McGraw-Hill, Singapore, 1991.

(2) Personal communication - Quadro Chemicals Engineering (Pty) Ltd., Dunswart, RSA.

(3) Personal communication - Germ Africa (pty) Ltd., Durban, RSA.

(4) Municipality, Pietermaritzburg, RSA.

J.2 Marshall and Swift cost indices & exchange rate

Cost indices were found in *Chemical Engineering*, and the relevant volumes are tabulated below:

Table J-1

Year	Cost Index	*Chemical Engineering* Volume
1990 (1st quarter)	915.4	Vol 97 (6), June 1990
2001 (1st quarter)	1084.7	Vol 107 (13), December 2000

Exchange rate taken as R9.20 = $1

$$cost_{year\ a} = cost_{year\ b}\ (index_{year\ a} / index_{year\ b})$$

J.3 Estimation of purchased equipment cost

Table J-2

Equipment	Capacity		Units	Cost (R)	Cost ($)	Cost year	Reference	Comments
Induction unit				68400		2001	2	25 kW, 1000Hz
Reactor				57000		2001	2	including cooling jacket, insulation, induction coils and ceramic inserts
Dosing pump	flow	1.1	l/hr	2280		2001	3	2x expected flow
Vacuum pump	vacuum	100.0	kPa	4674		2001		2x expected flow, sliding vane
Packed tower absorber	diameter	1.0	m		750	1990	1, 16-28	
	height	2.1	m					x1.5 factor
Single cyclone	C flow	0.2	kg/hr		1000	1990	1, 14-87	on-line emptying, 2x expected flow
	gas flow	1.6	kg.hr					

Table J-3

Equipment	Index 1990	Index 2001	Cost ($) 2001	Cost (R) 2001
Induction unit				68400.00
Reactor				57000.00
Dosing pump				2280.00
Vacuum pump				4674.00
Packed tower absorber	915.4	1084.7	888.71	8176.13
Single cyclone	915.4	1084.7	1184.95	10901.51
GC				100000.00
Total purchased equipment cost				**301431.64**

J.4 Estimation of fixed capital investment

Table J-4

	% of total	Cost (R)	
Direct Costs			630266.15
Purchased equipment	33	301431.64	
Equipment installation	8	73074.34	
Instrumentation & Control	8	73074.34	
Piping (installed)	5	45671.46	
Electrical (installed)	5	45671.46	
Service facilities	10	91342.92	
Indirect Costs			283163.05
Engineering & supervision	10	91342.92	
Construction expense	8	73074.34	
Contractor's fee	3	27402.88	
Contingency	10	91342.92	
Total fixed capital investment			913429.21