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The preparation of pitches from anthracene oil

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Declaration

I, Mashau Ntevheleni Sharon declare that the thesis hereby submitted in partial fulfilment for the requirement of the degree Master of Science (Chemistry) at the University of Pretoria is my own work and has not been submitted by me for any other degree at any institution.

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Date: 20 November 2007…………….……………………………………………

Abstract

Eskom has embarked on the development of the Pebble Bed Modular Reactor to generate electricity at low cost compared to that of coal with no greenhouse gas emissions. The proposed PBMR requires about 600 tons of nuclear-grade graphite blocks in its construction. A considerable amount of pitch is required as impregnants for the manufacture of this graphite.

Anthracene oil is a high-boiling coal-tar distillate fraction consisting of a complex mixture of mainly unsubstituted polyaromatic hydrocarbons, with some methyl substitution. Conversion to pitch may be effected by dehydrogenation, i.e. volatile oil molecules condensing together to yield material of high molecular mass. Two dehydrogenation reagents, elemental sulfur and a novel reagent, hexachlorocyclohexane (HCH), an industrial waste product, were used to give three series of pitches with differing softening points. These products were characterised by standard pitch analyses, elemental analyses, thermogravimetric analysis (TGA), proton nuclear magnetic resonance spectroscopy (^{1}HNMR), gas chromatography (GC), gas chromatography–mass spectrometry (GC-MS), Maldi-TOF mass and mass probe spectrometry and then compared with commercial pitch grades from Mittal Coke and Chemicals.

The results obtained showed that the reaction products reacted with 15 and 20 wt % of sulfur, with the softening points of 61.3 and 91.4 ^{o}C, would be suitable as commercial products. All pitches showed very little, if any, ash, making them suitable for use in the manufacture of high-purity graphite. Pitches prepared with 15-20 wt % of sulfur and HCH pitches may have more applications in impregnation because of their low QI content. Total sulfur content detected by elemental analysis is high. This is undesirable because sulfur may cause puffing which will result in poor quality of graphite. All pitches show very little, if any, ash, making them suitable for use in the manufacture of high-purity graphite.

TGA results showed that pitches prepared with higher concentrations of sulfur can be suitably used as impregnants because of their high coking yields. The coking yields of HCH-derived pitches are lower than those of Mittal Coke and Chemicals commercial pitches.

Results from the ^{1}HNMR showed that cross-linking on reaction with sulfur is through aliphatic carbon atoms; the percentages of aliphatic protons decrease with the increase in the sulfur concentration, and aromatic percentages increase. There is a slight increase in the proportion of aromatic protons of the HCH pitches; therefore cross linking is through aromatic-aromatic carbon atoms.

Model reactions were prepared by reacting pure aromatic hydrocarbons with HCH, demonstrating the incorporation of the dehydrogenation reagent. These reactions were used to determine the reactivity of the main components of anthracene oil. The reaction products were characterised by Maldi-TOF and GC-MS. The results obtained from HCH pitches showed the formation of chlorobenzenes. This is undesirable because chlorine may cause corrosion of the equipment during coking.

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Table of contents

List of figures

List of Tables

List of abbreviations

$AlCl_3$	Aluminium chloride
AO	Anthracene oil
BF_3	Boron trifluoride
$CDCl_3$	Deuterated chloroform
CS_2	Carbon disulphide
CY	Coking yield
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
DTG	Differential thermogravimetry
FID	Flame ionisation detector
GC	Gas chromatography
GC-MS	Gas chromatography – Mass spectrometry
H_2S	Hydrogen sulphide
HCH	Hexachlorocyclohexane
HCl	Hydrogen chloride
HF	Hydrogen fluoride
HNMR	spectroscopy
ITD	Ion trap detector
MCO	Coal tar oil (from Mittal Coke and Chemicals)
MIT	matter-insoluble toluene
NaOH	Sodium hydroxide
NMP	N-methylpyrrolidinone

NMR	Nuclear magnetic resonance
PAH	Polycyclic aromatic hydrocarbon
PBMR	Pebble Bed Modular Reactor
ppm	Parts per million
QI	Quinoline insoluble
T_g	Glass transition temperature
SG	Specific gravity
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TOF	Time of flight
UO_2	Uranium oxide

CHAPTER 1: INTRODUCTION

South Africa is a country rich in natural resources, but she sadly lacks in the energy field. The coalfields found in the east of the country are of low-grade coal and have a limited life span. Improving the efficiency of power stations, importing electricity from Cahora Bassa and the gas pipeline from Maputo can somewhat alleviate the shortage of energy in the short and medium term. However, alternative sources of energy must be found for the long-term alleviation of the shortage of energy.

Eskom, the national energy supplier, has embarked on the development of the Pebble Bed Modular Reactor (PBMR) for the purpose of generating electricity at a price comparable to that of coal. This nuclear reactor technology was extensively tested in Germany, Europe, North America and Asia, but only one power reactor, was ever built in Germany (Nicholls, 2001). The power reactors were closed down when the Green Party came into power and testing was also stopped (Nicholls, 2001; Der Heyde and Thomas, 2002). Eskom believes that this project will generate a market both in South Africa and abroad, for which 30 reactors per year could be built within a period of 12 to 15 years (Nicholls, 2002). The ease of operation will permit effective functionality away from developed centres.

The proposed PBMR requires about 600 tons of nuclear-grade graphite blocks in its construction (Nicholls, 2001). A considerable amount of pitch is required for the manufacture of this graphite, both as a binder and as impregnants (void filler). South Africa has limited amounts of suitable pitches. However, it has sizeable quantities of low-value anthracene oils. These oils would give relatively pure synthetic pitches, appropriate for these applications (Nicholls, 2001; Nicholls, 2002). Pitch is also used as a binder for the manufacture of electrodes in aluminium anodes. It is used for anode applications because of its resistance to corrosion and low porosity (Betts, 1997).

1.1 Objective of the study

The main objective of this study was to prepare pure synthetic pitches suitable for use as binders or impregnants for the manufacture of nuclear-grade and other synthetic graphites. The reaction of hexachlorocyclohexane with pure polycyclic hydrocarbons would be studied as models for the complex oils.

Pitches would be prepared using two methods: by dehydrogenative cross-linking of the anthracene oil with sulfur, and with a novel reagent, hexachlorocyclohexane. Both these reactions are effective at temperatures between 250 and 275^{o}C.

CHAPTER 2: LITERATURE REVIEW

2.1 Pebble Bed Modular Reactor

The Pebble-bed Modular Reactor (PBMR) is a high-temperature gas-cooled nuclear reactor that utilises a closed Brayton Power Conversion Unit with helium as the working fluid (Greyvenstein and Rousseau, 2003). The PBMR consists of a structure made up of synthetic graphite blocks (the reflector), enclosed within a steel pressure vessel. The reflector acts as a transitional container for the fuel pebbles and it is assembled with 600 tons of nuclear-grade graphite (Nicholls, 2001).

Depending on their position within the structure, the blocks vary in their qualities, with the inner ones being able to withstand the higher temperatures (up to 950 °C) and the high neutron fluxes experienced during operation. The external blocks are filled with boron carbide, which acts as a neutron shield to stop irradiation of the steel shell (Nicholls, 2001; Nicholls, 2002).

The fuel elements are graphite spheres referred to as *pebbles*, 60 mm in diameter, containing many uranium oxide (UO_2) kernels of approximately 0.5 mm in diameter. The kernels are coated with two pyrolytic graphite shells of different porosity, a silicon carbide shell, and a third layer of pyrolytic graphite shell (Nicholls, 2002; Morgan, 2002). The silicon carbide shell is highly stable and retains all fission products formed during the operation. The fuel element is prepared by mixing the coated particles with finely powdered graphite and a resin binder, pressed into a spherical shape, and baked at 1 900 °C. Each fuel element contains 9 g of uranium and the total mass of a fuel sphere is 210 g. The pebbles are 5 to 8 %

uranium-enriched, which enables the PBMR to sustain the chain reaction (Nicholls, 2001; Nicholls, 2002).

During operation, the pebbles are loaded into the top of the reactor, passed through the reactor and then released at the bottom where their degree of burn-up is measured. The kernels are returned to the reactor (if useful energy is left), or retained within the building (if fully burned out) to allow the bulk of the decay of the short-lived fission products to take place (Nicholls, 2002). Heat generated by the reactor is removed by helium gas, which enters the reactor vessel at a temperature of about 450 °C, is heated to 900 °C and then drives a gas turbine, giving a useful capacity of 160 MWe. The modular nature of the structure would allow ten reactors to be built on a site, sharing services and a single control room (Nicholls, 2001).

The reactor was defined as being intrinsically safe, because the silicon carbide shell around the uranium oxide kernels is able to retain all fission products at higher temperatures (Nicholls, 2002). If the coolant gas stopped flowing, fission products from radioactive decay would continue to heat the fuel to a temperature of 1 600 °C, the heat losses through the reactor shell would balance the heat production, and the reactor core would slowly cool down. There would be no release of radioactive fission products below the temperature of 1 600 °C (Nicholls, 2001; Nicholls, 2002).

Graphite is chosen as one of the best materials for nuclear fission reactors due to its high moderating efficiency, which is required for nuclear reaction, and its low absorption cross-section for neutrons. It has a high sublimation point and oxidises slowly at higher temperatures (Pierson, 1993; Mantell, 1968). The graphite blocks must be of high strength and highly isotropic to give the best dimensional stability under irradiation. Graphite is used as the structural material and moderator for the reactor core because it is a readily available material with low thermal neutron-capture. A good moderator material must not react with neutrons because if the neutrons are captured in the moderator, they cannot sustain the fission process (Delhaes, 2001). The graphite blocks utilised for fission and fusion reactors are derived from blocks of petroleum or pitch cokes (Long, 1992; Collin *et al.*, 1995).

Pitch is introduced into nuclear-grade graphite as a binder or impregnant for the manufacture of well-graphitised coke particles (Betts, 1997; Collin, 1995). The binder is used to wet the surface of the carbon grain to produce mixtures of high plasticity and high carbon yield after the process of pyrolysis (Long, 1992). The purpose of the impregnant pitch is to decrease the porosity of the carbon, thus increasing the density of the resultant graphite (Nightingale, 1962). Pitch is preferably used as a binder or impregnant in the manufacture of graphite because of its low cost, good wettability to carbons, and its capacity for generating matrices with different microstructures on graphitisation (Pierson, 1993). Pitch consists of hundreds of polycyclic aromatic compounds, which condense on thermal treatment, leading to a graphitisable material that effectively binds the particles together. The main source of well-graphitising coke is needle coke, made by coking petroleum residue in a delayed coker (Long, 1992).

2.2 Manufacture of synthetic graphite

Synthetic graphite is a material consisting mainly of graphitic carbon that has been obtained by the thermal treatment of non-graphitic carbon or chemical vapour deposition (Delhaes, 2001; Collin *et al.*, 1995). It is an allotropic form of carbon, consisting of layers of hexagonally arranged carbon atoms in a planar condensed ring system. The layers of graphite are held together by σ and π bonds. The bonds within the layers are covalent with sp^2 hybridisation (Delhaes, 2001; Pierson, 1993).

Synthetic graphite is manufactured by the pyrolysis of a highly graphitisable filler coke, such as petroleum coke and coal tar pitch binder. Petroleum coke and coal tar pitch are also used as impregnants to strengthen the final graphite artifact. Figure 2.1 outlines the materials and processes used in the manufacture of synthetic graphite (Nightingale, 1962). Petroleum coke is mixed with the pitch binder, the mixture is then moulded into shape, baked to a temperature of about 800 to 1 000 °C and further graphitised at 3 000 °C to produce nuclear-grade graphite (Collin *et al.*, 1995; Nightingale, 1962; Turk, 1992).

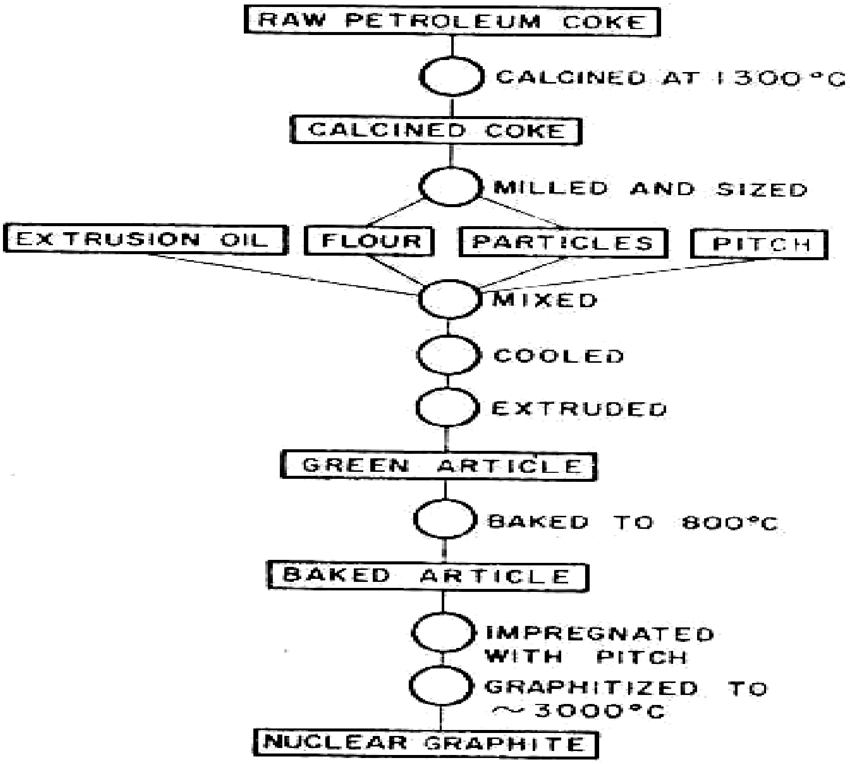

Figure 2.1: Materials and processes used in the manufacture of synthetic graphite

The resulting product is a porous material and for special applications such as nuclear graphite it is re-impregnated with molten pitch fluid in a rebaking or graphitising operation. The purpose of re-impregnation is to fill the voids and make the material denser in order to obtain pure synthetic graphite (Turk, 1992; Nightingale, 1962).

2.3 Coal tar

Coal tar is a complex mixture of organic compounds, primarily hydrocarbons, produced in the carbonisation process of bituminous coal at higher temperatures to give volatile products and a residue called ‘coke’. It is made up of the colloidal dispersed solid materials with high molecular weights of hydrocarbons (Wilson and Wells, 1950; Collin *et al.*, 1995). The composition and properties of a coal tar depend on the temperature of carbonisation and the nature of the coal that has been used as a starting material. The generation temperatures of tar are between 500 and 1 300 °C. An increase in the generation temperature results in a decreased tar yield and a reduced alkyl substitution of the aromatic and phenolic components (Marsh and Rodriguez-Reinoso, 2000). The yield of tars from coal carbonisation at a higher temperature is about 3 to 4 wt %, and pitch represents 50 to 55 wt % of the crude tar (Betts, 1997; Collin, 1995; “Tars and Mineral Oils”, undated). High-temperature tars contain large amounts of polyaromatic compounds, i.e. phenols, cresols, naphthalene, benzene and anthracene, as the main important constituents (Nightingale, 1962; Pierson, 1993). Figure 2.2 outlines the molecular structures of typical components present in different coal tar fractions.

Low-temperature tars are obtained from the carbonisation of coal tar at lower temperatures, i.e. below 700 °C. They are less aromatic than high-temperature tars, containing 40 to 50 wt % of polycyclic aromatic hydrocarbons and giving a pitch yield of 26 to 30 wt % (Betts, 1997; Collin, 1995; “Tars and Mineral Oils”, undated).

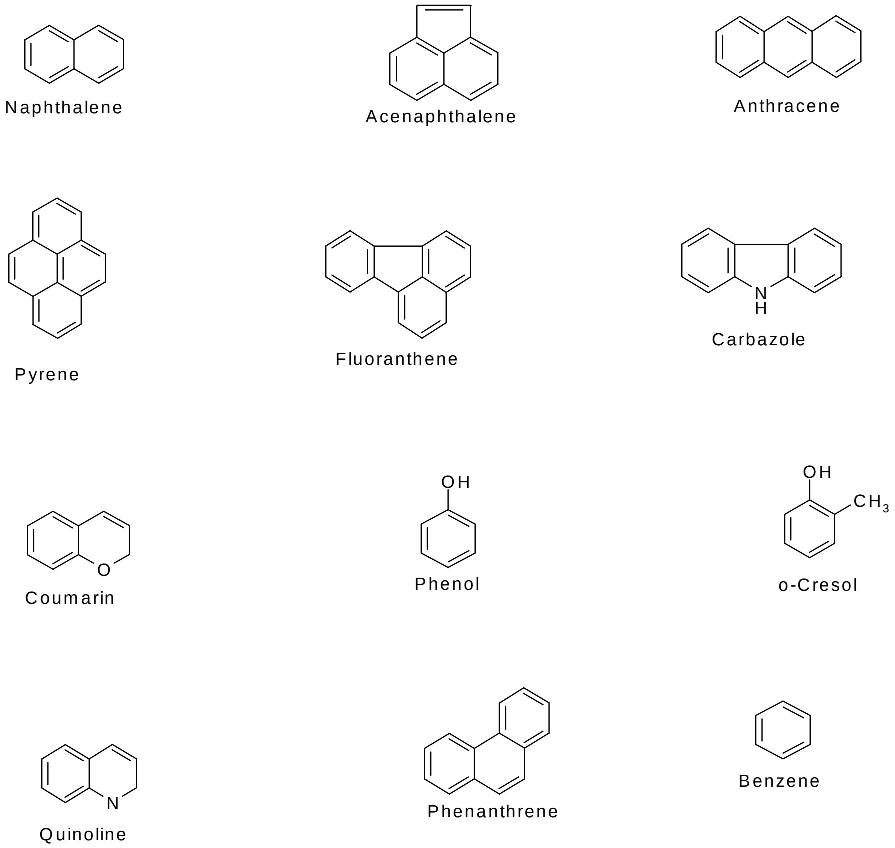

Figure 2.2: Typical components present in different coal tar fractions

2.4 Pitch

Pitch is produced by the thermal treatment or distillation of coal tars in the absence of air. It is a shiny, dark brown residue that follows the removal of the heavy oil (creosote oil) or anthracene oil fractions. Pitches are carbonaceous materials derived from organic precursors by relatively low-temperature processes (Marsh, 1989; Lewis, 1992; Betts, 1997). They give a residue of carbon upon pyrolysis (Collin *et al.*, 1995). Typical distillation data for coal tar pitches are shown in Table 2.1. Pitches are made up of complex mixtures of many individual organic compounds, with different compositions depending on the source tar and the method of removing compounds of low molecular weight (Speight, 1994). They are solid at room temperature but gradually soften with an increase in temperature (Pierson, 1993). Very hard pitches are pulverised and used as a fuel. About two-thirds of the compounds that have been isolated from coal tar pitch are aromatics, the remainder being heterocyclic (McNeil, 1981; Pierson, 1993). Most of the isolated compounds contain two to six aromatic rings (McNeil, 1981; Lewis, 1992). Coal tar pitches contain a large amount of carbon and hydrogen with small amounts of nitrogen, oxygen and sulfur. The aromaticity of coal tar pitch is determined by the ratio of carbon to that of hydrogen (Marsh and Rodriguez-Reinoso, 2000).

Table 2.1: Typical distillation data of coal tars at lower temperatures

Product	Boiling range, °C	Weight, %
Light oil	<195	0.5–1
Naphthalene oil	195–230	10–12
Creosote oil	230–300	6
Anthracene oil	>300	20–30
Pitch	Residue	50–55
Tar acids	-	1

2.5 Petroleum pitch

Petroleum pitch is a thick, dark-coloured bituminous substance obtained from the heavy residue or petroleum fractions during the catalytic cracking process described as ‘distillation’ (Newman, 1975; Pierson, 1993; Marsh, 1989). Like coal tar pitch, it is also solid at room temperature and its composition varies depending on the temperature and the nature of the materials used as a starting material (Pierson, 1993). The distillation of petroleum fractions for longer times at higher temperatures results in more aromatic pitches with higher anisotropic contents.

Note: Anisotropy is when pitches viewed under an optical microscope have different characteristics in different direction.

Petroleum pitches are less aromatic by 10 to 20 wt % and have higher molecular weight distributions than coal tar pitches. Petroleum pitch has a higher content of alkylated and partially hydrogenated polycyclic aromatic hydrocarbons (PAHs), and smaller amounts of heterocyclic compounds containing nitrogen (Newman, 1975; Marsh, 1989).

2.6 Anthracene oil

Anthracene oil (AO) is distilled from coal tar and has a boiling point in the range of 250–370 °C. The distillate consists mainly of non-substituted poly-aromatic hydrocarbons with two to four aromatic rings. The major constituent compounds of anthracene oil are phenathrene, anthracene, fluoranthene and pyrene (Fernandez, Granda, Bermejo and Menendez, 1998). The structural formulae of these compounds are shown in Figure 2.2. Anthracene oil has a relatively low economic value, which can be increased if it is converted to pitch by dehydrogenation. Either thermal or chemical method is used for the process of dehydrogenation of AO (Greinke and Lewis, 1984; Lewis, 1980). The thermal method is achieved by using both sulfur (Fu and Harvey, 1978; Oi, Onishi, Yamada and Honda, 1978; Fernandez *et al.*, 1998) and a novel reagent, hexachlorocyclohexane (HCH), which is discussed in this dissertation. Chemical dehydrogenation can be achieved by using Friedel-Crafts catalysts (Rey Boero and Wargon, 1981; Mochida, Shimizu, Fujiyama, Yozo and Otsuka, 1988), by either blowing air during the reaction (Yamaguchi, Mondori, Matsumoto, Honma, Kumagai and Sanada, 1995; Greinke and Lewis, 1984) or by addition of sulfur at temperatures above 200 °C (Fernandez *et al.*, 1998; Van Krevelen, Goedkop and Palmen, 1959).

2.7 Synthetic pitches from anthracene oil

Previous results on the preparation of synthetic pitches from AO to be used as carbon precursors have been reported. Fernandez and co-workers prepared synthetic pitch from AO using aluminium chloride ($AlCl_3$) as a catalyst (Fernandez *et al.*, 1998). $AlCl_3$ is the most widely used catalyst for polymerising aromatic hydrocarbons present in AO because it promotes non-dehydrogenative processes. This polymerisation process results in oligomers that are rich in naphthenic structures (Mochida, Korai, Ku, Watanbe and Sakai, 2000). After the reaction, $AlCl_3$ was removed by acid washing (i.e. aqueous hydrochloric acid) and then followed by water washing (Bermejo, Menendez, Figueras and Granda, 2001).

Hydrogen fluoride or boron trifluoride (HF/BF_3) have long been recognised as Friedel-Crafts acid catalysts. Mochida and co-workers reported that synthetic pitch can also be produced from aromatic hydrocarbons using HF/BF_3 as a catalyst (Mochida *et al.*, 1988). The treatment of aromatic hydrocarbons with these acids results in protonated compounds, which attack the other aromatic molecules at the position with the greatest basicity to give larger aromatic molecules. HF/BF_3 catalysts can be removed from the pitch by atmospheric distillation because of their lower boiling points and can then be recycled (Mochida *et al.*, 2000).

The results obtained from the polymerisation of aromatic hydrocarbons with HF/BF_3 were very similar to those obtained from treatment with $AlCl_3$. Polymerisation of aromatic hydrocarbons with BF_3 requires larger facilities and higher investment and fabrication costs compared with polymerisation with $AlCl_3$ (Fernandez *et al.*, 1998). As a result, synthetic pitches prepared with $AlCl_3$ have been preferred for use as carbon precursors.

Pitches with a high coking yield may produce porous materials due to the fact that they swell on pyrolysis. The increase in the softening point and coking yield of pitches prepared from AO, to be used as precursors in carbon-carbon composites, can be accomplished by air-blowing treatment, due to its low cost and simple application in this industry (Yamaguchi, Mondori, Matsumoto, Honma, Kumagai and Sanada, 1995; Menendez *et al*., 2002). Barr and Lewis (1978) reported that the oxidation of pitches can be controlled without destroying their coke structures. Fernandez and co-workers (Fernandez, Figueiras, Granda, Bermejo, Parra and Menendez, 1995a; Fernandez, Figueiras, Granda, Bermejo and Menendez, 1995b) found that synthetic pitches can be prepared by heating in the temperature range of 250–300 °C under air flow. High coking yield of the pitches was achieved from this reaction and this suggests that air-blown pitches can be used as precursors for carbon-carbon composites.

Thermal polymerisations of PAHs occur at a temperature of about 500 °C and at high pressures (Lewis, 1980). Russian researchers have obtained needle coke from anthracene oil by thermal treatment at 455 °C and 7 MPa (Cheshko, Pityulin, Pyrin and Shustikov, 1995). Elemental sulfur was the reagent most widely used for the dehydrogenation of PAHs because it extracts hydrogen at temperatures above 200 °C (Fu and Harvey, 1978; Van Krevelen *et al*., 1959). Fernandez *et al.* (1998) reported the polymerisation of AO with sulfur under nitrogen flow at temperatures between 250 and 300 °C. They found that sulfur reacts completely with AO to form pitch-like materials and these pitches have potential application as precursors of anisotropic carbons.

2.8 Hexachlorocyclohexane

A 1,2,3,4,5,6-hexachlorocyclohexane or benzene hexachloride (HCH) mixture of isomers is a musty-smelling crystalline solid, which is produced by reacting benzene with chlorine (Patent

No. GB586439, 1947, 1954); Krauer, Duvall and Alquist, 1947; Matthews, 1891; Daasch, 1947; Grundey and Kraus, 1976). Its molecular formula is $C_6H_6Cl_6$ with the molecular weight of 290.8, and it sublimes at higher temperatures. It is not water-soluble but soluble in organic solvents at higher temperatures (Beck, 1995; Matthews, 1891). 1,2,3,4,5,6-hexachlorocyclohexane was first prepared by Faraday in 1825 (quoted in Matthews, 1891; Daasch, 1947). It was prepared by chlorination of benzene in the presence of a catalyst or chlorination in the presence of light (Dockner, 1988; Beck, 1995).

Chloro-substituted compounds react more rapidly with alkali because of the electron-withdrawing effect, which influences the rate of reaction. Reactions of HCH with PAH yield mainly two PAHs, hydrogen chloride gas and minor amounts of chlorobenzenes (Dockner, 1988; Beck, 1995; Patent No. GB717007, 1954; Patent No. GB717792, 1954). Vacuum residue oil, consisting mainly of PAHs such as phenanthrene and anthracene, serves as a reducing system (Dockner, 1988). Figure 2.3 illustrates the reaction of HCH with PAHs.

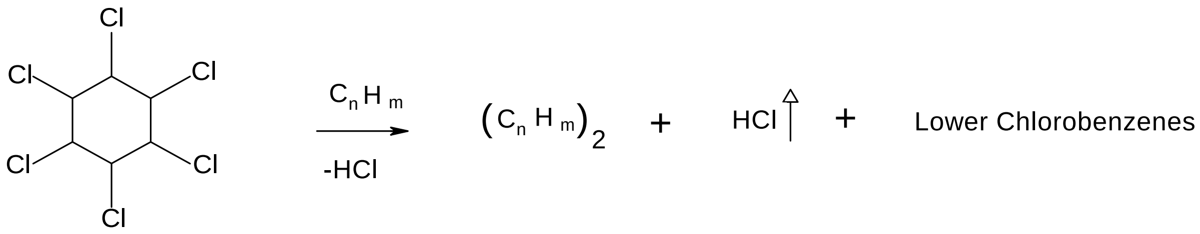

Figure 2.3: Reaction of HCH with PAHs

Industrially, benzene hexachloride has been manufactured and marketed globally as the crude 1,2,3,4,5,6-hexachlorocyclohexane mixture containing 14 % of the γ-HCH isomer. The γ-HCH isomer, also called lindane, is known for its application as an insecticide. It was first separated and purified by solvent extraction and a concentrate with approximately 40 % of lindane was obtained (Slade, 1945; Patent No. GB586439, 1947). The mixed a- and ß-isomers used in the study were the results of extraction.

About 5 to 10 million tons of the residues from the production process of HCH have been dumped all over the world. These residues, which are a major environmental problem, have often been dispersed to the environment by wind, leakage into the ground and thus seepage into surface waters. The HCH industry has attempted to make use of these residues to reduce this environmental problem. In this study, HCH was used as a dehydrogenation agent of anthracene oil for the manufacture of pitch (Vijgen, 2006).

Isomers can be separated from the crude mixture by recrystallisation, solvent extraction or chromatography (Grundey and Kraus, 1976). An attempt was made by Meunier (quoted in Matthews, 1891) to separate the ß-isomers from a mixture of a- and ß-isomers by boiling the mixture in an alcoholic solution. Meunier believed that boiling the mixture would completely decompose the a-isomer, leaving the ß-isomer which could then be recrystallised in alcohol and further purified by sublimation.

Matthews (1891) also attempted to isolate the a- and ß-isomers from each other by steam distillation of the crude HCH mixture. This was done by dissolving the crude mixture in a solvent in which only the a-isomer is volatile. The a-isomer was collected in a Leibig's condenser, leaving the ß-isomer behind. Both isomers were further purified by recrystallisation from alcohol (Slade, 1945).

The ß-isomer was isolated from the crude mixture by refluxing the mixture in xylene and dimethyl sulfoxide, to completely dissolve the a-isomer (Roemer-Maehler, Bieniek and

Korte, 1972). Ionescu and Mager (1970) also attempted to separate the ß-isomer by refluxing the crude isomer in anhydrous pyridine, pyridine hydrogen chloride or pyridine hydrogen bromide in dioxane. The a -isomer was isolated by treating the solution with cyclohexene. None of the aforesaid methods for the separation of the a- and ß-isomers from the crude mixture was successful.

2.9 Characterisation of pitches

Pitch is a complex mixture of many individual organic compounds. It can be characterised according to three different factors (Marsh, 1989; Marsh and Rodriguez-Reinoso, 2000):

i) Physical characterisation by material properties such as softening points, density, coking value and solubility in organic solvents

ii) Chemical characterisation of materials with regard to individual compounds

iii) Description of the materials in terms of structural features, high aromaticity, broad molecular weight and molecular weight distributions.

2.9.1 Physical characterisation of pitches by material properties

Pitches are characterised by physical properties such as the boiling range, density, solubility in different solvents, softening points and the coking yield (Marsh and Rodriguez-Reinoso, 2000; Madshus, 2003). Solvent solubility or fractionation and determination of the softening point are the methods used mostly to determine the physical characteristics of pitches (Zander, 1987a). The most widely used solvents are quinoline, toluene, n-hexane and pyridine. Soxhlet extraction is normally used for dissolving pitches in different solvents. Table 2.2 lists the physical characteristics of pitch (Marsh and Rodriguez-Reinoso, 2000).

Table 2.2: Physical characteristics of pitch

Density, g.cm^{-3}	1.175
Toluene insoluble, wt %	5.50
Quinoline insoluble, wt %	2.0
Distillation range:	
Up to 180 °C: water, wt %	2.5
Light oil, wt %	0.9

The percentages of primary and secondary quinoline insolubles and the toluene insolubles were studied to differentiate pitches based on their empirical formulas (Marsh, 1989). The difference between the toluene insoluble and the quinoline insoluble is called theβ-resin.

2.9.2 Physical properties of commercial pitch grades from Mittal Coke and Chemicals

Table 2.3 lists the properties of commercial pitches available from Mittal Coke and Chemicals. The softening points and coking yields were measured to characterise the physical properties of Mittal Coke and Chemicals' commercial pitch grades. Their softening points range from 45–117.4 °C and their coking yields are between 38.75 and 56 wt %.

Quantitatively, similar softening points are needed as a result of the removal of creosote oils in different quantities for different pitch grades. The ratio of coking value to softening point required for these pitches must be higher than 0.5, with a minimum specific gravity of 1.3. The quinoline-insoluble concentration is within 6–10 % and the matter insoluble (MIT) concentration in toluene is 25–32 %. These properties make the commercial pitches suitable for use as binders.

Table 2.3: Properties of Mittal Coke and Chemicals' commercial pitches

Pitch grade	SP, °C	CY, %
41-46	45.0	38.75
55-59	56.5	44.40
90 Mettler	91.3	45.60
68-73	68.8	47.55
110 Mettler	109.6	53.27
114-118	117.4	56.00

Notes: SP = softening point; CY = coking yield

2.10 The difference between binder and impregnation pitch

Coal tar pitch is used as a commercial impregnant and binder in the preparation of graphite because of its availability in large quantities and its high coking value (Nightingale, 1962). A binder material is used to wet the surface of carbon grains, give mixtures of high plasticity when mixed with the grains, and give a high yield of carbon residue after pyrolysis (Collin *et al.*, 1995; Marsh, 1989). The binders used in the manufacture of carbon graphite blocks are produced from the distillation of coal tar. The principal binding materials that have been used are liquid tars, electrolytic pitch and coal tar pitch with thermoplastic characteristics, solid at room temperature and liquid at higher temperatures (Mantell, 1968; Pierson, 1993). The characteristics of binder pitch (Marsh and Rodriguez-Reinoso, 2000; Nightingale, 1962) are as follows:

i) The viscosity must be high at room temperature.

ii) The softening point must be approximately 100 °C, so that mixing and forming can be accomplished in steam-heated equipment.

iii) It must be thermoplastic, being solid at room temperature and liquid at higher temperatures to allow mixing with the coke filler.

iv) It must have high carbon content: approximately 56 % after pyrolysis is needed for the production of high-density cokes.

v) It must have high specific gravity at room temperature.

The principal use of impregnation pitch is to reduce the porosity and increase the density of coke graphite. Carbon is impregnated with the fluid, which is pitch, and graphitised at higher temperatures. For the pitch to be used as impregnant, it must have the following characteristics (Mantell, 1968; Nightingale, 1962):

i) The aromatic ratio of carbon to hydrogen must be about 1.65.

ii) The specific gravity of this pitch at room temperature must be 1.25.

iii) The viscosity and coking value of impregnation pitch must be very small compared with that of the binder pitch.

iv) Fifteen per cent of an impregnation pitch must be insoluble in benzene.

v) The quinoline-insoluble fraction must be below 5 %.

2.10.1 Rheology of pitch

The rheological properties of pitch play the most important role in the manufacturing process of carbon products. Isotropic pitches are defined as non-graphitisable because they are glass-forming materials. They do not have a definite melting point but pass through a glass transition region on heating, before forming a viscous liquid phase (Marsh and Rodriguez-Reinoso, 2000). The temperature region of great importance in the manufacture of carbon or graphite is that region where the mixing and wetting of coke granules or carbon fibres take place. The flow properties of pitch are affected strongly by temperature and viscosity. Viscosity is used to determine the extrusion and moulding characteristics of pitch coke mixtures. The flow properties of pitch are divided into two types, i.e. non-Newtonian and Newtonian flow (Rand, 1987; Marsh, 1989).

The rheology of an isotropic pitch is different from that of a mesophase pitch, i.e. the flow characteristics of an isotropic pitch at 100 °C above the glass transition temperature is called Newtonian, while that of a mesophase pitch is called non-Newtonian (Marsh 1989; Marsh and Rodriguez-Reinoso, 2000). This is the stage where the variation rate of the shear strain, γ, with the shear stress, τ, is linear, and the viscosity coefficient, $\eta = d\tau/d\gamma$, depends only on the shear stress. A change in the shear rate also changes the molecular composition and the viscosity coefficient of a pitch, i.e. an increase in shear rate causes a decrease in the viscosity coefficient. Therefore the viscosity must be low enough to allow flow into capillaries in infiltration stages (Rand, 1987; Marsh, 1989).

The method most widely used to determine the glass transition state is differential scanning calorimetry (DSC) (Rand, 1987; Marsh, 1989; Marsh and Rodriguez-Reinoso, 2000). Spectroscopic methods such as broad-line proton nuclear magnetic resonance (NMR) techniques are excellent for use in determining the glass transition (T_g) temperature values. The spin lattice relaxation times in the NMR technique and the electron nuclear dipolar interactions are very sensitive to molecular motion. Therefore, the glass transition state increases with an increase in the average molecular weight and molecular structure, and with a decrease in the effect of plasticity (Singer and Lewis, 1984; Rand, 1987).

The rheology of pitch is not characterised by T_g only, but it can also be characterised by determining its softening point. The softening point of the mixture can be determined by several methods, such as the Kraemer-Sarnow (KS), Ring and Ball (R and B), the Mettler (M) and the Cube-in-Air method (Marsh and Rodriguez-Reinoso, 2000).

2.10.2 Chemical characterisation of pitches by individual compounds

Although pitch has an extremely complex chemical composition, its constituents belong to only a few classes of compounds (Zander, 1987b)

- polycyclic aromatic hydrocarbons (PAHs)
- alkylated PAHs
- PAHs with cyclopenteno moieties (acenaphthalenes type)
- partially hydrogenated PAHs
- oligo aryls, oligo aryl methanes
- hetero-substituted PAHs (amino and hydroxy derivatives)
- carbonyl derivatives of PAH
- polycyclic hetero-aromatic compounds (benzologs of pyrrol, furan, thiophene and pyridine).

Pitches are complex mixtures of many individual organic compounds. They are composed mainly of aromatic hydrocarbons and smaller amounts of heterocyclic compounds. The average molecular weight and the molecular weight distribution can be obtained from gel permeation, high-pressure liquid and gas chromatography. The aromaticity and aliphatic character of fractions can be determined by proton and ^{13}C NMR spectroscopy (Karr 1978, Marsh, 1989).

2.11 Analytical techniques used in the structural characterisation of pitches

The standard pitch method, elemental analysis, gas chromatography (GC), gas chromatography–mass spectrometry (GC-MS) and probe mass spectrometry, Maldi-TOF MS, nuclear magnetic resonance (^{1}HNMR), thermal analyses and reflective polarised light microscopy are the analytical methods usually used to obtain statistical structural information about tar and pitch composition. Thermal analyses and mass spectrometry were the main methods used in this study.

2.11.1 Thermogravimetric analyses

Thermogravimetric analysis (TGA) is a technique in which the mass of a substance is measured as a function of temperature while the substance is subjected to a controlled temperature. TGA is used to determine the percentage volatiles (i.e. the coking value and the weight loss of the sample) that are released during the process of pyrolysis as the temperature increases (Wendlandt, 1986). Differential thermal analysis (DTA) is used to measure the difference between the substance and the reference material. Thermal analyses are used for a quantitative and qualitative analysis of the sample mixture in which a ‘thermogram’ is recorded and a single step in the thermogram may be related clearly to one component of the mixture (Fifield and Kealey, 1995). A thermogram is a curve of temperature against weight loss and its derivative curve can also be recorded. The use of thermal analytical techniques applied mainly to pitch has given important information on the behaviour of pitch materials during the pyrolysis process (Wendlandt, 1986).

TGA is made up of a thermo-balance equipped with a sample pan suspended inside a furnace. The heating rate of the furnace can be programmed and a suitable atmosphere can be selected according to the test requirement (Fifield and Kealey, 1995). The temperature programme mostly used for pitch analyses is from 25–1 000 °C at 10 °C/ min and the atmosphere is nitrogen (Fernandez *et al.*, 1995a,b). The residue left after analysis is called the ash content of the sample.

2.11.2 Gas chromatography

Gas chromatography (GC) is a widely used chromatographic technique for qualitative and quantitative analyses of mixtures of components. It is particularly used for the rapid analysis of volatile mixtures containing few or even hundreds of components. A small amount of vaporised sample is fractionated as a result of partition between a mobile gaseous phase and a liquid stationary phase held in a column. The rate of elution of individual components depends on the boiling point, solubility and adsorption. The components of the mixture are eluted according to the increase in the boiling point (Willet, 1987; Fifield and Kealey, 1995; Perry, 1981; Karr, 1978). The instrument is equipped with an injection port, column, detector and recorder. It is also connected to a gas regulator for controlling the flow rates and to an oven for controlling the temperature of the sample (Skoog, West, Holler, Kinsel and Crouch, 2004).

Pitch samples are dissolved in a solvent and the solution is injected directly into the cooled top part of the oven, also called the ‘injection chamber’, which is then heated to volatilise the components of the mixture. A syringe of 1 to 10 µl is fitted with a very fine quartz needle used for injecting the sample (Fifield and Kealey, 1995; Karr, 1978).

For quantitative analysis, the integrated peak area is directly proportional to the amount of solute eluted. In order to determine the ratio of the peak area of the standard to that of the component, a known amount of the standard is added before it is injected into the column (Fifield and Kealey, 1995).

2.11.3 Mass spectrometry

Mass spectrometry (MS) is used to identify the structural characteristics of organic compounds, i.e. the molecular weights and molecular formulae of compounds, according to the manner in which they fragment when bombarded with high-energy electrons (Skoog and West, 1971; Fifield and Kealey, 1995). The data obtained are in spectral form and the relative abundance of mass fragments from a sample is recorded as a series of lines or peaks carrying a charge. The spectra must be recorded under high vacuum to prevent loss of the charged fragments; therefore high-vacuum pumps are used (Fifield and Kealey, 1995). The mass spectrometer is equipped with a sample-inlet system, an ionisation source and an accelerator in which sample molecules are ionised, fragmented and accelerated into an analyser or separator, an ion detector and a recorder (Davis and Freason, 1987). GC-MS and Maldi-TOF MS were also used for the pitch analyses in this study.

2.11.4 Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (NMR) is mostly used to provide structural information such as the aromaticity and the aliphatic groups present in pitches (Yamaguchi *et al.*, 1995; Zander, 1987a; Fischer, Stadelhofer and Zander, 1978). Measurements of the absorption of electromagnetic radiation in the radio-frequency region, roughly between 4 and 900 MHz are made. The analyte is placed in an intense magnetic field in order to develop the energy state required by the nuclei for the absorption to occur.

Proton NMR spectroscopy is used to determine the different types of hydrogen that are present in tar and pitches. Pitches are dissolved in carbon disulphide (CS_2) solutions and then analysed. Proton NMR spectra give a direct measurement of the distribution of protons in different chemical shifts (see Table 2.4), which include hydrogen in olefinic and aliphatic groups α-, β and γ to an aromatic ring (Karr, 1978).

Table 2.4: Assignments of the chemical shifts for proton NMR spectra

Range of signal, δ- ppm	**Assignment and symbol**
6.0–9.5	Aromatic hydrogens (H_{ar}) in mono- and di-aromatic hydrocarbons
0.5–4.5	Aliphatic hydrogen (H_{al})
4.5–3.69	Aliphatic hydrogen in methylene groups α to two aromatic rings (fluorene type)
3.69–3.0	Aliphatic hydrogen in methylene groups α to an aromatic ring and β to another (acenaphthene type)
3.0–2.0	Aliphatic hydrogen in methyl or methylene groups α to an aromatic ring
2.0–1.0	Aliphatic hydrogen in methyl or methylene groups β to an aromatic ring
1.0–0.5	Aliphatic hydrogen in methyl or methylene groups γ to an aromatic ring

2.11.5 Reflective polarised light microscopy

The major application of polarised light microscopy is to examine thin sections of transparent materials. It is capable of yielding accurate quantitative information about the optical properties of the constituents present in the material. It enables the isotropic and anisotropic characteristics of the crystals to be distinguished quickly. Isotropic crystals are cubic in structure at room temperature and non-crystalline. They are defined as isotropic because they have similar properties in all directions. Light vibrates easily through these sections and isotropic pitches have no effect on rays of polarised light that pass through them. The polished cokes are viewed under an optical microscope equipped with a monochromatic light source. When white light is used, anisotropic crystals may appear coloured when viewed between crossed polars and isotropic crystals appear to be black and white (Haynes, 1984).

2.12 Carbonisation chemistry of pitches

2.12.1 Stages of carbonisation

Carbonisation is the conversion of pitch to carbon by polymerisation at higher temperatures in the absence of air (Benn, Edewor and McAuliffe, 1981). During this process, pitches undergo a series of physical and chemical transformations at higher temperatures, resulting in the formation of an infusible hydrocarbon polymer called coke. If the carbonisation temperature is increased, the original organic matter loses its non-carbon elements (Berkowitz, 1979).

Carbonisation is categorised into three stages:

i) the early condensation stage
ii) the mesophase stage
iii) the carbonisation or graphitisation stage.

Early condensation takes place in the temperature range of 150 to 350 °C. This is the stage in which carbon dioxide, water and the volatile components are evolved (Speight, 1994).

The mesophase is the liquid state, formed when pitch is heated to a temperature of 350 to 500 °C to form a large planar aromatic molecule. This is the stage in which devolatilisation and condensation of organic matter take place, resulting in the formation of residual carbon (Barr, Chwastiak, Didchenko, Lewis, Lewis, and Singer, 1976). It is during this stage that softening and the formation of liquid from the original organic matter may accompany the pyrolysis process, which leads to the greater molecular mobility that is necessary for the development of a high degree of ordered graphite (Brooks and Taylor, 1965). A number of changes of stages can be identified during this second carbonisation stage. During heating, some volatiles are removed without altering the wetting characteristics of the pitch, which improves the structure and properties of the resultant carbon material. The development of the mesophase is satisfactorily achieved in pitch fractions, natural bitumen, certain polymers and other simple organic substances (Barr *et al*., 1976; Berkowitz, 1979; McNeil, 1981).

The third carbonisation stage is from 500 to 1 300 °C, leading to the formation of semi-coke. It takes place in the solid state and there is little change in the growth of aromatic ring systems. Methane and hydrogen are the main products from carbonisation at a temperature above 550 °C (Speight, 1994). Carbonisation of pitches at 1 000 °C results in the residual hydrogen being removed with some of the heteroatoms. Dehydrogenative polymerisation and intra-molecular dehydrogenation are the main reaction pathways that polycyclic aromatic compounds undergo at higher temperatures (McNeil, 1981; Berkowitz, 1979).

2.12.2 The reaction-pathway of pitch carbonisation

Carbonisation involves the aromatic growth and polymerisation of small structures of polycyclic aromatic hydrocarbons (PAHs) to form a large aromatic polymer (Bermejo *et al*., 1995). In order to understand the carbonisation of pitches, the reaction-pathways for the model reactions have been studied in detail with pure PAHs to provide information about the reaction pathways that the pitch undergoes at higher temperatures (Mochida *et al*., 2000; Lewis, 1987; Zander and Collin, 1993; Yamaguchi *et al*., 1995). The reaction pathway in Figure 2.4 occurred during the liquid phase thermolysis of PAH at temperatures between 400 and 500 °C (Marsh and Rodriguez-Reinoso, 2000; Madshus, 2003; Schobert, 1990), and is termed ‘aromatic growth’ because it leads to molecular size enlargement of aromatic ring systems (Schobert, 1990).

Dehydrogenative polymerisation occurs in positions 9 and 10 in the anthracene ring (Fig 2.4) and this results in the formation of free radicals. Free radical molecules condense into aromatics with higher molecular weights. They are electrically neutral and highly reactive (Pierson, 1993). A reaction pathway for the dehydrogenation of anthracene is shown in the Figure 2.5. The radical in A is assumed to attack hydrocarbon B to give a dimeric radical C, which loses hydrogen to give a biaryl D.

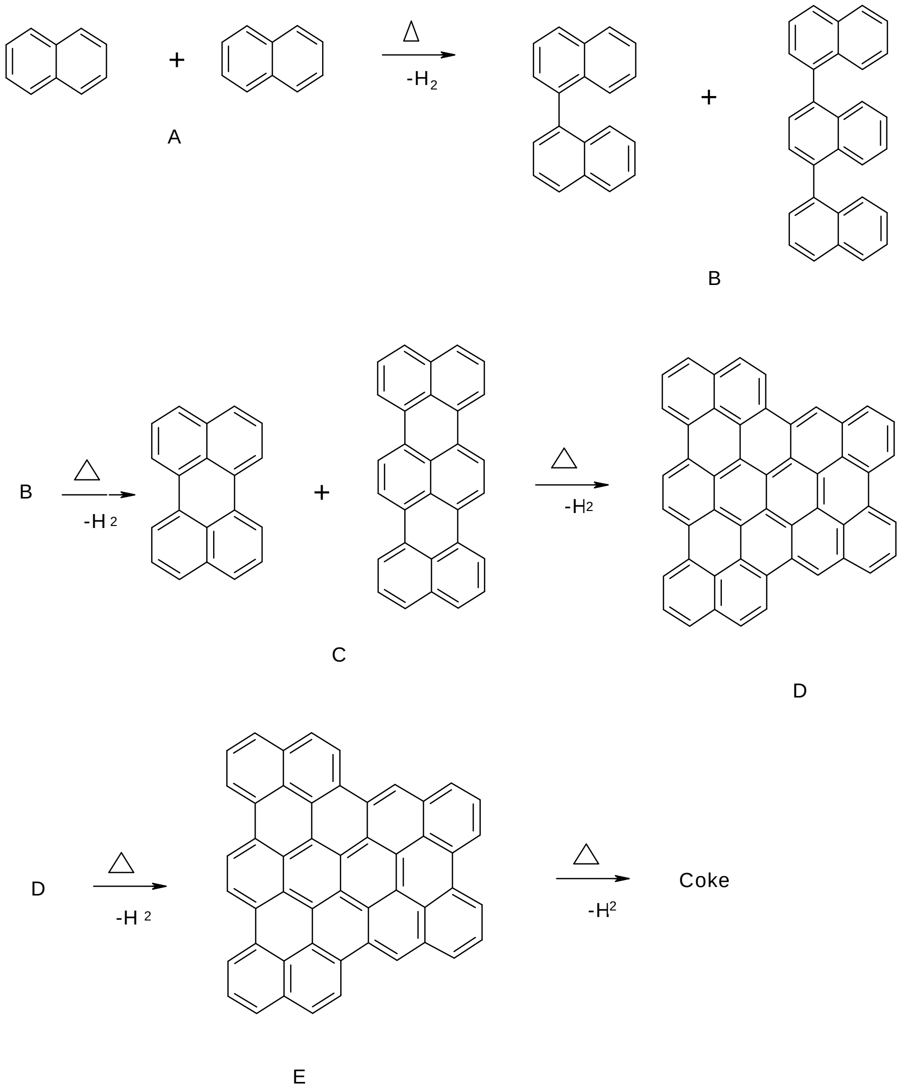

Figure 2.4: The reaction pathway that occurs during pyrolysis of PAH

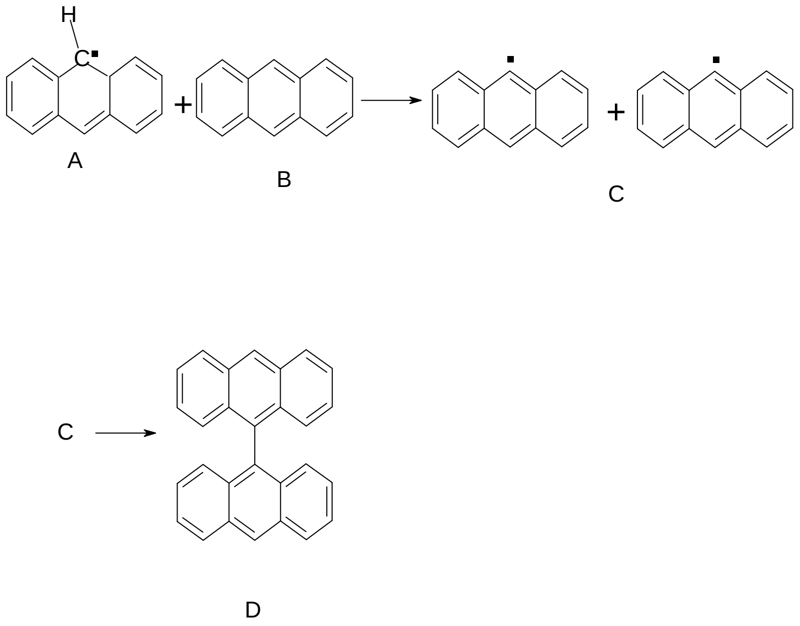

Figure 2.5: A reaction pathway for the dehydrogenation of anthracene

2.13 Applications of tars and pitches

The applications of coal tar are related to those of its distillation product, which is pitch. Coal tar is used primarily for the production of refined chemicals, fertilisers, ammonium salts, nylon, styrene, solvents, saccharine, explosives and resins. Coal tar is also used in open-hearth and blast furnaces as a fuel in the steel industry (Karr, 1978; “Tars and Mineral Oils”, undated). Coal tars can be considered as the source of most poly-aromatic and heterocyclic compounds that are of interest as raw materials in the production of coal tar pitch. Coal tars have been used as substitutes for petroleum fuel oil because they emit a larger amount of flame to promote heat transfer (Marsh and Rodriguez-Reinoso, 2000; Pierson, 1993).

Pitch has been widely used as carbon electrodes in refractories, in fibre pipes, for protective coatings, for roofing, damp-proofing and waterproofing, for road tars for paving, in coal tar fuels for the production of pitch cokes and in coal briquetting (Karr, 1978; Betts, 1997; Marsh and Rodriguez-Reinoso, 2000). In nuclear applications, coal tar pitch is usually used as binders and impregnants for artificial carbon products, such as graphite electrodes for the production of steel in electric furnaces (Peirson, 1993; Delhaes, 2001). It is also used in the preparation of carbon anodes and in Soderberg paste for the aluminium industry (Betts, 1997; Perez, Granda, Santamaria and Menendez, 2004; Fitzer, Kompalik and Yudate, 1987; Turner, 1987).

Pitch is used mainly as a binder for the production of pure graphite to avoid the adsorption of low-energy neutron capture. It can be considered as an ideal precursor for graphite materials because of its availability, low cost, low sulfur content and high carbon content (Queipo, Granda, Santamaria and Menendez, 2004; Mantell, 1968; Pierson, 1993; Criscione, 1992). The binder pitch is characterised by the high carbon to hydrogen content for a specified softening point, the high yield of coke on carbonisation and the high ß-resin content (Collin *et al.*, 1995; Criscione, 1992; Marsh and Rodriguez-Reinoso, 2000). The ratio of carbon to hydrogen is used to determine the quality and the degree of aromaticity of the pitch. Pitches are stable at higher temperatures and their behaviour with respect to fission and fusion electrons makes them suitable as good moderators and reflectors (Pierson, 1993).

The use of pitch as a binder depends on the chemical composition of the parent pitch, which contains the formation of the mesophase during pyrolysis. The mesophase is an intermediate state during the carbonisation of coal tar. It is a nematic liquid crystal stage of highly anisotropic spheres observed under a polarised light microscope (Pierson, 1993; Palmer, Marx and Wright, 1996).

Coke-forming characteristics are widely used to determine the suitability of pitches as binders for carbon electrodes. Coal tar pitches used as a binder, especially for carbon anodes, usually give a yield of over 50 % of the coke residue (Karr, 1978). Graphite electrodes are prepared by mixing a highly graphitisable coke filler with the binder pitch. The mixture is then extruded and graphitised at a temperature of about 3 000 °C (Nightingale, 1962; Turk, 1992).

CHAPTER 3: EXPERIMENTAL PROCEDURES

3.1 Materials

Anthracene oil from Mittal Coke and Chemicals with a boiling point of 220–250 °C and coal tar oil (MCO) with a boiling point of 220 °C were used as raw materials for the preparation of pitches. The chemicals used were: sulfur (chemically pure, powder, LabChem), anthracene (sublimated, 98 wt %, Fluka), phenanthrene (90 wt %, Fluka), fluorene (98 wt %, Aldrich), naphthalene (scintillate grade, Merck), methylnaphthalene (98 wt %, Merck) and the crude sample of mixed isomers (hexachlorocyclohexane) obtained from an encapsulated dump at an industrial site. Hexachlorocyclohexane (HCH) was purified by recrystallisation before it was used.

3.2 Purification of coal tar oil

Coal tar oil (MCO) was distilled at a temperature of 220 °C under reduced pressure. The distillate was collected and used for the preparation and analysis of pitches.

3.3 Purification of pure α- and β-HCH from the HCH mixed isomers

3.3.1 Purification by steam distillation

The crude HCH mixed isomer (20 g, 68.7 mmol) was suspended in 250 ml of distilled water and steam-distilled for 24 hours. Pure α-isomer was carried over azeotropically and crystallised in a Leibig condenser, from which crystals were removed periodically. The β-isomer remained behind in the reactor flask. The separation of the two isomers was monitored by GC analysis.

3.3.2 Purification by sublimation

A mixture of α- and β-isomers (89 % α; 11 % β by GC) (6.0 g, 20.6 mmol) was placed in a small conventional sublimation apparatus. High vacuum was applied and the product was slowly heated to 110 °C. Sublimation started at 80 °C. After 3.5 hours most of the product had sublimed to the cold finger as white, solid crystals, leaving a little residue behind.

3.3.3 Purification using conventional steam distillation

The HCH mixed isomer (40 g, 137.5 mmol) was suspended in distilled water (250 ml) and steam-distilled for 18 hours. The α-isomer was carried over azeotropically and crystallised in the Leibig condenser from which crystals were removed periodically. The resulting water distillate containing white crystals was also recovered and filtered. After filtration, the crystals were recrystallised twice with toluene and washed with a small amount of hexane.

3.3.4 Purification by isomerisation in xylene and dimethyl sulfoxide

An amount of 1.0 g (3.4 mmol) of recrystallised HCH mixed isomer (89 % α, 11 % β by GC) was dissolved in a mixture of 45 ml of dry xylene and 5 ml of dimethyl sulfoxide (DMSO) and then refluxed for 8 hours.

3.3.5 Purification by isomerisation in *N*-methylpyrrolidinone

An amount of 1.0 g (3.4 mmol) of recrystallised waste isomer (89 % α, 11 % β by GC) was dissolved in 50 ml of *N*-methylpyrrolidinone (NMP) and refluxed for 8 hours to obtain the β-isomer. The crystals were collected and analysed. The separation of the two isomers was monitored by GC analysis.

3.3.6 Purification using pyridinium hydrochloride

The crude HCH mixture of isomers (10 g, 34.5 mmol) was dissolved in 20 ml of tetrahydrofuran (THF) and 2 ml of dimethylformamide (DMF). An amount of 0.8 g of pyridinium hydrochloride was also added. The solution mixture was then closed tightly and left for a week. It was then filtered, washed with 4 ml of THF and the crystals were dried under nitrogen. About 0.523 g (1.80 mmol) of the crystals was weighed, washed with water and dried in an oven.

The a-isomer was isolated from the mother liquor. The mother liquor after filtration was evaporated in a rotary evaporator. The crystals were washed with small amounts of distilled water, left for 6 hours and dried at room temperature overnight. The separation of the isomers was monitored by determining the melting point.

3.4 Preparation of pitches

3.4.1 Reaction of distilled coal-tar oil with sulfur

Distilled oil (250 g) was placed in a one-litre reactor flask fitted with a reflux condenser and a thermocouple. The evolved gases were passed through a trap flask with 70 ml of 0.25 M sodium hydroxide (NaOH) to scrub the hydrogen sulphide (H_2S) gas evolved during the reaction. The distilled oil was heated under nitrogen flow, using an electric heating mantle. Figure 3.1 outlines the apparatus used in the preparation of the pitches. Once the reaction had reached the temperature of 250 °C, varying concentrations of sulfur (5–20 wt %) were added and the mixture was allowed to react for 2 hours at 250 °C, after which it was cooled to room temperature under nitrogen flow. The products were analysed by standard pitch methods, elemental analyses, NMR spectroscopy, GC, GC-MS, Maldi–TOF mass and mass probe spectrometry.

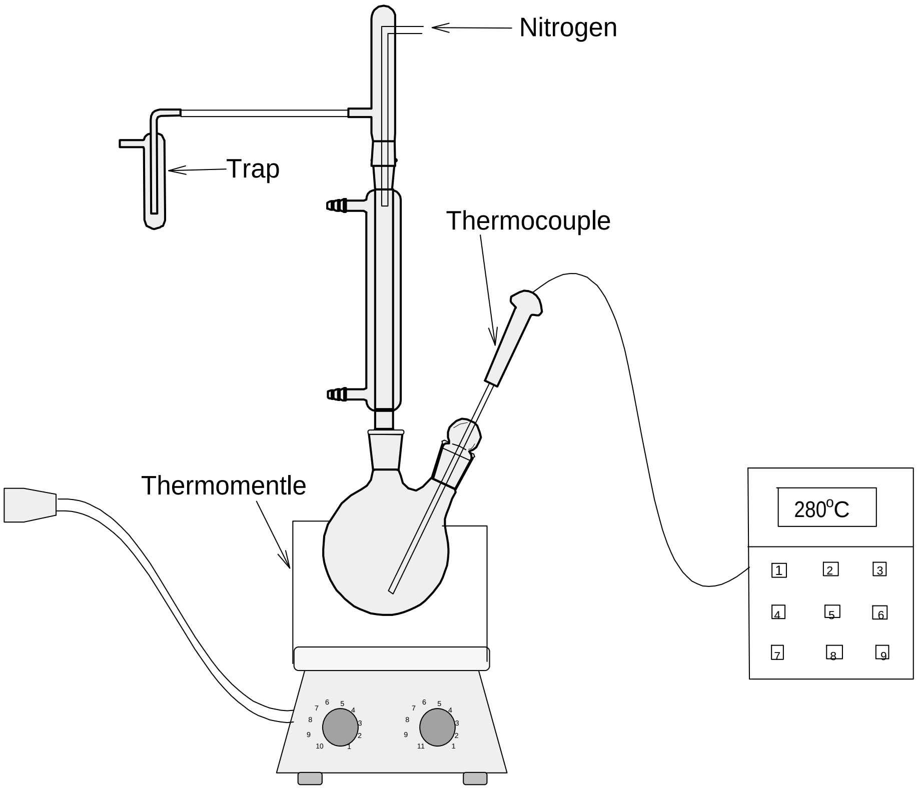

Figure 3.1: Outline of the reaction apparatus

3.4.2 Reaction of anthracene oil with sulfur

Anthracene oil (460 g) was heated with varying amounts (15 to 30 wt %) of sulfur in a two-litre reaction flask fitted with a reflux condenser and a thermocouple as shown in Figure 3.1. The reactions were done under nitrogen. The temperature was maintained for 2 hours at 275 °C. The evolved gases were passed through a trap flask with 3 500 ml of 1.0 N NaOH to scrub the H_2S produced. The H_2S gas evolved during the reaction was measured by iodometric titration of the NaOH solution. At completion, the products were cooled to room temperature and analysed by standard pitch methods, elemental analyses, NMR spectroscopy, GC, GC-MS, Maldi –TOF mass and mass probe spectrometry.

3.4.3 Reaction of anthracene oil with hexachlorocyclohexane mixed isomer

Anthracene oil (350 g) was heated with varying amounts (40 to 900 wt %) of HCH in a two-litre reaction flask fitted with a reflux condenser and a thermocouple. The reactions were done under nitrogen. The temperature was maintained for 2 hours at 275 °C. The off-gases were passed through distilled water (3 500 ml) to scrub the hydrogen chloride (HCl) gas evolved during the reaction. The gas evolved was measured by titration with 1.0 M of NaOH solution. At completion, the products were cooled to room temperature and analysed by standard pitch methods, elemental analyses, proton NMR spectroscopy, GC, GC-MS, Maldi–TOF mass and mass probe spectrometry.

3.4.4 General method for the reaction of pure polycyclic aromatic hydrocarbons with HCH

The pure aromatic hydrocarbons (anthracene, phenanthrene, acenaphthalene and naphthalene) were used. The amount each hydrocarbon will vary depending on the compound used. Each pure hydrocarbon and HCH was placed in a 50 ml glass flask and heated using an electric heating mantle. The flask was fitted with a condenser, a thermocouple and a trap flask containing water (100 ml) to trap any HCl gas evolved during the reaction. The reaction was run under nitrogen flow at 300–340 °C for 5 hours. About 5 ml of the chloride solution was taken out every 5 minutes and titrated with 1.0 M NaOH to measure the amount of chlorine removed from HCH during the reaction. At completion, the reaction products were cooled to room temperature under nitrogen flow, weighed to determine the pitch yield and the products were analysed by Maldi-TOF mass and mass probe spectrometry.

3.4.5 Preparation of pitch from pure anthracene

Pure anthracene (200 mg, 1.1 mmol) was sealed in a thick-walled glass capillary tube and heated to 475 °C in an electric furnace for 2 hours. At completion, the capillary tube was allowed to cool to room temperature and the resulting pitch was used as the reference material for Maldi-TOF mass spectrometry analysis.

3.5 Partial carbonisation of pitch

The pitch products (0.4–0.8 g) were placed in pre-weighed test tubes and carbonised under nitrogen flow. The samples were heated to 600 °C at a flow rate of 5 °C/min in an electric furnace for 3 hours, after which the products were cooled to room temperature under nitrogen flow. The test tubes were removed from the furnace, weighed and the coking value was determined using the following equation:

$$\text{Coking value, \%} = \frac{\text{Mass of residue after heating}}{\text{Mass of original sample}} \times 100 \qquad (1)$$

The pitch cokes were observed under a reflective polarised light microscope after having been mounted on a resin and polished.

3.6 Carbonisation of the pitches

The carbonisation of pitch was carried out in a horizontal tube furnace. The heating rate was constant at 10 °C/min. The reactor tube was made of Pyrex glass, 3.6 cm in diameter and 96.0 cm in length. Pyrolysis was carried out under nitrogen flow. The pitch was heated to a final temperature of 900 °C and maintained at the maximum for 30 minutes. The product was cooled to room temperature and the resulting coke was observed under a reflective polarised light microscope after being mounted on a resin and polished.

3.7 Analyses of the reaction products

3.7.1 Standard method for pitch analyses

The coking value, softening point, quinoline-insoluble, toluene-insoluble and elemental analyses were the methods used to characterise the pitch products. The ash content and specific gravity were also determined by the standard pitch method.

3.7.2 Thermogravimetric analyses (TGA and DTA)

TGA analyses were carried out in a Mettler Toledo TGA/SDTA851 thermal analyser. About 14 mg of sample was placed in an aluminium crucible of 70 μl capacity and heated to 900 °C at a heating rate of 10 °C/min under nitrogen flow of 30 ml/min. The single differential curve was also recorded.

3.7.3 Gas chromatography (GC)

GC analyses were carried out using a Varian-3300 gas chromatograph with a flame ionisation detector (FID). Distilled coal tar oil, anthracene oil and the pitch products were dissolved in toluene and the soluble fractions were analysed by injecting 1 μl into the GC capillary column (SE-30, 25 m in length and 0.3 mm internal diameter) using helium gas a carrier gas. The column’s temperature was programmed from 100 to 300 °C at 5 °C/min and maintained at the maximum for 30 minutes.

3.7.4 Mass probe spectrometry and GC-MS

GC-MS was carried out in a Varian-3300 gas chromatograph equipped with an ion trap detector (ITD). Probe mass spectrometry was performed in a Micromass GCT spectrometer equipped with a time-of-flight (TOF) detector. The samples were dissolved in toluene and the soluble fractions were analysed.

3.7.5 Maldi-TOF mass spectrometry

A Maldi Micromass (Microbe Lynx System ^{TM}) was used in a linear mode with a nitrogen laser (337 nm) and a time-of-flight detector. An amount of 7,7,8,8-tetracyanoquinodimethane (98 wt %, Aldrich) was used as a matrix. The sample for Maldi-TOF MS was prepared by mixing the solution of the matrix compound with that of the analyte. A droplet of the mixture was then dried on the sample target, resulting in a solid deposit of the analyte-doped matrix crystals. The dried sample spot was introduced into the mass spectrometer for laser desorption or ionisation. The amount of the matrix must be larger than that of the analyte to avoid reduction of the matrix signal (Edwards, Jin and Thies, 2003; Skelton, Dubois and Zenobi, 2000).

3.7.6 Proton NMR spectroscopy

The proton NMR of the reaction products and the distilled anthracene oil was determined using a Bruker ARX-300 spectrometer. About 15 mg of the samples was dissolved in deuterated chloroform, $CDCl_3$, and the soluble fractions were analysed at 300 MHz.

3.7.7 Determination of hydrogen sulphide by iodometric titration

Hydrogen sulphide (H_2S) was determined by oxidation with potassium iodate in an alkaline medium. Hydrogen sulphide solution was prepared by bubbling H_2S gas through NaOH solution. Amounts of the sulfide solution (10ml), 0.1 N potassium iodate (15ml) and 10 M sodium hydroxide (10ml) were boiled gently for 10 minutes, cooled and then 5 % potassium iodide solution (5ml) and 4 M sulfuric acid (20ml) were added. The liberated iodine was titrated with standard 0.1 N sodium thiosulphate using sodium starch glycollate as an indicator (Bassett, Denney, Jeffrey and Mendham, 1978).

3.7.8 Sulfur analyses

The sulfur content of the distilled anthracene oil and pitch products was determined directly using a LECO S-144DR elemental analyser. Experiments were carried out with 0.25 g of the sample at a temperature of about 1 350 °C.

3.7.9 Optical texture of coke

The optical texture of the cokes obtained from the carbonisation of pitches in an electric furnace at 600 °C was determined by mounting samples in an epoxy resin, polishing them and examining them under a reflective polarised light microscope. Representative photographs of the polished samples were taken at 50x magnification.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Characterisation of pitches by standard pitch methods

Tables 4.1 and 4.2 give the properties of the pitches prepared from anthracene oil reacted with HCH and sulfur at 275 °C.

Table 4.1: Properties of pitches obtained at 275 °C from anthracene oil reacted with hexachlorocyclohexane (HCH)

HCH , wt %	SP, °C	R_{900}, %	QI, wt %	MIT, wt %	CY, %	Ash, %	SG
40	-	6.86	-	-	-	-	-
80	too soft	9.93	0.07	4.70	12.31	0.05	1.16
120	too soft	14.08	0.11	8.63	15.94	0.16	1.17
160	too soft	16.32	0.16	9.59	17.62	0.17	1.18
200	-	17.56	-	-	-	-	-
250	too soft	15.24	0.91	13.04	18.00	0.28	1.19
300	-	31.17	1.27	25.05	32.58	-	1.41

Notes: HCH = initial concentration of hexachlorocyclohexane; R_{900} = residue at 900 °C (TGA); SP = softening point; QI = quinoline insolubles; MIT = matter-insoluble toluene; CY = coking yield; SG = specific gravity; - = insufficient sample.

Table 4.2: Properties of pitches obtained at 275 °C from anthracene oil reacted with sulfur

S_o, wt %	SP, °C	R_{900}, %	QI, wt %	MIT, wt %	CY, %	Ash, %	SG
15	61.3	27.09	0.09	24.52	28.37	-	too soft
17.5	-	30.99	0.22	24.67	33.59	-	1.241
20	91.4	35.49	2.26	34.67	36.67	-	1.251
22.5	-	37.83	17.36	39.97	41.2	0	1.262
25	144.2	45.22	37.72	44.45	44.8	-	1.278
30	does not melt	52.96	82.43	54.04	51.64	0	too hard

Note: S_o = initial concentration of sulfur.

The properties of the pitches prepared from coal tar oil with sulfur at 250 °C are presented in Table 4.3. The three series of pitches are compared with the Mittal Coke and Chemicals commercial pitches presented in Table 2.3. All the pitches prepared from anthracene oil (AO) with HCH had lower softening points (they are too soft) than those of the commercial pitches, which have softening points ranging from 45 to 117 °C. The sulfur pitches showed undesirable SPs, except those reacted with 15 and 20 wt % of sulfur at 275 °C, which had SPs of 61.3 and 91.4 °C. The pitch with 30 wt % of sulfur was too hard and did not melt at the coking temperatures. The pitch prepared with 25 wt % of sulfur had the highest SP compared with those of the commercial pitches. Therefore, the reaction products of AO reacted with 15 and 20 wt % of sulfur could be suitably used as commercial products.

Table 4.3: Properties of coal tar pitches reacted with sulfur at 250 °C

S_o, wt %	SP, °C	R_{900}, %	QI, wt %	MIT, wt %	CY, %	Ash, %	SG
5	-	8.88	-	-	-	-	-
8	-	14.79	-	-	-	-	-
10	-	17.69	-	-	-	-	-
12	-	20.32	-	-	-	-	-
14	too soft	25.95	0	21.1	26.71	0	too soft
15	too soft	27.74	0.08	22.94	28.13	0	too soft
18	-	29.65	-	-	31.01	0	-
20	-	33.37	-	-	34.95	0	-

The solubility of pitches in toluene and quinoline solvents increases with the increase in the initial concentration of sulfur at 275 °C, whereas the solubility of sulfur pitches prepared at 250 °C is insufficient. The toluene-insoluble content of sulfur pitches at 275 °C is higher than that of HCH pitches. Pitches reacted with 15 and 17.5 wt % of sulfur and 300 wt % of HCH can be used as they have properties similar to those of the Mittal Coke and Chemicals commercial pitch properties, with MIT values between 25 and 32 wt %. The reaction products of AO with HCH and sulfur at 250 °C may have more application as impregnants than as the binders due to their relatively low content of quinoline insolubles.

The SGs for all the sulfur and HCH pitch products are lower than those of the impregnation pitch, namely 1.25–1.30, except for the AO reacted with 17.5–25 wt % of sulfur, which has an SG range from 1.24–1.27. Pitches prepared at 250 °C have insufficient SGs. A low SG is undesirable as it leads to a lower carbon conversion per unit volume during carbonisation. Ash is almost absent from the sulfur pitches and accounts for 0.05–0.28 % in the HCH pitches and sulfur pitches prepared at 250 °C. This makes the pitches suitable as impregnants in the manufacture of graphite.

The coking yields of the sulfur pitches increase with an increase in the sulfur contents. The coking yields (CYs) of sulfur pitches prepared with 22.5–30 wt % of sulfur make them suitable for use as commercial pitches. The CYs of HCH pitches are low compared with those of the commercial pitches, which have CYs from 38.8–56 %. A high CY is desirable so that the pitch does not lose the entire carbon residue upon coking.

Table 4.4 gives the elemental analyses of the reaction products from AO reacted with 15–30 wt % of sulfur at 275 °C and Table 4.5 gives the elemental analyses of coal tar oil reacted with 5–20 wt % of sulfur at 250 °C. Sulfur was totally removed in the form of H_2S gas during the reaction with AO; the results obtained from titration show that 96-97 % of sulfur has reacted with AO. The titration results contradict the elemental analyses of the pitches. The elemental analyses show that the total sulfur content increases as the initial concentration of sulfur increases, and therefore optimisation for the determination of H_2S is required. High sulfur content in the pitch is undesirable because it may cause ‘puffing’, which would result in poor quality of graphite.

Table 4.4: Elemental analyses of the reaction products obtained from anthracene oil reacted with sulfur at 275 °C

S_o, wt %	Carbon, wt %	Hydrogen, wt %	Nitrogen, wt %	Total sulfur, wt %
15.0	84.4	4.08	1.18	6.45
17.5	84.3	4.05	1.35	-
20.0	82.0	3.79	1.21	7.62
22.5	76.1	3.93	1.78	10.5
25.0	82.2	3.77	1.14	11.0
30.0	80.1	3.57	1.07	13.7

Table 4.5: Elemental analyses of the reaction products obtained from coal tar oil reacted with sulfur at 250 °C

S_o, wt %	Carbon, wt %	Hydrogen, wt %	Nitrogen, wt %	Total sulfur, wt %
5.0	84.6	4.26	1.35	-
8.0	85.6	4.16	1.49	6.32
10	83.0	3.92	1.40	-
12	84.9	3.86	1.26	8.19
14	83.9	4.18	1.18	6.99
15	83.5	3.92	1.22	7.82
18	77.9	3.60	1.33	14.0
20	79.8	3.60	1.37	12.7

The results from the elemental analyses show a small difference in the elements detected from the pitches prepared with sulfur at 275 °C and 250 °C. This indicates that the properties of anthracene oil are similar to those of coal tar oil and that temperature has no effect on their properties.

Table 4.6 gives the elemental analyses of anthracene oil pitch products prepared from anthracene oil reacted with hexachlorocyclohexane (HCH). The hydrogen and the total sulfur contents were slightly affected by an increase in the concentration of HCH. There was also a slight change in the nitrogen and carbon contents and this indicates that not all the HCH has reacted with AO to form pitch. This is undesirable because chlorine may cause corrosion of the equipment during the manufacture of graphite.

Table 4.6: Elemental analyses of pitches prepared from anthracene oil reacted with hexachlorocyclohexane at 275°C

HCH, wt %	Carbon, wt%	Hydrogen, wt %	Nitrogen, wt %	Total sulfur, wt %
40	85.3	4.35	2.78	-
80	84.8	4.27	2.67	-
120	85.3	4.39	2.46	0.59
160	85.7	4.39	2.47	0.67
200	85.6	4.44	1.93	0.67
250	87.2	4.15	1.26	-
300	87.2	4.03	1.70	0.69

4.2 Thermal analyses of pitches

Figure 4.1 illustrates the TGA curves of AO at 275 °C under similar conditions. The weight loss of AO begins at 100 °C and finishes at 350 °C. The difference in the weight loss between run 1 and 2 is due to volatility during evaporation of the AO.

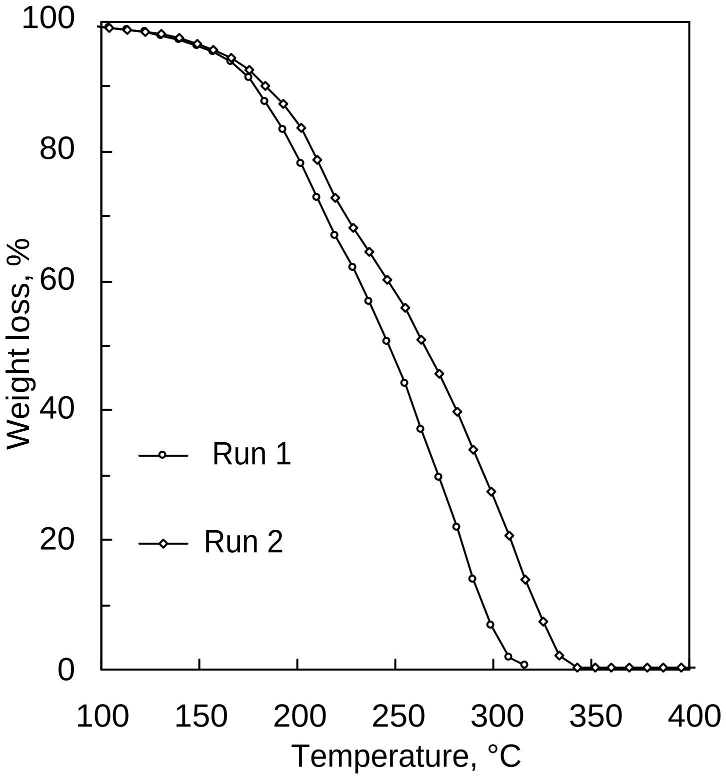

Figure 4.1: TG curves of anthracene oil at 275 °C

Figure 4.2 represents the TG curves of AO and the products from AO reacted with 15–30 wt % of sulfur at 275 °C. The reaction was complete at 600 °C and the decomposition of the pitches, indicated in the differential thermogravimetry (DTG) curves in Figure 4.3, was observed at temperatures between 150 and 450 °C.

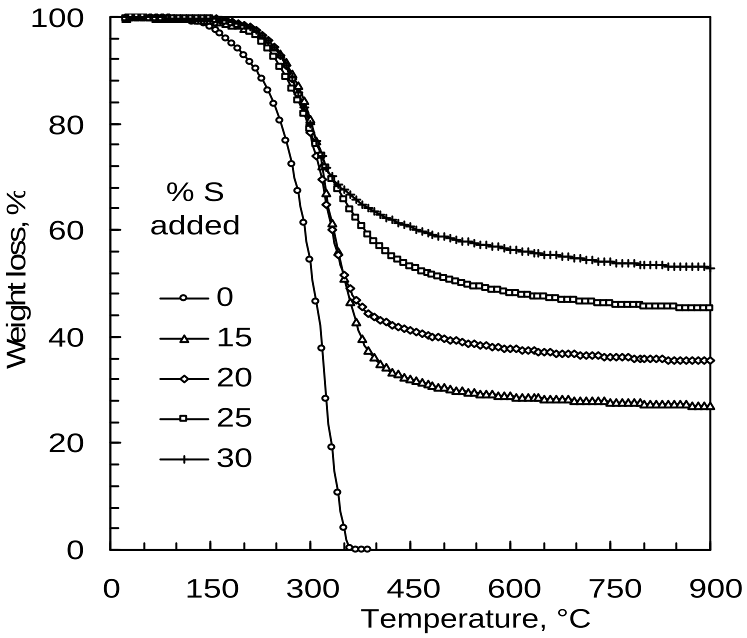

Figure 4.2: TG curves of AO and AO reacted with 15–30 wt % sulfur at 275 °C

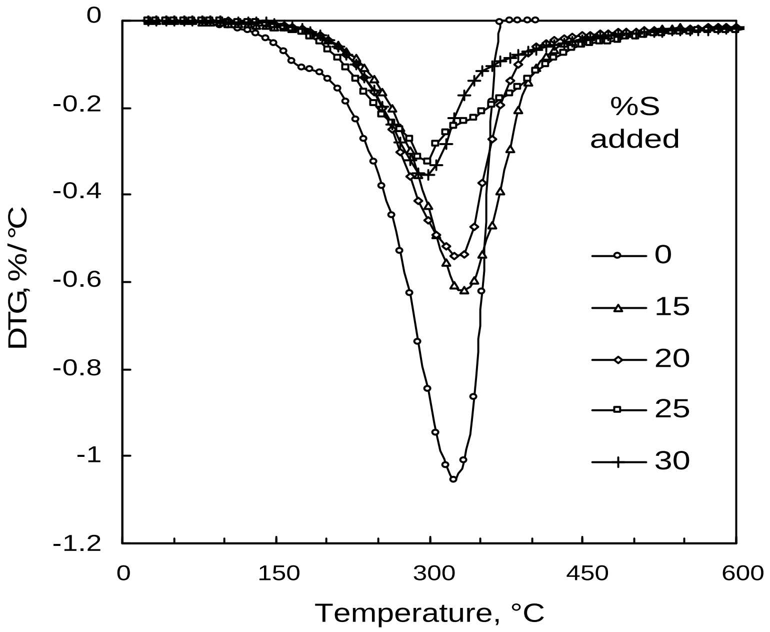

Figure 4.3: DTG curves of AO and AO reacted with 15-30 wt % sulfur at 275 °C

The weight loss of the reaction products is due to the distillation of light compounds and the removal of gases generated by dehydrogenative cross-linking during the process of pyrolysis. Table 4.7 gives the coking values of pitch products prepared with 15–30 wt % of sulfur after carbonisation in an electric furnace at 600 °C. The values obtained for the coking yield from TGA at 900 °C are similar to those obtained from the standard pitch analysis method and from carbonisation in an electric furnace.

Table 4.7: Coking results of AO reacted with 15–30 wt % of sulfur obtained in an electric furnace at 600 °C

$S_{o,}$ wt%	CY, %	Volatiles, %
15	30.4	69.6
17.5	34.5	65.5
20	39.6	60.4
22.5	42.0	58.0
25	49.7	50.3
30	55.9	44.1

Figure 4.4 shows that the coking yields of sulfur pitches increase linearly with the initial concentration of sulfur. The points corresponding to the products of AO reacted with sulfur fit in a straight line (r = 0.9990) with a slope of 1.7651. This shows that AO is incorporated into the pitches and these pitches may have more application in impregnation because of their high coking yields.

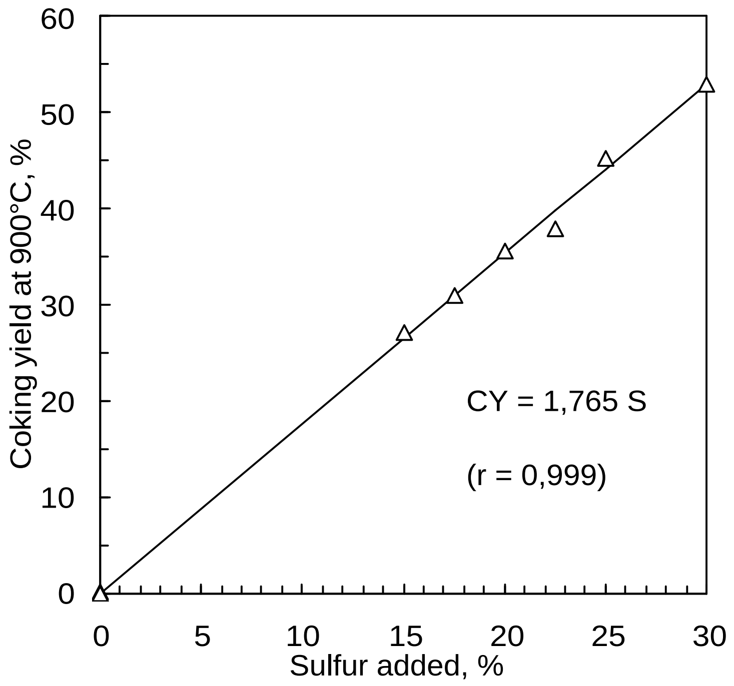

Figure 4.4: Variation of R_{900} of AO with 15-30 wt% sulfur at 275 ° C

The characteristics of pitches derived from coal tar oil reacted with sulfur at 250 °C, shown in Figures 4.5 to 4.7 are similar to those of the reaction products of AO with sulfur at 275 °C. The coking yields also increased as the sulfur concentration was increased. The points corresponding to the pitch products reacted with sulfur fit in a straight line (r = 0.9946) with a slope of 1.73, which differs slightly with the reaction products of AO reacted with sulfur at 275 °C due to the volatility in evaporation of the oils. From this it has been concluded that

AO has characteristics similar to those of coal tar oil. Therefore, the CYs of pitches prepared with 22.5–30 wt % of sulfur show that they can be used as commercial pitches.

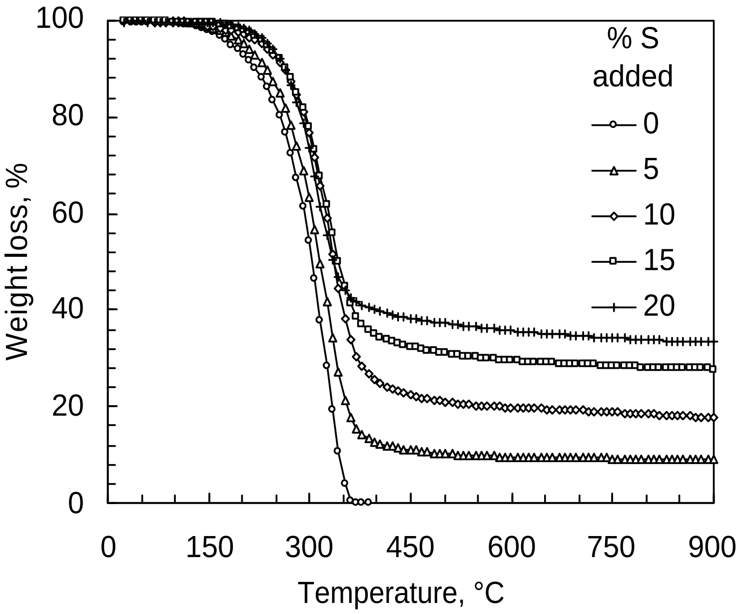

Figure 4.5: TG curves of coal tar and coal tar reacted with 5–20 wt % of sulfur at 250°C

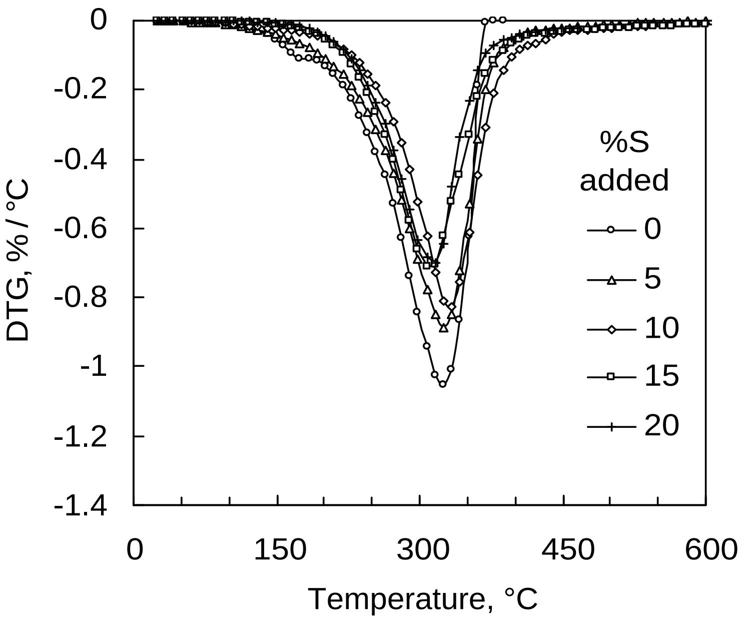

Figure 4.6: DTG curves of coal tar and coal tar reacted with 5–20 wt % of sulfur at 250°C

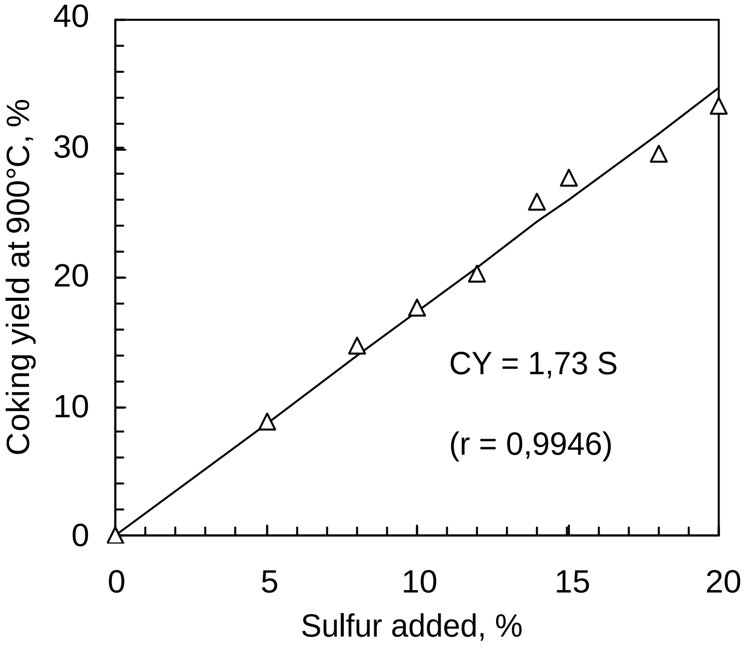

Figure 4.7: Variation of R_{900} of coal tar oil with 5–20 wt% sulfur at 250 °C

Figure 4.8 illustrates the TG curves of AO and AO reacted with 40-900 wt % of HCH at 275 ^{0}C and Figure 4.9 shows the DTG curves.

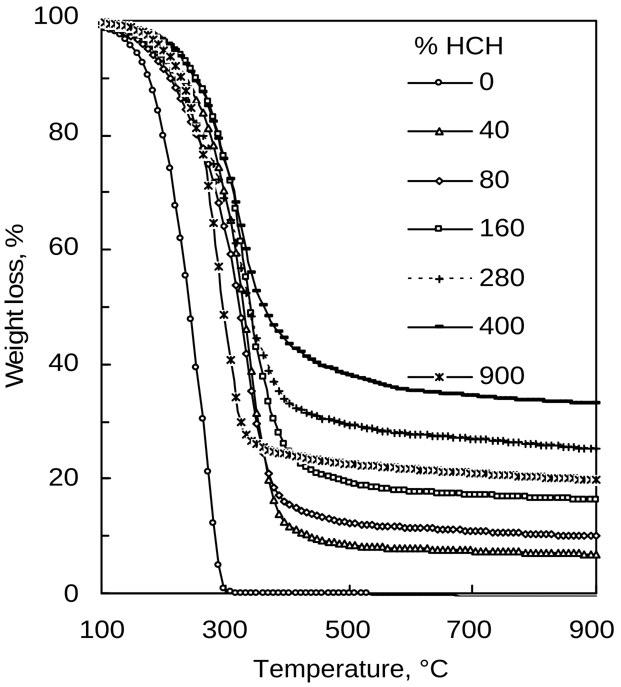

Figure 4.8: TG curves of AO and AO reacted with 40–900 wt % of HCH at 275 °C

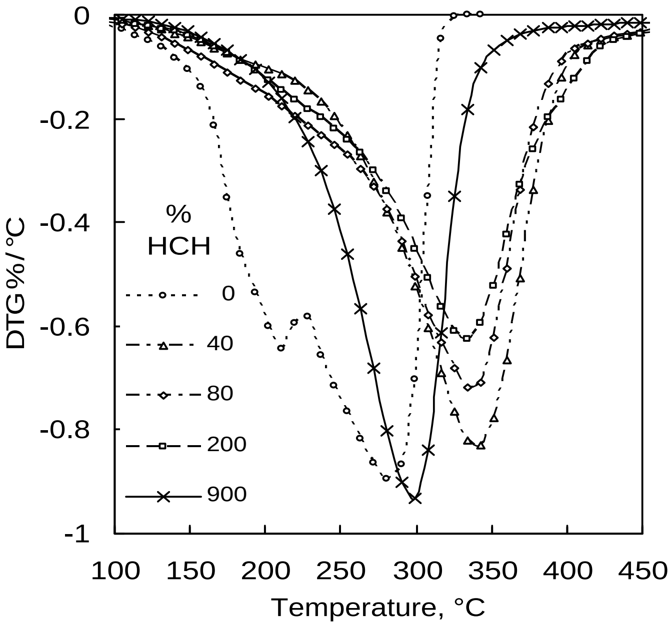

Figure 4.9: DTG curves of AO and AO reacted with 40–900 wt % of HCH at 275 °C

The TG curve of the reaction product of pitch with 900 wt % of HCH does not follow the same trend as the other curves. This may be due to some chlorobenzene volatiles not having been totally removed during the reaction. The DTG curves show that the weight loss of AO occurs in two steps, showing peaks at 210 and 280 °C. The weight loss of HCH pitches occurs within a shorter range as compared with the reaction products of AO reacted with sulfur. The weight loss of AO components at these lower temperatures is due to the distillation of compounds with lower boiling points.

The coking yields of these pitches reach the maximum value at 33 % (Figure 4.10), i.e. the coking yield increased as the concentration of HCH was increased to 80 % (400 wt %) and decreased when 86 % (600 wt %) of HCH was added, which is due to the possibility of HCH chlorobenzene products, such as trichlorobenzene and tetrachlorobenzene, not being totally removed in the reaction products. Chlorine is undesirable because it may cause corrosion of the equipment during coking.

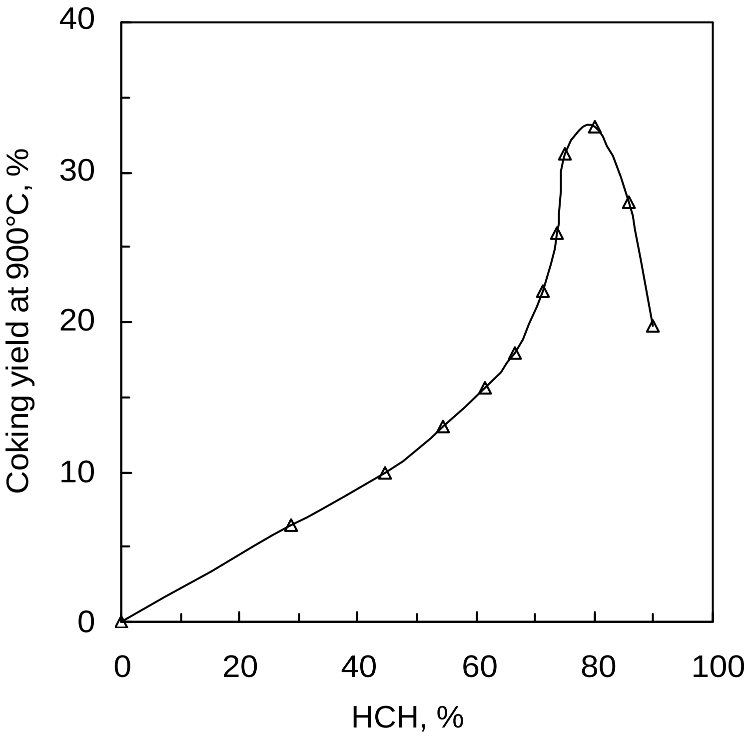

Figure 4.10: Variation of R_{900} of AO oil reacted with 29–90 % HCH at 275 °C

Thermal analyses of the three series of pitches are compared with the Mittal Coke and Chemicals commercial pitches in Figure 4.11.

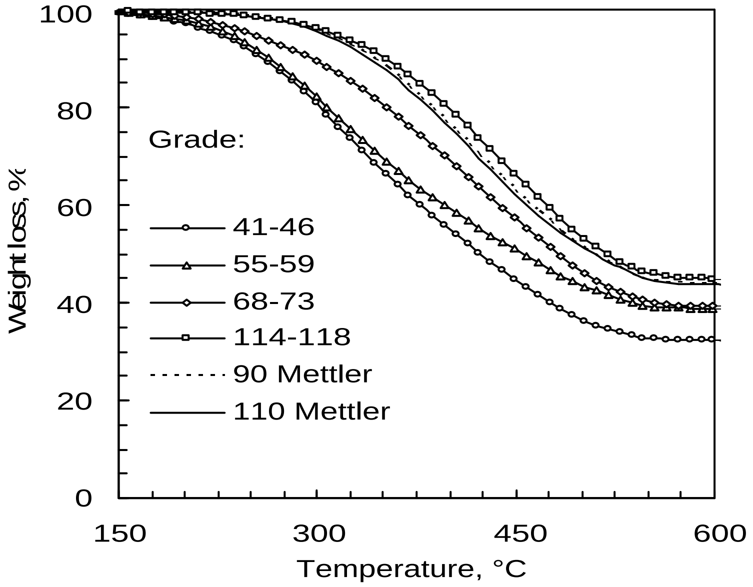

Figure 4.11: TG curves of Mittal Coke and Chemicals' commercial pitches

The weight loss for the reaction products starts at lower temperatures than for the Mittal Coke and Chemicals pitches, which begin at 150 °C and finish at 600 °C (Figure 4.12).

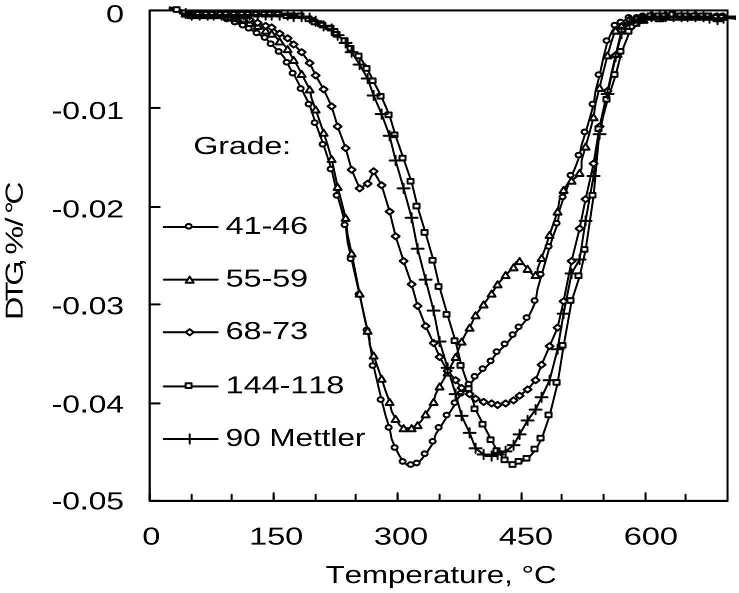

Figure 4.12: DTG curves of Mittal Coke and Chemicals' commercial pitches

The coking yield is lower than 40 % when using 41-46, 55-59, and 68-73 Mettler pitch and above 40 when using 90, 110, and 114-118 Mettler pitch. The coking yield for Mittal Coke and Chemicals pitches is from 31.2–44 % as obtained from the TGA results at 900 °C as illustrated in Figure 4.13.

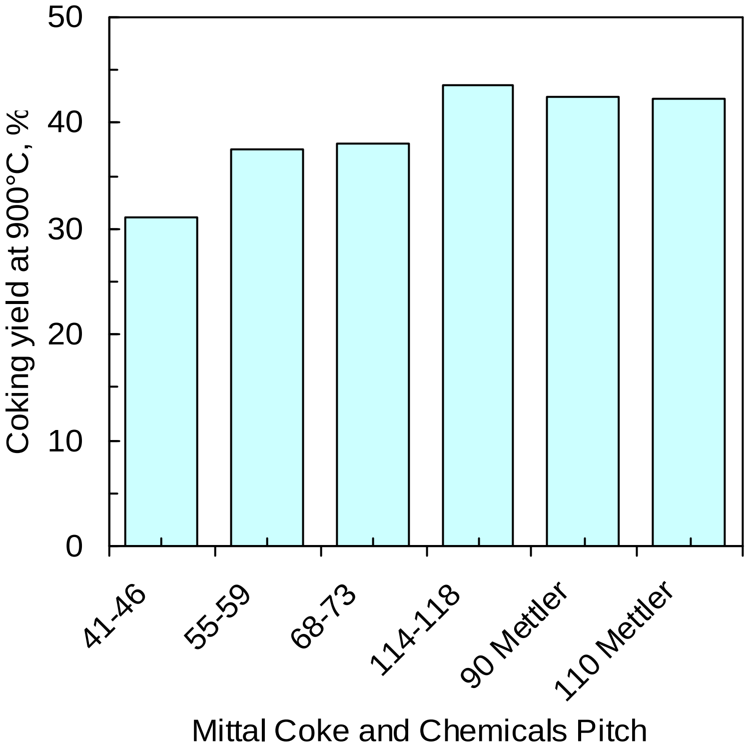

Figure 4.13: Coking yields of Mittal Coke and Chemicals' commercial pitches at 900°C

The TG curves show that the reaction products reacted with 17.5–25 wt % of sulfur and the one reacted with 300–400 wt % of HCH have the desired coking yields as impregnants.

4.3 Analyses of pitches by GC and GC-MS spectra

4.3.1 Analysis of HCH isomers after purification

The result obtained from GC analysis after recrystallisation was that the mixture contained 89 % a- and 11 % ß-isomers. The results of the sublimation and steam distillation of crude HCH also showed a mixture of the two isomers. Purifications of HCH by isomerisation in xylene and DMSO, NMP and pyridine-hydrochloride were also unsuccessful, resulting in a mixture of the a- and ß-isomers. Therefore, the attempts to purify HCH were unsuccessful.

4.3.2 Analysis of the main components of AO

Figure 4.14 shows the gas chromatogram of the toluene-soluble fraction of AO to characterise the more volatile and less polar components of AO.

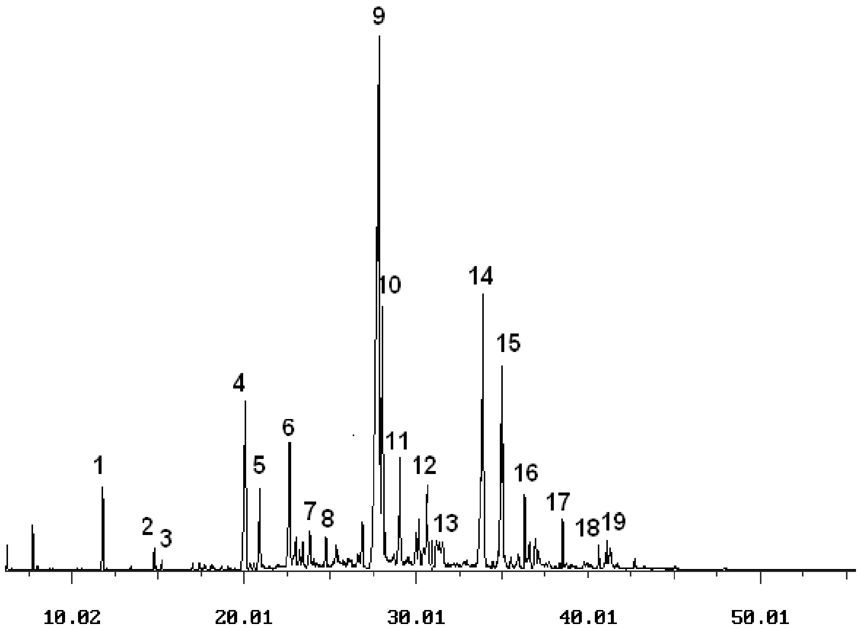

Figure 4.14: Gas chromatogram of the toluene-soluble fraction of AO

Figure 4.15 gives the gas chromatograms of the toluene-soluble fractions of the reaction products of AO reacted with sulfur. This method did not allow direct comparison of the conversion percentages of AO because of inconsistency in the retention times. The elution times of PAH were inconsistent for different samples and therefore the chromatograms could not be used to detect the concentration of smaller molecules.

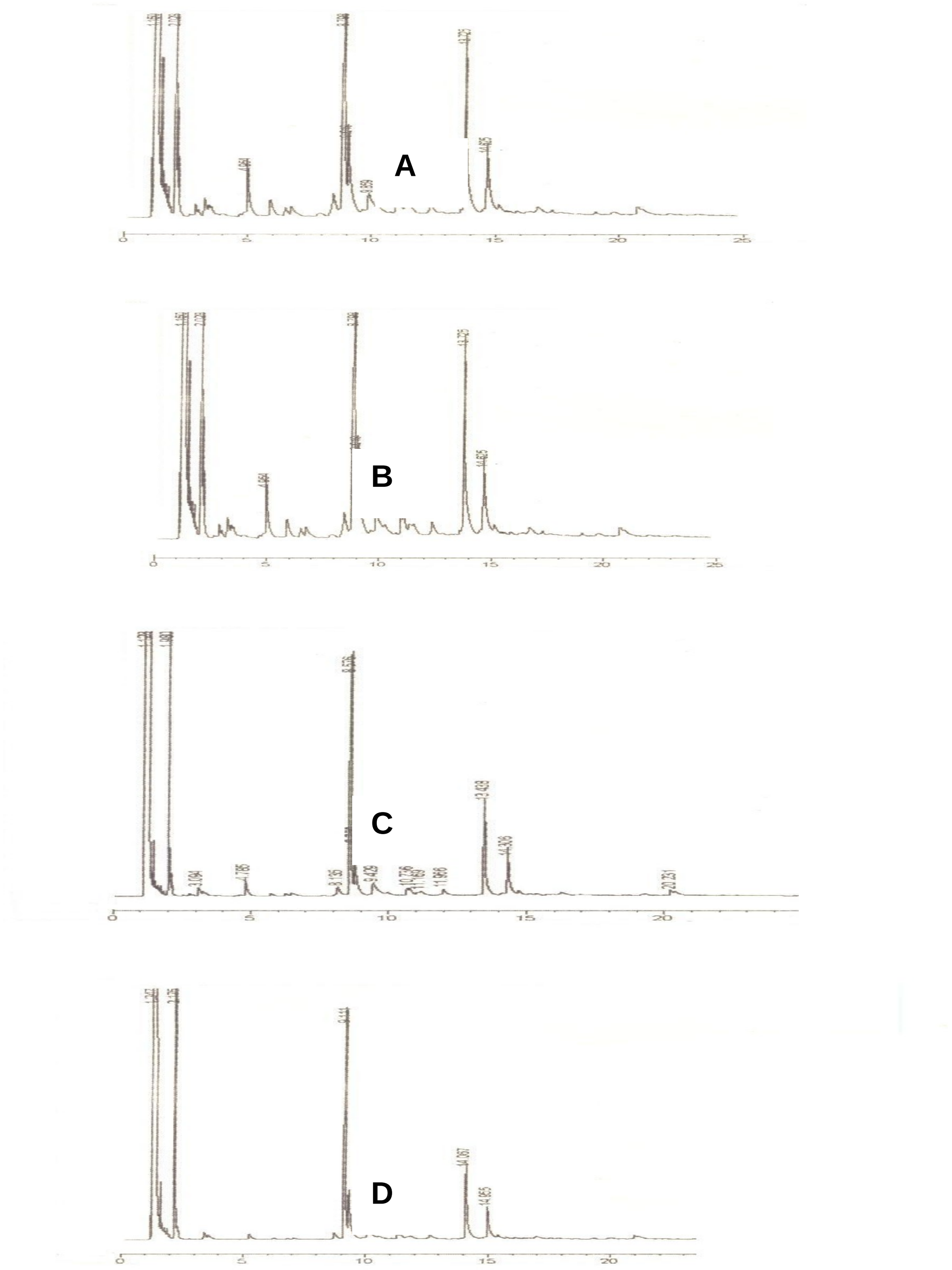

Figure 4.15: FID gas chromatograms of the toluene-soluble fraction of (A) anthracene oil and anthracene oil reacted with (B) 15, (C) 17.5 and (D) 20 wt % of sulfur

The PAH components detected by GC of the toluene-soluble fractions of anthracene oil are assigned by GC-MS as presented in Table 4.8. These components were identified using their MS fragmentation patterns, compared with a library, and the methyl-substituted positions were not known.

Table 4.8: Components detected in anthracene oil by GC-MS

Peak number	Compound name	Molecular mass
1	Naphthalene	128
2	Methyl-naphthalene	142
3	Methyl-naphthalene	142
4	Acenaphthene	154
5	Dimethyl-naphthalene	156
6	Fluorene/Phenalene	166
7	Diphenyl-methane	168
8	Methyl-fluorene	180
9	Phenanthrene	178
10	Anthracene	178
11	Carbazole	167
12	Methyl-phenanthrene	192
13	Methyl-anthracene	192
14	Fluoranthene	202
15	Pyrene	202
16	Methyl-pyrene	216
17	Methyl-pyrene	216
18	Benzoanthracene	228
19	Naphthacene	228

Naphthalene was detected as the first peak in the AO chromatogram. The components detected from the reaction products indicate that the aliphatic groups attached to the aromatics completely reacted with sulfur (methyl-naphthalene, acenaphthalene, phenalene, methyl-phenanthrene, methyl-anthracene and methyl-pyrene), followed by carbazole. The least reactive components are phenanthrene, anthracene, fluoranthene and pyrene. Phenanthrene appeared to be the most intense peak after the addition of a high concentration of sulfur.

Figure 4.16 shows the gas chromatogram of the pitch obtained from AO reacted with 80 wt % of HCH. The components detected by GC-MS are similar to those of sulfur pitches, but with traces of chlorobenzene, trichlorobenzene and tetrachlorobenzene. When AO was reacted with a high concentration of HCH, trichlorobenzene was observed (Figures 4.17 and 4.18). Dichlorobenzene was not detected in any of the HCH pitches. The incorporation of chlorine into the pitches is undesirable because chlorine may cause corrosion of the equipment during coking.

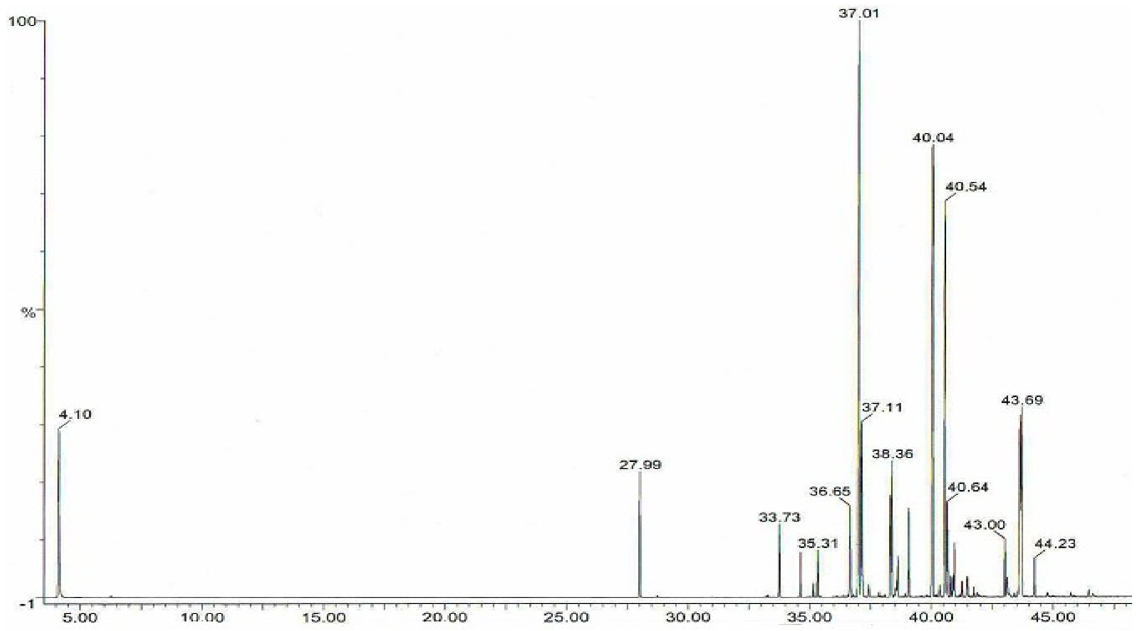

Figure 4.16: Gas chromatogram of the toluene-soluble fraction of pitch obtained from AO reacted with 80 wt % of HCH

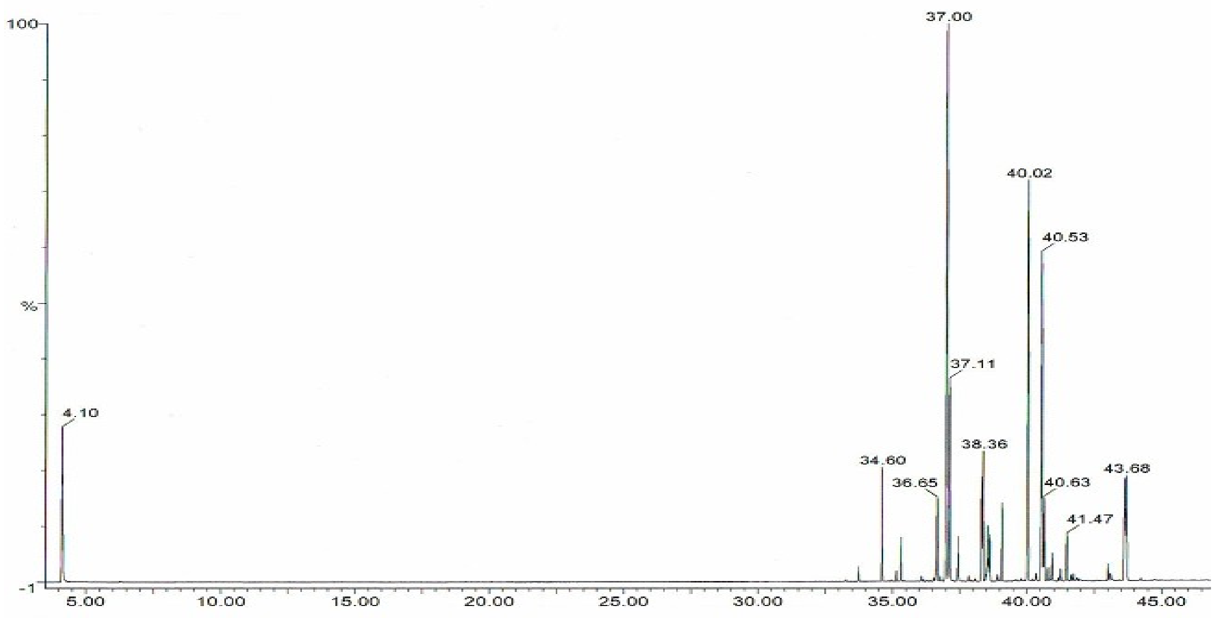

Figure 4.17: ITD gas chromatogram of the toluene-soluble fraction of pitch obtained from AO reacted with 250 wt % of HCH

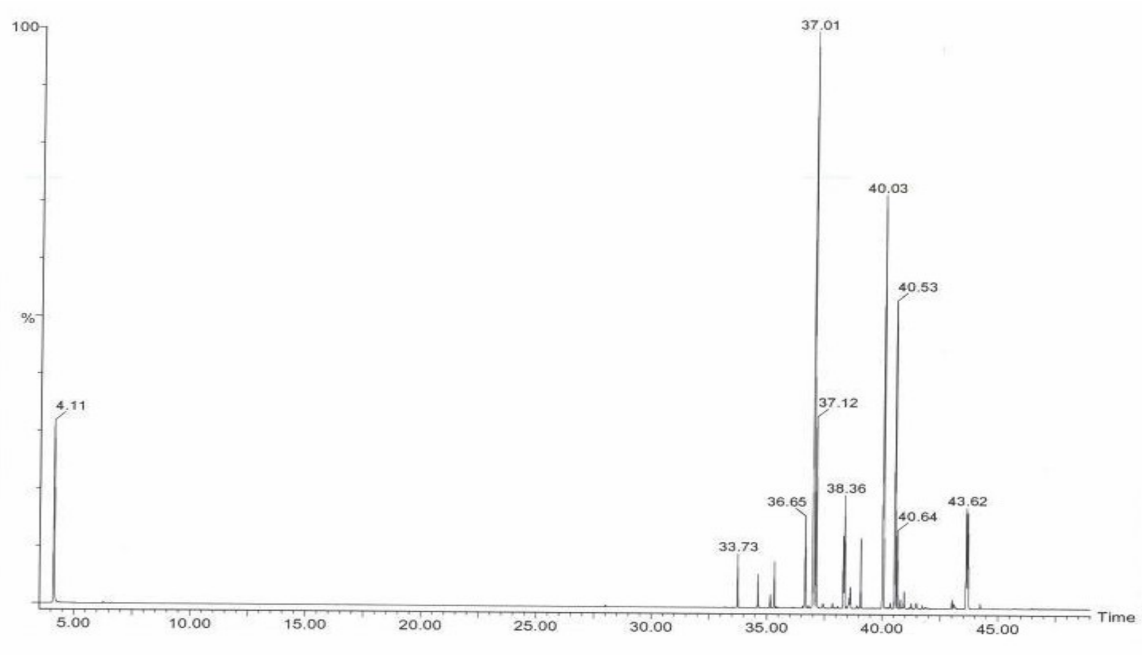

Figure 4.18: ITD gas chromatogram of the toluene-soluble fraction of pitch obtained from AO reacted with 300 wt % of HCH

4.4 Analyses of pitches by Maldi-TOF and mass probe spectra

The Maldi-TOF mass spectra of AO and the pitch products from AO reacted with 20 wt % of sulfur acquired using tetracyanoquinodimethane as a matrix are presented in Figures 4.19 and 4.20. The dimer of anthracene is visible in the Maldi spectrum of AO with the peak at m/e = 352.

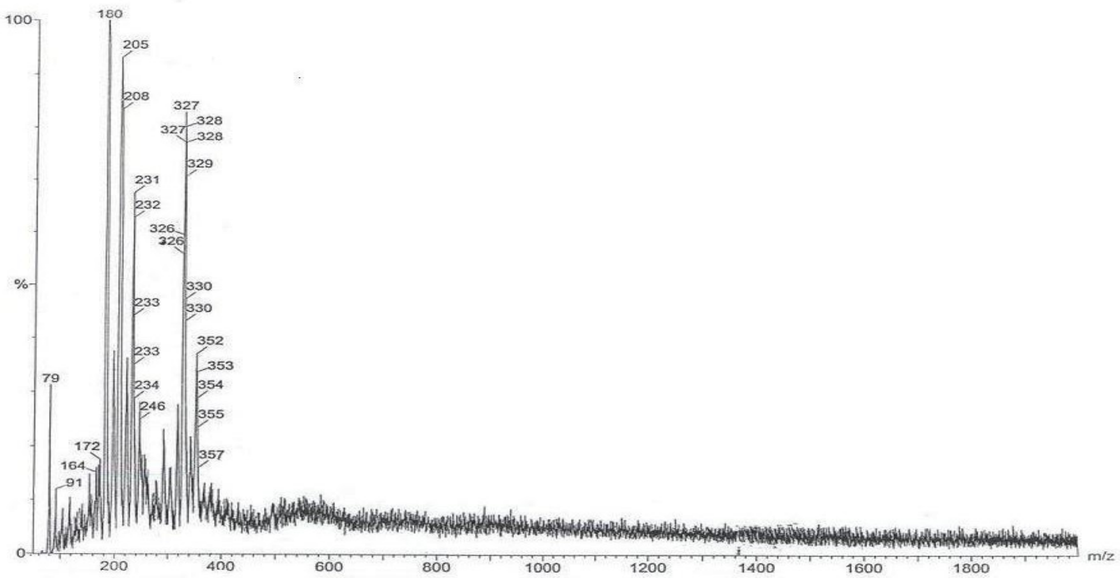

Figure 4.19: Maldi-TOF mass spectrum of AO at 275 °C

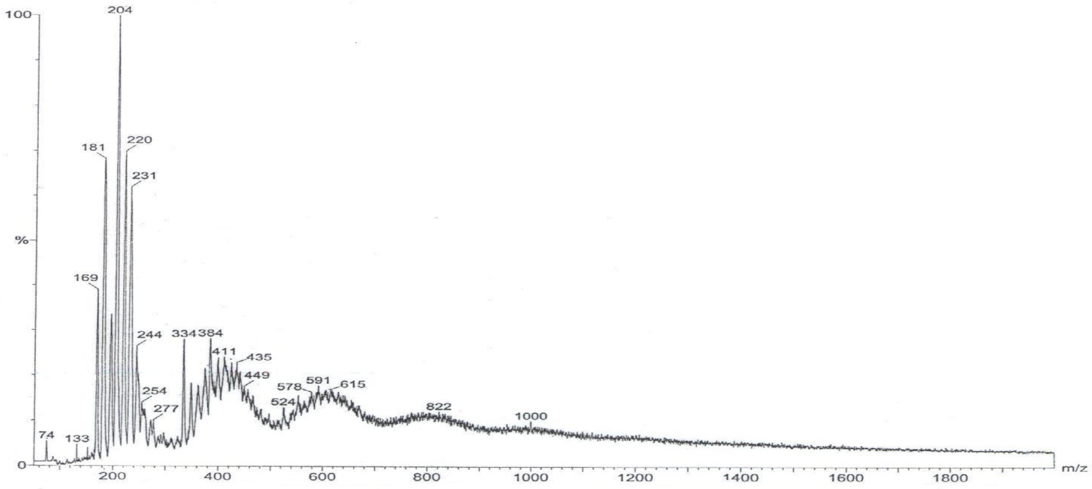

Figure 4.20: Maldi-TOF mass spectrum of AO reacted with 20 wt % of sulfur at 275°C

Pitch obtained from the coking of pure anthracene at 600 °C was used to study the reaction that the pitches prepared with various concentrations of sulfur undergo at high temperatures (Figure 4.21). The mass of anthracene was observed as m/e = 180. This indicates that anthracene has reacted with some elements during coking. Anthracene was considered as a monomer because the molecular weight of the pitch products is centred around it. The results obtained from the sulfur pitches display peaks corresponding to the monomer, dimer, trimer, tetramer and pentamer of anthracene.

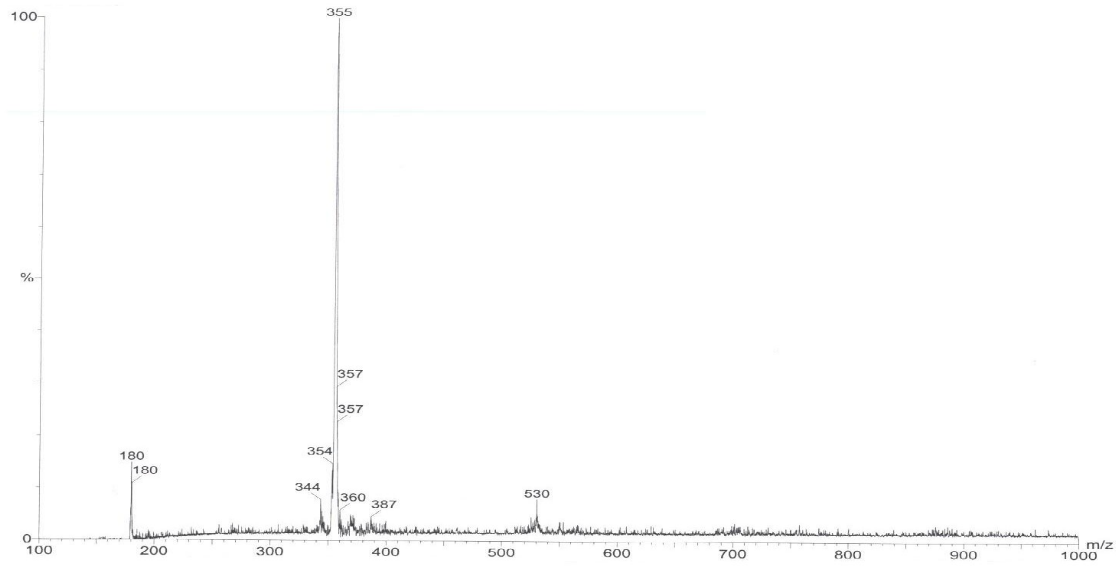

Figure 4.21: Maldi-TOF mass spectrum of pitch derived from pure anthracene reacted at 600 °C

Figure 4.22 summarises the plausible reaction pathway of anthracene reacted with sulfur at 275 °C. The results indicated that AO undergoes dehydrogenation when reacted with sulfur and that hydrogen is removed in the form of H_2S gas.

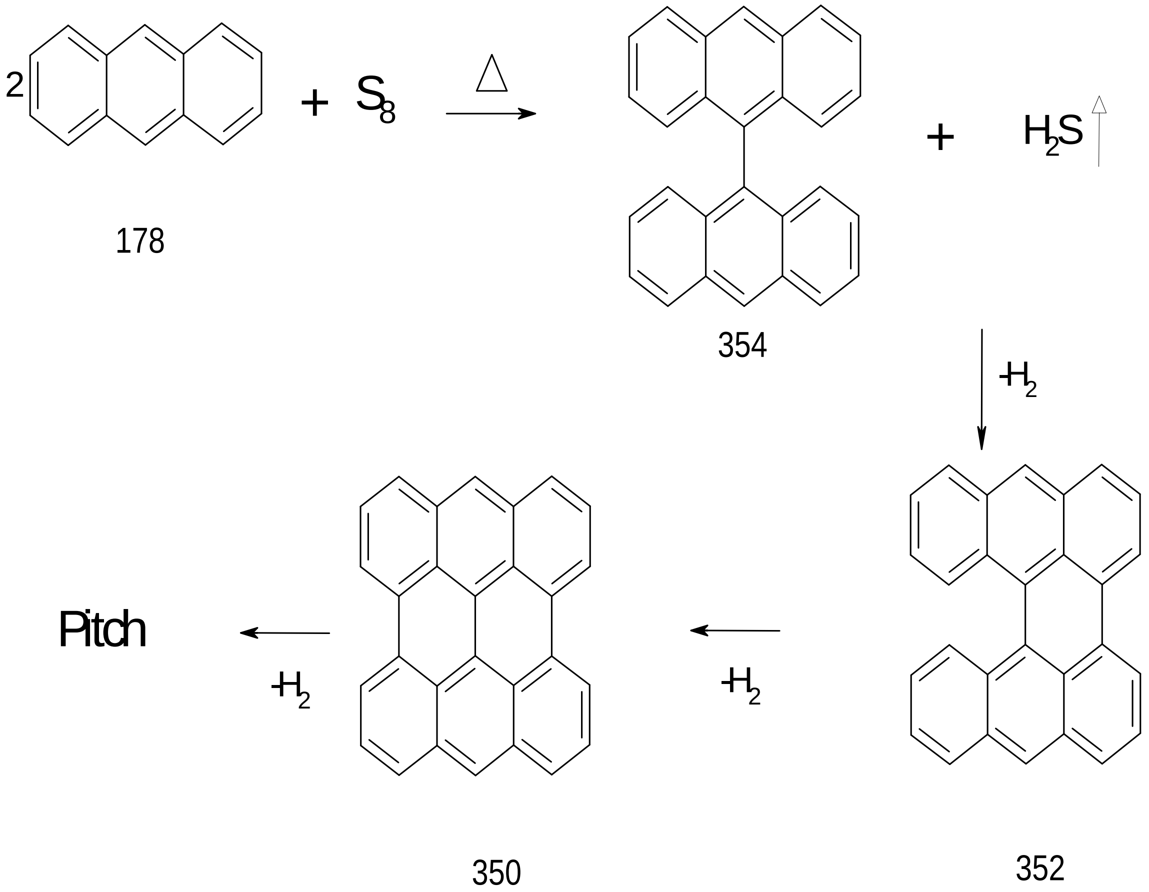

Figure 4.22: The simplistic reaction pathway of anthracene with sulfur at 275 °C

The Maldi-TOF results for HCH pitches display peaks corresponding to the monomer, dimer and trimer of anthracene, assigned as follows: m/e = 180, 347 and 560 (Figure 4.23) and these results are confirmed by the mass probe spectrum.

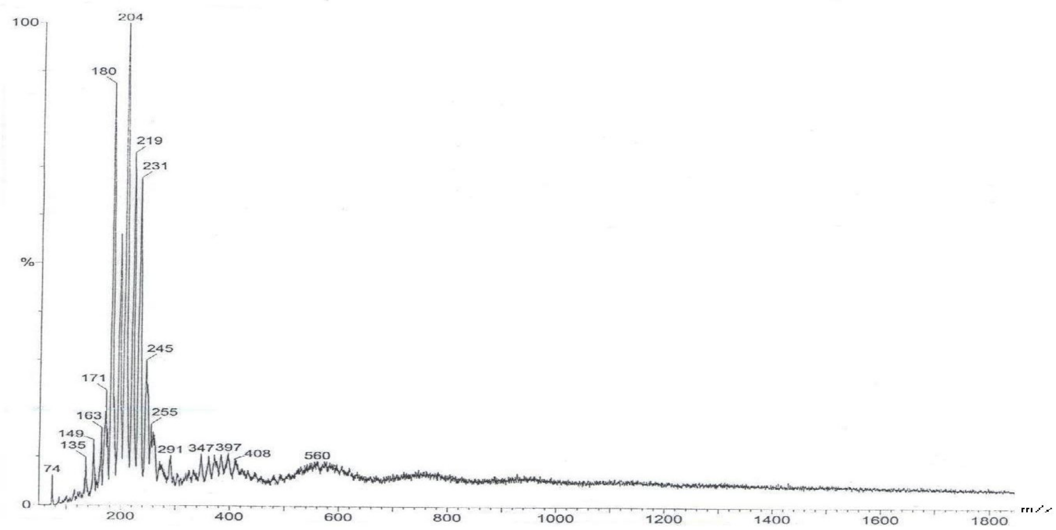

Figure 4.23: Maldi-TOF mass spectrum of anthracene oil reacted with HCH at 275 °C

Figure 4.24 shows the AutoSpecETOF mass spectrum of the reaction product of anthracene with HCH.

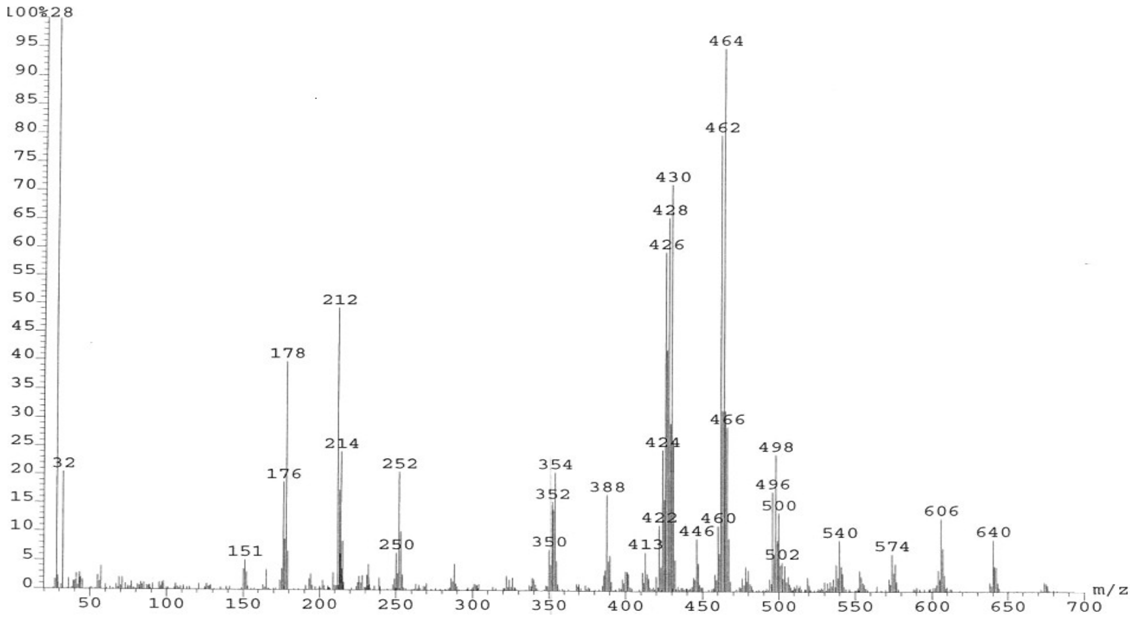

Figure 4.24: Mass probe spectrum of anthracene reacted with crude HCH at 275 °C

The mass spectra detected with the TOF-MS and AutoSpecETOF-MS were compared and the latter was used because it can detect samples at higher molecular weights.

To compare the information about the reactions of AO reacted with HCH; the reactions of pure anthracene and pure phenanthrene were studied separately. The highly aromatic nature of the compounds means that mainly molecular ions are formed, with very little fragmentation. When pure anthracene was reacted with the crude HCH at 275 °C for 2 hours, the mass spectrum was characterised by the following molecular ions: m/e = 151, 178, 212, 214, 252, 288, 322, 354, 424, 430, 498, 540, 574, 606 and 640 (Figure 4.24). Figure 4.25 give the mass spectrum of anthracene reacted with recrystallised HCH, in which prominent peaks similar to those of anthracene reacted with crude HCH were detected. Plausible structures from the reaction products of anthracene with crude and recrystallised HCH are presented in Figure 4.26. Not all the chlorine was removed as HCl gas, some of it reacted with the anthracene molecule to form chlorobenzenes and chloro-hydrocarbons. Chlorine is undesirable in pitches because it causes corrosion of the equipment in the manufacture of graphite.

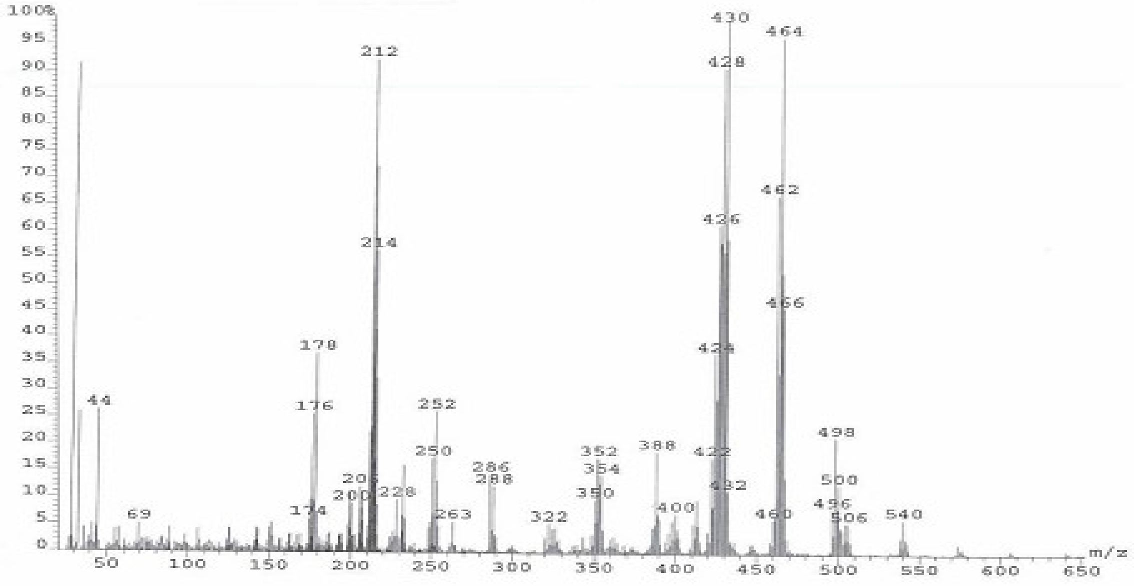

Figure 4.25: Mass probe spectrum of anthracene reacted with recrystallised HCH at 275 °C

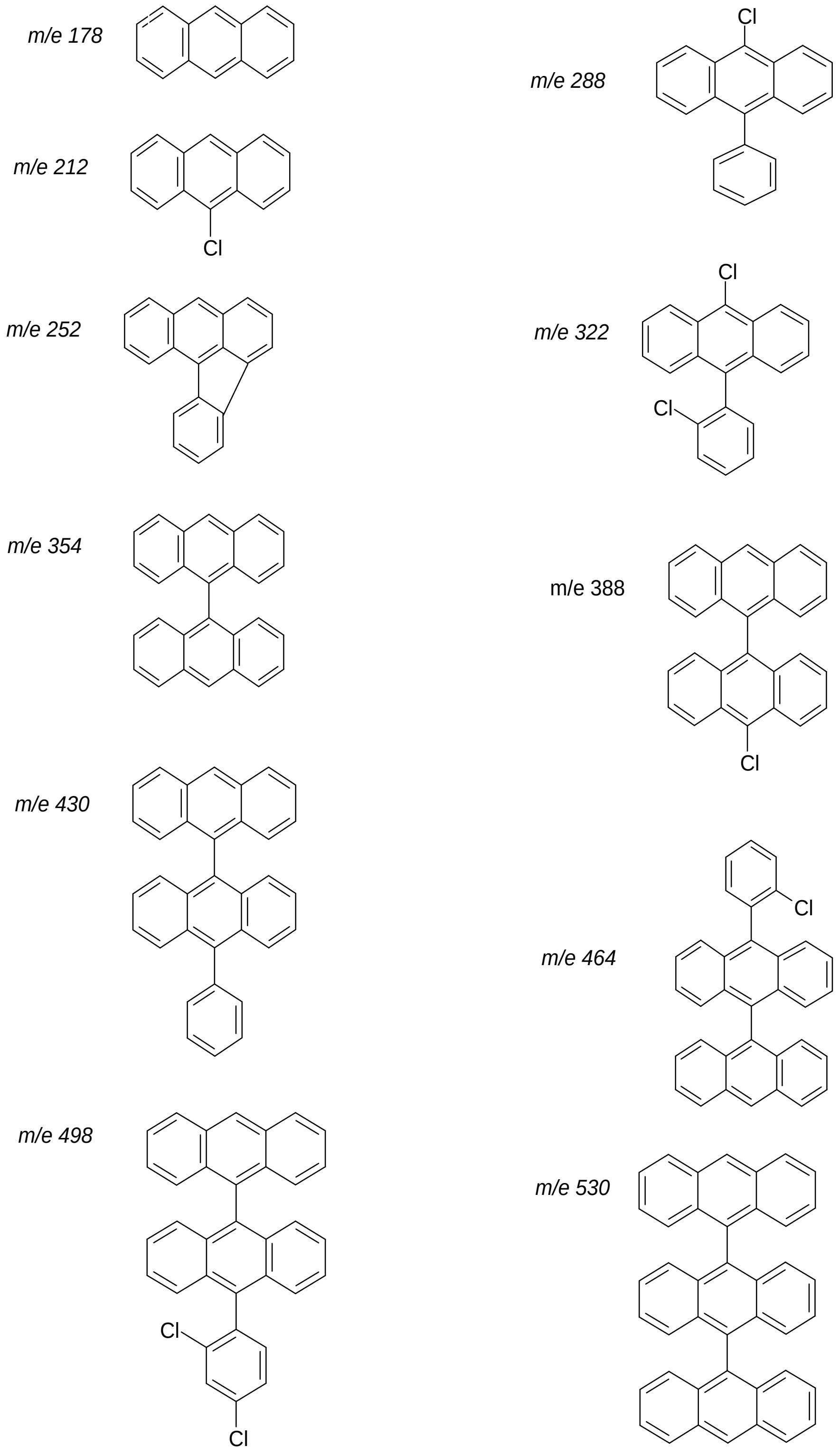

Figure 4.26: Plausible structures from reaction products of pure anthracene reacted with HCH

Note: The substitution positions of the compounds were speculated.

The mass spectrum for the reaction product of phenanthrene with HCH is similar to that for anthracene (Figure 4.27). The plausible structures from the reaction products are presented in Figure 4.28.

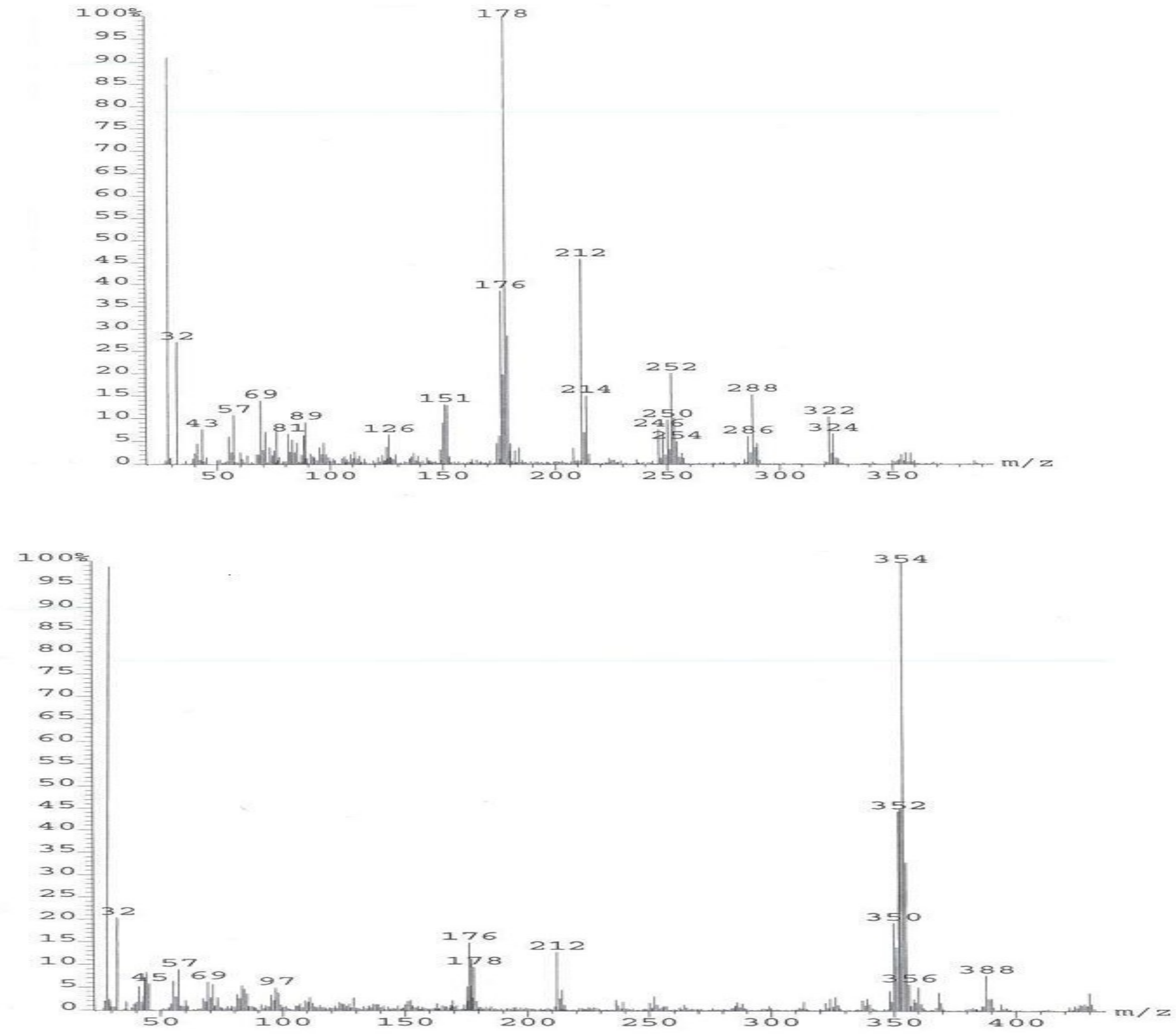

Figure 4.27: Mass probe spectrum of phenanthrene reacted with recrystallised HCH at 275 °C

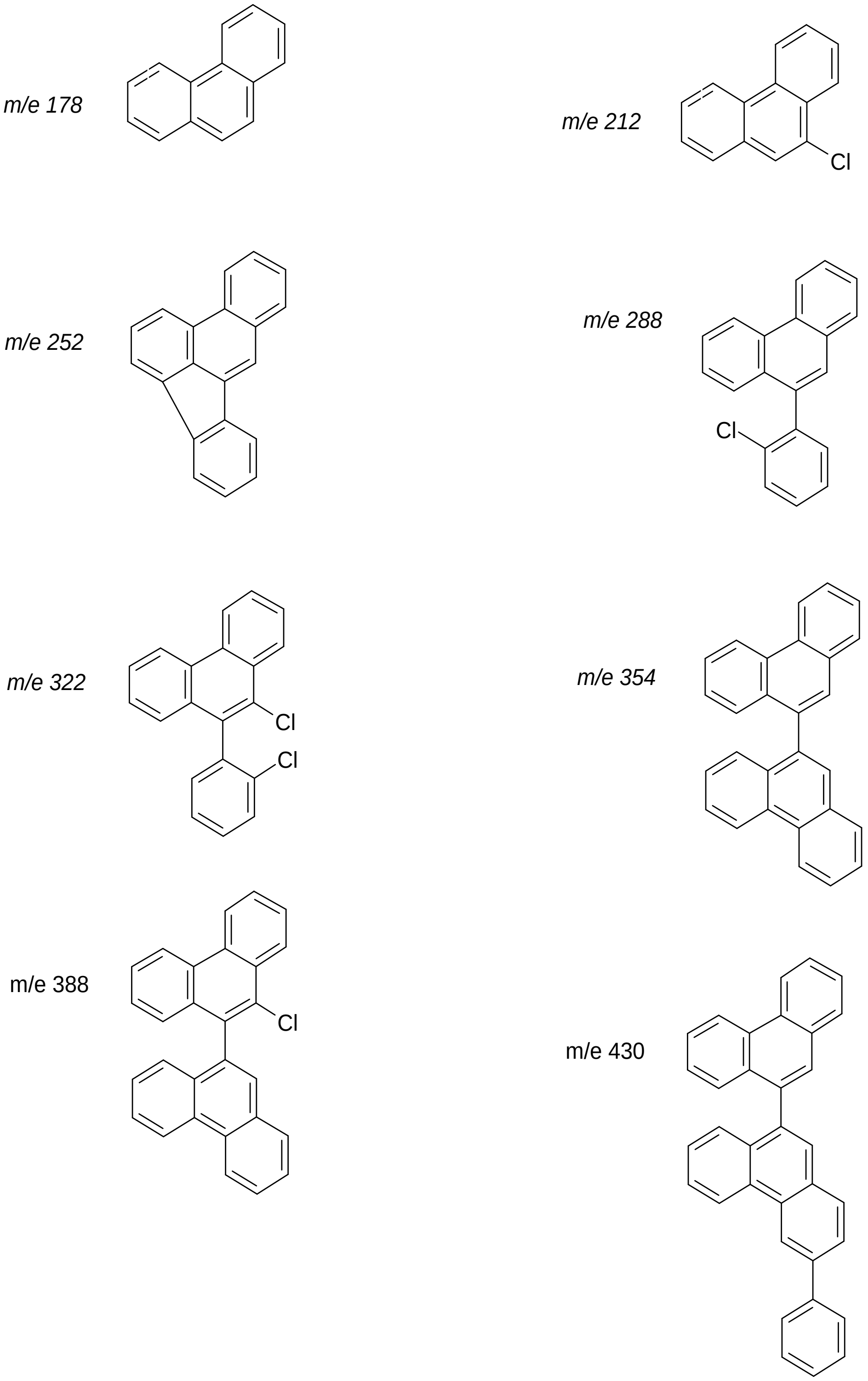

Figure 4.28: Plausible structures from reaction products of pure phenanthrene reacted with HCH at 275 °C

Dehydrogenation of anthracene occurs by two anthracene molecules reacting with HCH, losing HCl gas to form the dimer of anthracene and chlorobenzenes. Figure 4.29 summarises the simplistic pathway of the reaction that anthracene undergoes when reacted with HCH at 275 °C.

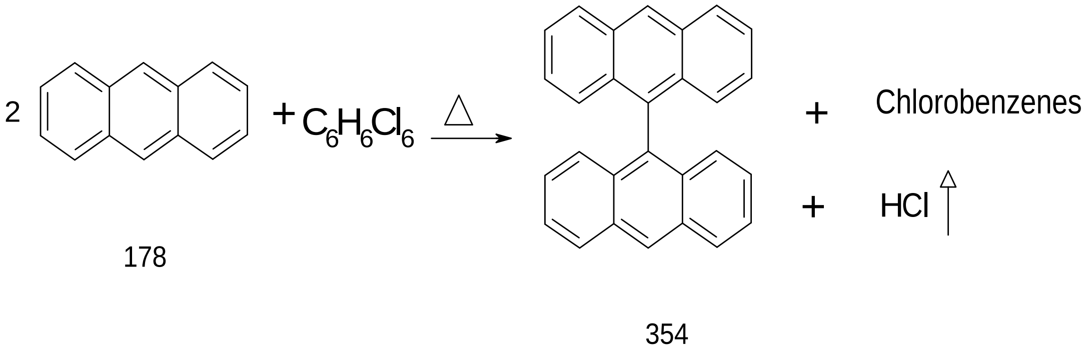

Figure 4.29: The simplistic reaction pathway of anthracene with crude HCH at 275 °C

Naphthalene did not react with the HCH because it sublimes at lower temperatures. The prominent peaks observed are chlorobenzene, dichlorobenzene, trichlorobenzene and tetrachlorobenzene, assigned by the following molecular ions: *m/e* = 111, 113, 145, 147, 181, 183, 219 and 221 (Figure 4.30). The molecular ions from the mass spectrum indicate the possibility of the presence of the isotopic mass of chlorine 35 and chlorine 37.

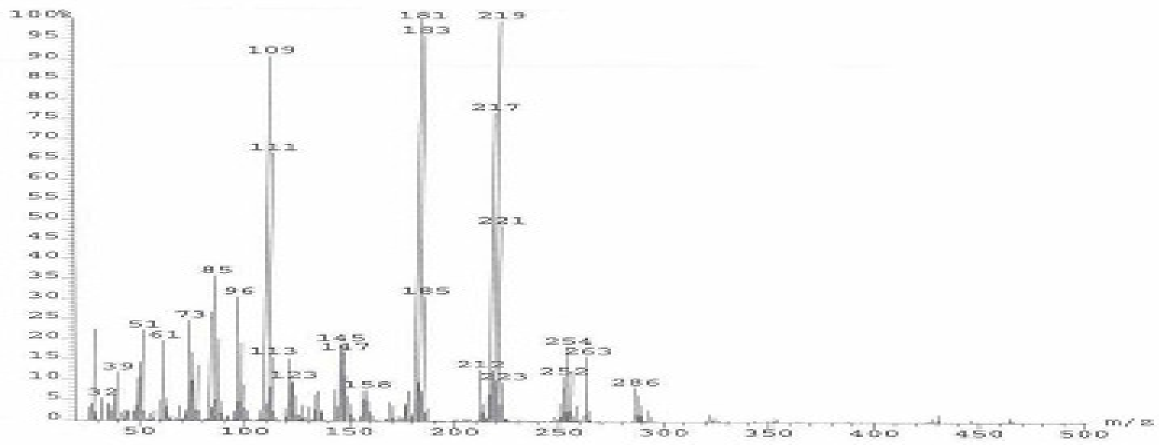

Figure 4.30: Mass probe spectrum of naphthalene reacted with recrystallised HCH at 275 °C

4.5 Structural characterisation by proton NMR (^{1}HNMR)

Figure 4.31 represents the ^{1}HNMR spectrum of AO and Figure 4.32 represents the ^{1}HNMR spectrum of the reaction product of AO reacted with 25 wt % of sulfur. The spectra show a greater presence of aromatic protons, with few aliphatic protons. The aliphatic protons include the methylene group hydrogens, with signals in the region of 4.50–3.69 ppm, alpha to two aromatic rings (the fluorene type). The aliphatic protons in the methyl or methylene groups, with signals in the region of 0.5–2.0 ppm, gamma or beta to an aromatic ring, are also present.

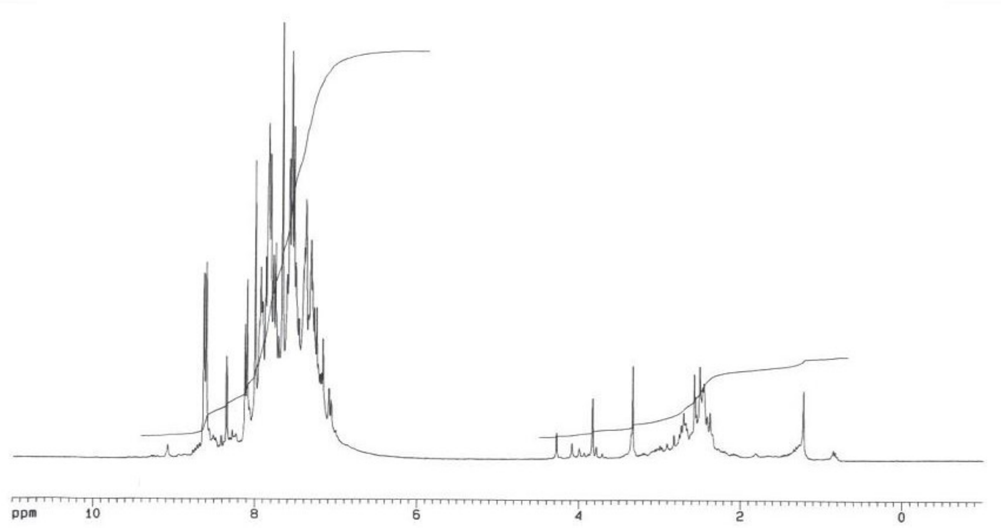

Figure 4.31: ^{1}HNMR spectrum of the CDCl$_3$-soluble fraction of anthracene oil

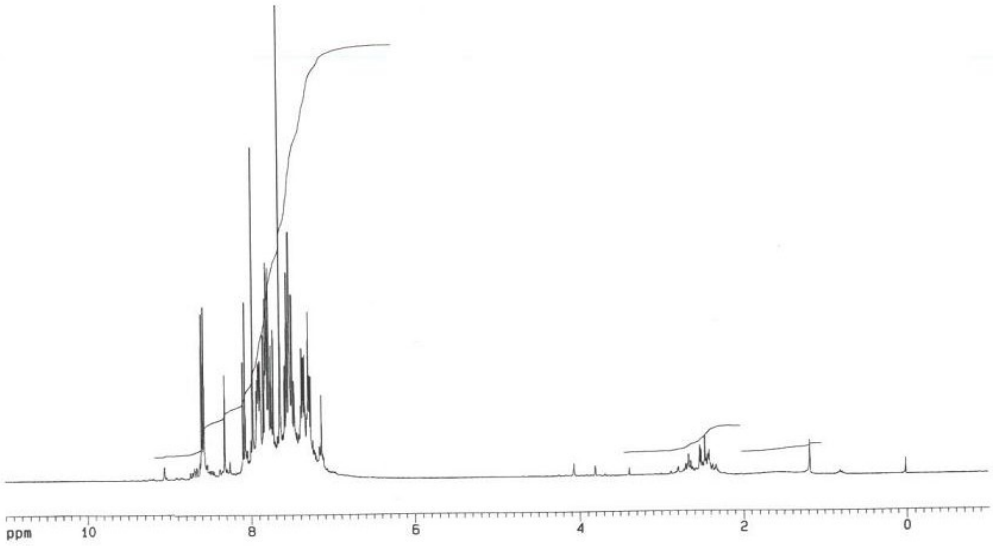

Figure 4.32: ^{1}HNMR spectrum of the $CDCl_3$-soluble fraction of AO reacted with 25 wt % of sulfur at 275 °C

Figures 4.33 to 4.35 represent the spectra of AO reacted with varying concentrations of sulfur.

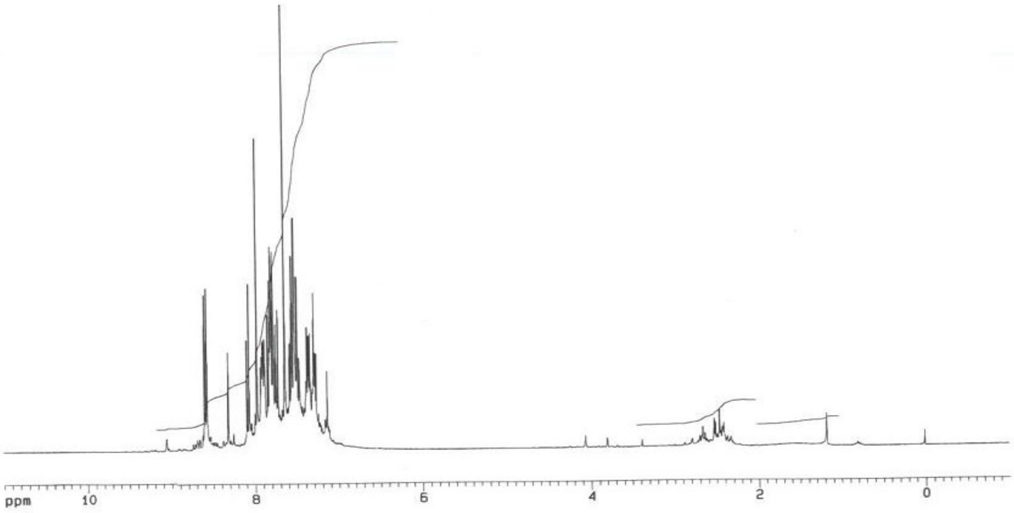

Figure 4.33: ^{1}HNMR spectrum of AO reacted with 17.5 wt % of sulfur at 275 °C

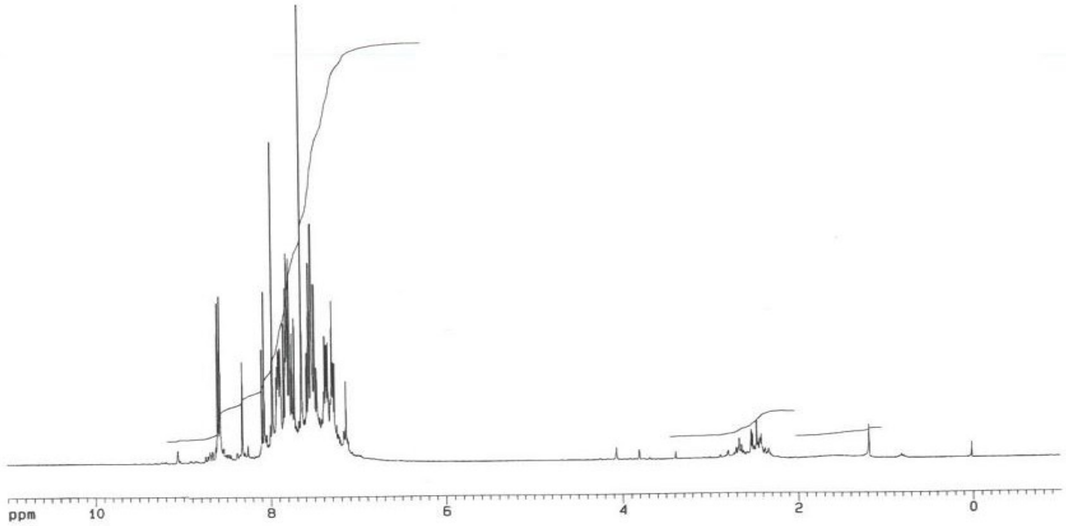

Figure 4.34: ^{1}HNMR spectrum of AO reacted with 20 wt % of sulfur at 275 °C

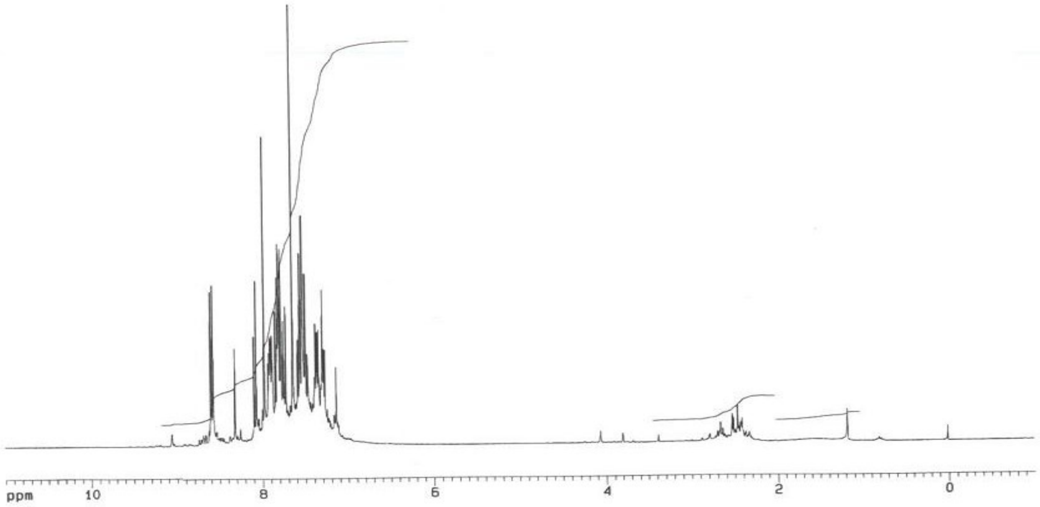

Figure 4.35: ^{1}HNMR spectrum of AO reacted with 22.5 wt % of sulfur at 275 °C

Table 4.9 gives percentages of proton distribution of AO and the reaction products of AO reacted with sulfur at 275 °C. The results obtained indicate that the percentages of aliphatic protons decrease with the increase in the sulfur concentration, and the aromatic percentages increase. This shows that cross-linking on reaction with sulfur occurs preferentially through aliphatic carbon atoms.

Table 4.9: Percentages of proton distribution of AO and the reaction products of AO reacted with sulfur at 275 °C by ^{1}HNMR

S_o, wt %	Aromatic, %	Aliphatic, %
0	79.7	20.4
20	92.6	7.37
22.5	92.9	7.07
25	93.5	6.45
30	95.9	4.08

Figures 4.36 to 4.38 represent the ^{1}HNMR spectra of the reaction products of AO with varying concentrations of HCH.

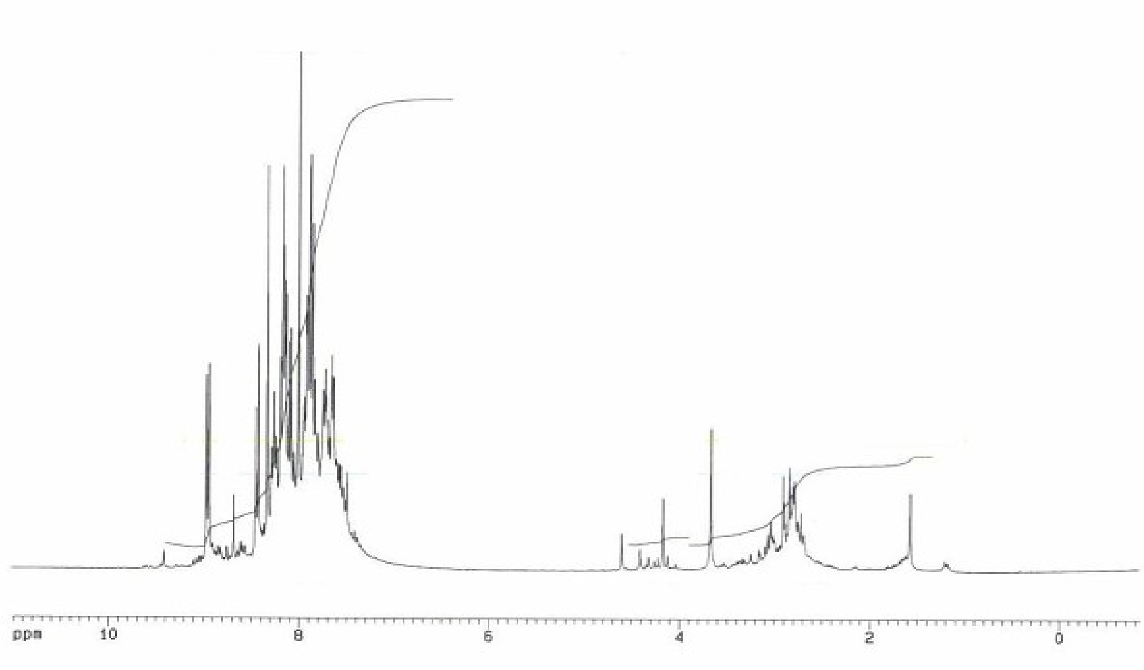

Figure 4.36: ^{1}HNMR spectrum of AO reacted with 40 wt % HCH at 275 °C

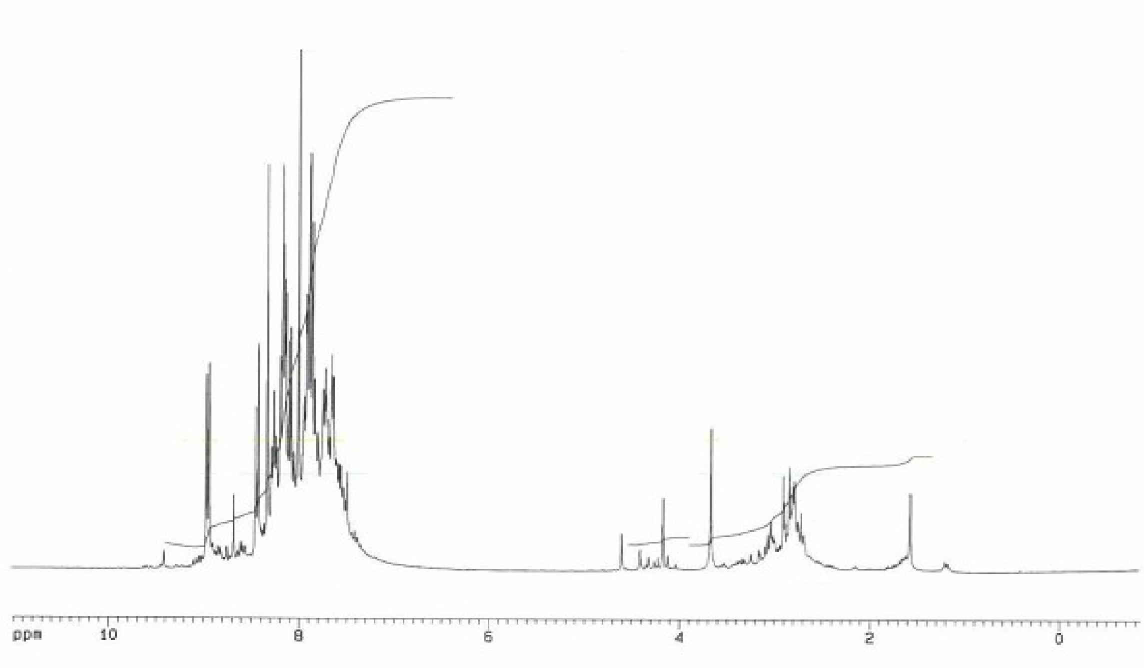

Figure 4.37: ^{1}HNMR spectrum of AO reacted with 200 wt % HCH at 275 °C

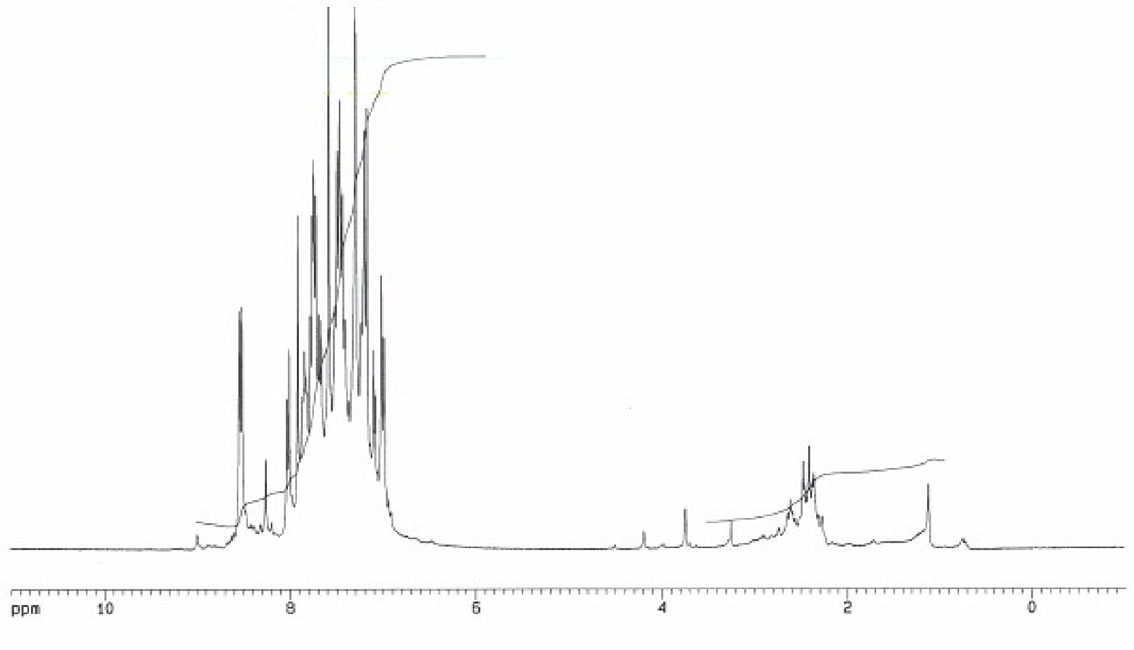

Figure 4.38: ^{1}**HNMR spectrum of AO reacted with 300 wt % HCH at 275 °C**

Table 4.10 gives the percentages of proton distribution of these reaction products at 275 °C. There was a slight increase in the aromatic protons with the signal shifts at 6.3–9.1 ppm. This indicates that cross-linking occurs through aromatic-aromatic carbon atoms.

Table 4.10: Percentages of proton distribution of the reaction products of AO reacted with HCH at 275 °C by ^{1}**HNMR**

HCH, wt %	**Aromatic, %**	**Aliphatic, %**
40	82.4	17.6
80	82.8	17.2
200	87.5	12.5
300	87.4	12.6

4.6 Analyses by optical microscopy

The optical micrographs of pitch cokes obtained at 600 °C from (A) anthracene oil reacted with 22.5 wt % of sulfur, (B) anthracene oil reacted with 25 wt % sulfur, (C) anthracene oil reacted with 300 wt % HCH and (D) 90 Mettler pitch are presented in Figure 4.39. The optical texture is related to the carbon content obtained from the elemental analysis. The domains for HCH, sulfur and the commercial cokes show the isotropic characteristics of carbons. The carbon contents of sulfur cokes show a decrease with the increased concentration of sulfur and that of HCH cokes increases with the increased concentration of HCH. These result in all the pitches not being suitable for use in graphite application because pitches with anisotropic characteristics are desired.

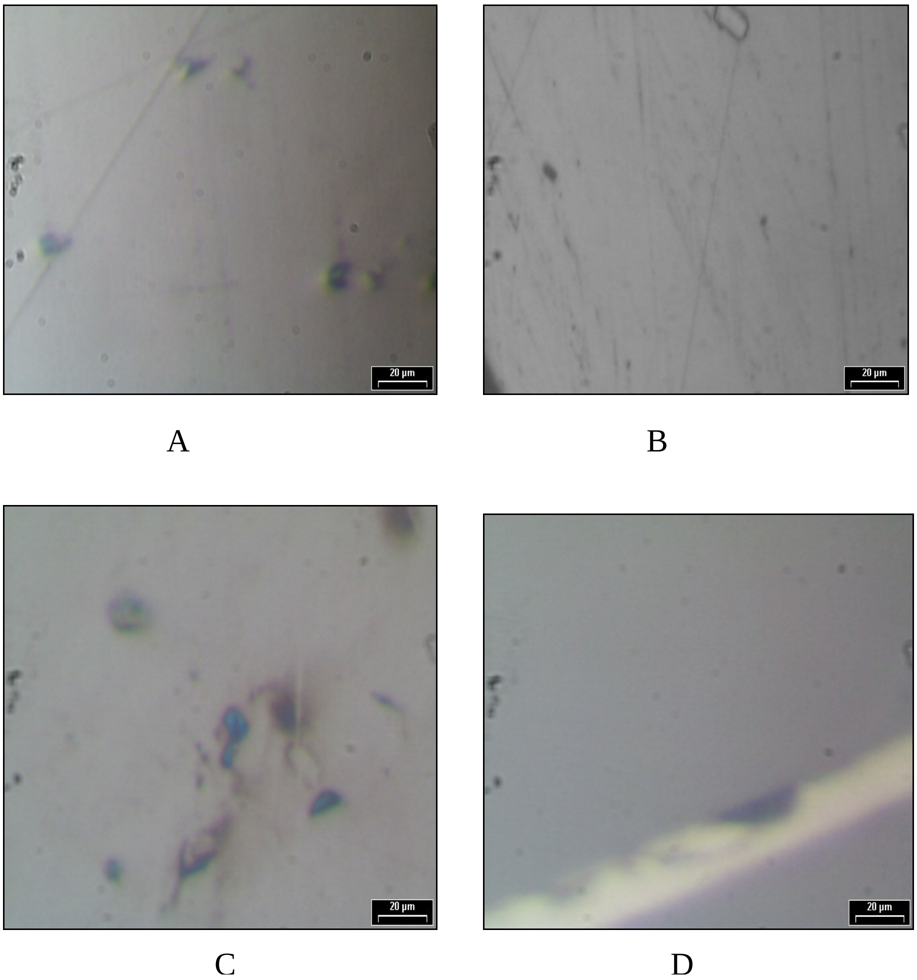

Figure 4.39: Optical micrographs of pitch cokes at 500x magnification

CHAPTER 5: CONCLUSIONS

Anthracene oil (AO) and coal tar oil react with sulfur in the temperature range of 250–275 °C for 2 hours, resulting in a significant increase of the carbon yield obtained by thermogravimetric analysis (TGA), i.e. the coking yields of pitch samples increase linearly with the initial concentration of sulfur. Therefore, pitches prepared with higher concentrations of sulfur are suitable for use as impregnants because of their high carbon yields. However, the total sulfur content detected by elemental analysis is high. This is undesirable because sulfur may cause ‘puffing’ which will result in poor quality of graphite.

The coking yields of pitches derived from hexachlorocyclohexane (HCH) are lower than those of Mittal Coke and Chemicals’ commercial pitches. The high density of the pitch is desirable so that it gives a high carbon yield, per unit volume, on coking. HCH pitches can also be used in other applications because of their low coking yields.

The quinoline-insoluble (QI) contents of the reaction products of AO reacted with sulfur at 275 °C are higher than those of sulfur pitches at 250 °C, which may make them less suitable as impregnation pitches. HCH pitches have a low QI content. Pitches prepared with 15–20 wt % of sulfur and HCH pitches may have more applications in impregnation.

From the proton NMR spectra, the percentages of aliphatic protons decrease with the increase in the sulfur concentration, and the percentages of aromatic protons increase. This shows that cross-linking on reaction with sulfur occurs preferentially through aliphatic carbon atoms. There is a slight increase in the proportion of aromatic protons in the HCH pitches; therefore cross-linking through aromatic-aromatic carbon atoms is relatively more important.

Not all the techniques used for the analyses of the pitch products proved to be equally useful. Gas chromatography (GC) was used to identify the more volatile and less polar components of AO. This method did not allow direct comparison of the conversion percentages of AO because of inconsistency in the retention times. The elution times of polycyclic aromatic hydrocarbon were inconsistent for different samples and therefore GC could not be used to detect the concentration of smaller molecules.

The model reaction of pure anthracene with HCH was used to determine the reactivity of the main components of AO. GC analysis of HCH pitches showed the formation of chlorobenzenes (monochlorobenzenes, trichlorobenzenes and tetrachlorobenzenes) and some chlorohydrocarbon compounds. This incorporation of chlorine into the pitches is undesirable as the formation of hydrogen chloride, during coking, would give rise to very undesirable corrosion of equipment.

Compared with the properties of Mittal Coke and Chemicals' commercial pitches, the reaction products reacted with 15 and 20 wt % of sulfur, with softening points of 61.3 and 91.4 ^{o}C, would be suitable as commercial products. All the pitches show very little, if any, ash, making them suitable for use in the manufacture of high-purity, nuclear-grade graphites.

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