THE UNIVERSITY OF CALGARY

Upgrading of Bitumen

by

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Abstract

In this work, the thermal (upgrading) reactions of bitumen were studied. Lab scale coking reactions of Syncrude bitumen (in the presence of small amounts of slurried additives) were carried out in order to learn about mechanisms important in coke formation. Analysis of the upgraded coker gas oil (CGO) was achieved using capillary GC-MS together with ^{1}H and ^{13}C NMR. It was found that the coking process was occurring by thermal mechanisms and attempts to influence the product distribution with small amounts of selected additives were unsuccessful. Large amounts of Lewis acids (>20 wt%) added to the bitumen prior to coking caused large undesirable increases in the amount of coke formed. Coking of bitumen in the presence of a deuterium source led to incorporation of the label, which could subsequently be followed using ^{2}H NMR and capillary GC-MS. Exchange of deuterium into the CGO was widespread but predominated in aromatic and benzylic hydrogen environments. The benzylic exchange was found to be reversible.

The pyrolysis of the bitumen asphaltene was also studied. Pyrolysis in various H-donor and non-donor H-shuttles was studied. H-donors and, to a lesser extent, diluents such as methylnaphthalene were found to be efficient at preventing coke formation. Examination of recovered asphaltene revealed that the degradation (compared to virgin material) was characterized by dealkylation, aromatization, condensation and at lower temperature, ring opening reactions. Using an isotopically labelled donor solvent (during pyrolyses) the exchanges occurring during thermal degradation of the asphaltene were probed and using GC-MS and ^{2}H NMR. An effective kinetic isotope effect was found when comparing H/D expressed from the donor. Widespread deuterium exchange into the pyrolysis products was found. Of

particular interest was the fact that the n-alkanes recovered have a high level of deuterium incorporated into their chains. A "hot" radical required for this exchange to occur was probably generated from the asphaltene pyrolysis.

Using model compounds (models of the asphaltene), the mechanisms important during pyrolysis, e.g. dealkylation, were studied in different media. Product distributions gave an idea of the mechanistic pathways important in the asphaltene pyrolyses, under a variety of conditions. The cleavage of alkyl aromatic compounds was found to depend on the size of attached ring. Alkyl chains attached to a ring larger than benzene were found to cleave predominantly α to the ring.

The reactions of the asphaltene with high temperature steam (hydrous pyrolysis) was also studied. The product distributions were found to be similar to those found in dry pyrolyses, however comparison of the recovered asphaltenes revealed that the presence of the H_2O had supressed the dealkylation and internal H-transfer reactions found in the dry pyrolyses. The use of D_2O allowed one to study exchange occurring with the asphaltene during hydrous pyrolysis. When comparing product distributions arising from pyrolyses of asphaltene and H_2O/D_2O, a kinetic isotope effect was found. Exchange from the D_2O involved radical processes since the presence of a sulphur radical initiator significantly. increased the rate of exchange.

To

My parents and family

Tracy, Michael, Andrew and Michele

Jenessa

Jim and Helen Black

and

all my closest friends

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Table of Abreviations

Abreviation	Meaning
H α,β,γ	Defined on page 25
CGO	Coker gas oil
DHA	9,10-dihydroanthracene
DHN	1,2-dihydronaphthalene
DHP	9,10-dihydrophenanthrene
DRB	Donor refined bitumen
Fac	^{13}C NMR derived aromaticity
FDMS	Field desorption mass spectroscopy
GC	Gas chromatography
CG-MS	Gas chromatography-mass spectroscopy
GPC	Gel permeation chromatography
HPLC	High performance liquid chromatography
IR	Infra-red spectroscopy
LC	Liquid chromatography
MN	1-methylnaphthalene
MT	Methyltetralin
NMR	Nuclear magnetic resonance
PDB	Pentadecylbenzene
PNA	Polynuclear aromatic hydrocarbon
SIC	Single ion chromatography
SCG	Supercritical gas
THA	Tetrahydroanthracene
TIC	Total ion chromatogram
TPP	Tetraphenylporphyrin
UV	Ultra-violet spectroscopy

Chapter 1

1.1 Introduction

Upgrading of bitumen is an important source of crude oil in Canada. Hydrocarbons derived from bitumen currently account for over 10% of the country's total crude production. Operational oil-sands (bitumen) plants in Alberta, use thermal coking as the primary upgrading method for converting bitumen into useable hydrocarbon fractions. The amount of syncrude that can be run at any particular refinery is usually set by the need to meet fuel aromatic specifications (especially in the jet and diesel fuel fractions). Of all the different boiling-point fractions, the most rapid growth in demand occurs for diesel fuel and this growth is expected to continue for 5-10 years [1]. This growth is placing great pressure on the ability of Canadian refiners to meet diesel fuel demand, and at the same time, maintain product quality. It is most probable that middle distillates from the tar sands will be expected to fill the gap in diesel fuel supply.

1.2 Upgrading Processes Used Industrially

Coking is a thermal process used commercially for the conversion of heavy bitumen to lighter products. Two variations of this process are used by Syncrude and Suncor in Alberta. The older process (Suncor), delayed coking, involves a semicontinuous process in which bitumen is heated at a long residence time, to allow cracking reactions to occur to completion. The temperature in the coking drums ranges from 415-450°C at pressures from 15-90 p.s.i.. The main disadvantage of this process is the relatively high coke production. Typically, 22 wt % of coke is formed [2]. The coke formed is then stockpiled and is not much use as a fuel because of its high sulphur content.

The yield of upgraded coker gas oil from this process is about 65%. The rest appears as low boiling gases. The other commercial process, fluid coking, is used by Syncrude. This is a continuous process which uses 40% of the coke formed as a renewable fluidizing medium and is generally a more efficient method of upgrading the bitumen. The advantages include a higher coker gas oil and lower coke yields. The main disadvantage is that the sulphur from the coke, used as the fluidizing medium, is released to the atmosphere and has undesirable environmental consequences.

1.3 Properties of the Syncrude

In an attempt to judge the coker gas oil's suitability as a replacement for conventional crudes, a comparison is made between the properties of the two fuel sources.

Table 1. Distillation characteristics of synthetic compared to conventional crude.

Distillate Yield, LV%	Synthetic crude	Conventional crude
I-C5	4	3
C5-195°C	18	36
195-345°C	47	31
345-560°C	31	18
560°C+	0	12

Looking at the distillation characteristics of the two crudes (Table 1), one can see that in the gasoline boiling range (lower temperature range) the syncrude (18% compared to 36% for the conventional) derived from the tar sands is much

lower. Obviously, this boiling range is in high demand and one would like to improve the yield of this fraction in the syncrude, if possible. The amount of diesel boiling within the the diesel range is favourably high for the syncrude (47% as opposed to 31% for the conventional).

Unfortunately, although the volume of material boiling in the diesel range is high in the syncrude, it is evident that the aromaticity is also high compared to the same fraction derived from a conventional crude (Table 2). This high aromatic content adversely effects the cetane number which is a measure of diesel fuel quality. The aromatic compounds cause high concentrations of unstable species to form, which under the conditions of high pressure found in diesel engines causes pre-ignition to occur, leading to overheating and a much reduced engine lifetime.

Table 2. Properties of Synthetic and Conventional Crudes.

	Synthetic	Conventional
Density, kg/dm^3	0.8974	0.833
Viscosity, cSt at 40°C	3.3	2.9
Cloud Point, °C	-27	-10
Pour Point,°C	<-50	-18
Sulphur, wt %	0.03	0.30
Nitrogen, ppm	25	15
Hydrogen, wt %	12.6	13.6
Aromatics, vol % (D 1319)	44	32
Cetane no. (D 613)	34	48

The standard cetane number required in Canada is 40 (50 in the U.K. and France). Evidently, the tar sands derived diesel fails to meet this standard (34 compared to 48 for conventially derived diesel). If possible, one would like to improve the cetane number of the diesel.

The maximum aromatic content allowable in jet fuel is about 20% and the syncrude fraction also fails to meet this specification. Investigation into mechanisms involved in the coking process would be useful, in order to learn how the high aromaticity (in the middle distillate fraction) and coke is formed. With this knowledge it might then be possible to modify the coking process and prevent the undesirably high aromaticity and coke formation.

1.4 Objectives of this Project

Preliminary work which involved the study of the initial coker feed bitumen and the various fractions formed on coking, using ^{13}C nuclear magnetic resonance, revealed that significant aromaticity was being formed during the coking process (Figure 1). A weighted average (carbon aromaticity) of the coking products had an overall aromaticity of 38.2 compared to the initial bitumen which had a value of 31.3% aromatic carbon content. This newly created aromatic carbon is of interest from the point of view of the middle distillate (aromaticity) and coke formation .

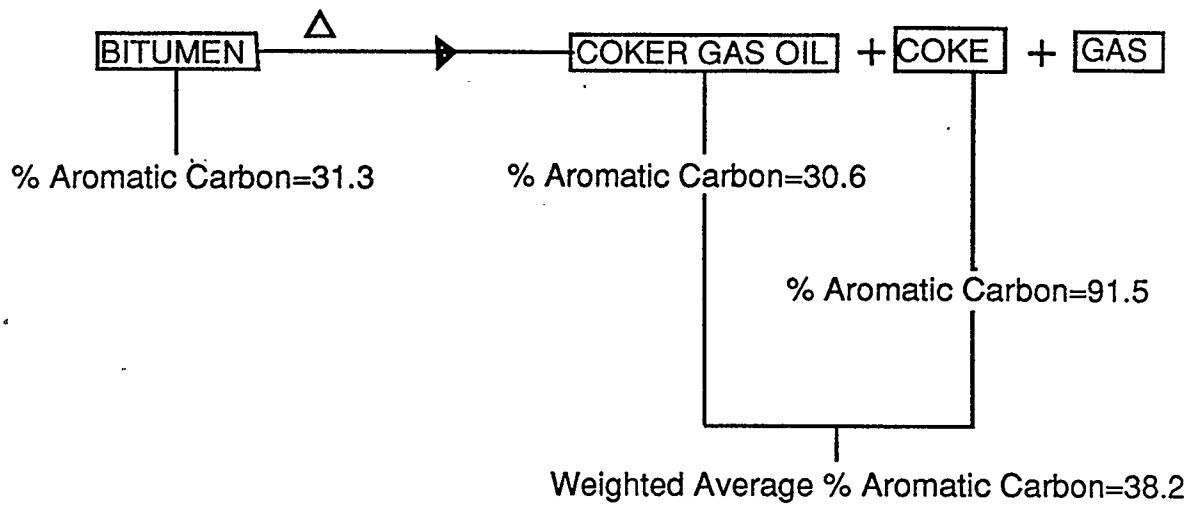


Figure 1. ^{13}C NMR analyses of the starting bitumen and products formed on coking.

With the previous information in mind the initial objective of this work was to study mechanisms involved in the coking process with the more practical aims of being able to:

(1) Decrease the amounts of coke formed whilst increasing the yields of the more valuable lighter fractions,

(2) Reduce the aromaticity of the middle distillate fraction.

1.5 Strategy

It was hoped that the objectives might be achieved by building a lab scale coker in which bitumen would be coked in an effort to model the commercial process involved. Variables in the coking process could be studied by adding small concentrations of compounds, with known chemical effect, to the bitumen prior to coking. It would then be possible to measure the effect of a particular additive, with respect to coke formation and liquid product quality (coker gas oil), using capillary GC-MS (for detailed analyses of the individual

components) and ^{1}H and ^{13}C NMR for a more global examination of product composition.

Subsequent to this work on the study of the coking process, it was realised that there were other possibilities for examining the upgrading of bitumen, i.e. the asphaltene fraction of the whole bitumen is known to be a very good coke precursor. The isolation and pyrolyses of this fraction was therefore studied in detail in chapter 4 using the alternative upgrading method of hydrogen addition with hydrogen atom donors. The use of deuterium isotopic labels, to follow upgrading reactions, was addressed in chapters 3 and 5. It is possible to model the complex system, involved in bitumen, by using pure synthetic compounds and studying their pyrolyses and this was studied in chapter 6. Another upgrading possibility involves the reaction of superheated steam , and obviously the deuterated equivalent, with the bitumen asphaltene (chapter 7).

Chapter 2

Model Coking Studies

Introduction

2.1 Properties of Whole Bitumen

Before dealing with the description of the model coking experiments, examination of the properties (Table 3) of Syncrude coker feed bitumen, will give the reader some idea of the nature of the material being studied. Looking at Table 3 it is evident that the whole bitumen is highly viscous.and contains no light ends, 87% boils at above 345°C. It has significant sulphur and nitrogen content as well as vanadium, nickel and iron. The presence of these contaminants could have significant effects on the upgrading of the bitumen feed.

2.2 Characterization of Bitumen

Strausz et al.[3] studied the make-up of different bitumens (including Athabasca). The elemental composition of 4 samples of Athabasca oil sands bitumen were found to be within the following ranges: C 82-84 wt %, H 10-10.4 %, N 0.2-.6 %, O 1-2 % and S 4.6-5.5 %. The molecular weight of the bitumen was found to be 490-620 and the H:C ratio was 1.46-1.49.

These fractions were then subjected to GC-FIMS [3] (field ionization mass spectroscopy) analysis. This is a soft ionization technique which results only in the production of parent ions. The saturate fraction was found to contain a series of cycloalkanes. The most abundant member of the series was the two ring species and the largest was a hexacyclic alkane. A large number of biomarkers were also found in this fraction. The aromatic fraction was

composed of aromatic and hydroaromatic species with up to 3 rings. The asphaltene fraction will be discussed at a later stage.

Table 3. Properties of Athabasca Bitumen.

Gravity, °API	13.5
Density at 15°C, kg/dm^3	0.975
Viscosity, cSt at 40°C	3000
Sulphur wt %	5.1
Nitrogen, wt %	0.6
Ash, wt %	0.7
Iron, ppm	440
Vanadium, ppm	200
Nickel, ppm	60
Distillate yield, LV%	
IBP-C5	0
C5-195°C	0
195-345°C	13
345+°C	87

2.2.2 Chromatographic Separation of Athabasca Bitumen

Selucky et al.[4] analyzed Athabasca bitumen using chromatographic separations and subsequently studied the resultant fractions using I.R., U.V., N.M.R., and GC-MS. The bitumen was initially deasphalted yielding 16.6% pentane asphaltene (pentane insoluble, benzene soluble material) and 83.4%

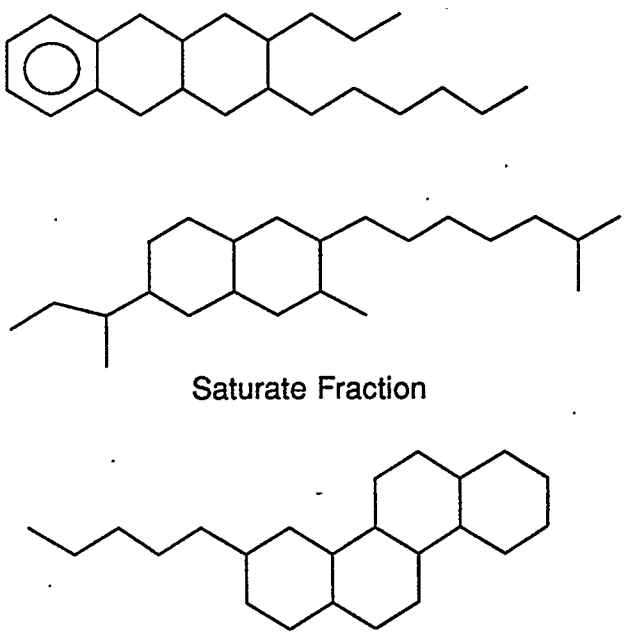
oil and resins (pentane soluble material). The separation used different polarity solvents eluting from a silica/alumina column and was capable of fairly cleanly separating saturates, monoaromatics, diaromatics and polyaromatics. The oil was found to contain 24.8 wt % saturates, 10.3% monoaromatics, 5.3% diaromatics and 58.2% polyaromatics. GC-MS analysis of the monoaromatic fraction revealed the presence of alkylbenzenes, naphthenebenzenes, dinaphthenebenzenes benzothiophenes and some other minor components. The diaromatic fraction was found to contain mainly naphthalenes, acenaphthenes and fluorenes. The alkane content of the bitumen was found to be small.

2.2.3 I.R. Analysis of Athabasca Bitumen Fractions

Bunger et al.[5] studied bitumen fractions using a number of different techniques. I.R. analysis was successfully used to discover the variety of functionalities present in the bitumen. A free phenol band was found at 3590cm^{-1}. The band due to intramolecular H-bonding was found at 3540cm^{-1}, this band is not affected on dilution of the sample. Bands found in the range 3490-3510cm^{-1} are assigned to the free O-H of carboxylic acids. Carbazoles bands are found at about 3460cm^{-1}. Ketone carbonyls are found at about 1695cm^{-1}. Bands found between 1625-1690cm^{-1} are assigned to amides but this has not been otherwise confirmed. The presence of sulphoxides is also noted in a band between 1025-1035cm^{-1}.

2.2.4 Global NMR Analysis of Athabasca Bitumen

Suzuki et al.[6] studied the chemical structure of Athabasca, Cold Lake and Orinoco tar-sand bitumens using ^{1}H and ^{13}C NMR. The bitumens were deasphalted (with heptane) and the resultant oils were separated on alumina columns, into saturate, aromatic and resin fractions. The saturate fraction was eluted with petroleum ether, the aromatic with benzene and the resin fraction using a 1:1 mixture of benzene and methanol. The ^{13}C and ^{1}H NMR spectra of the fractions were obtained. Using 'global' parameters from the NMR analysis, average structures for the different fractions were assigned (see Figure 2 for average structure of the Athabasca bitumen fractions). No single average structure can completely satisfy the NMR derived structural parameters. The authors expressed the average structure as a combination as shown in Figure 2. The average structures derived for the fractions of different bitumens had significant differences. Many attempts have been made using similar analyses of NMR data [7-24].



Saturate Fraction

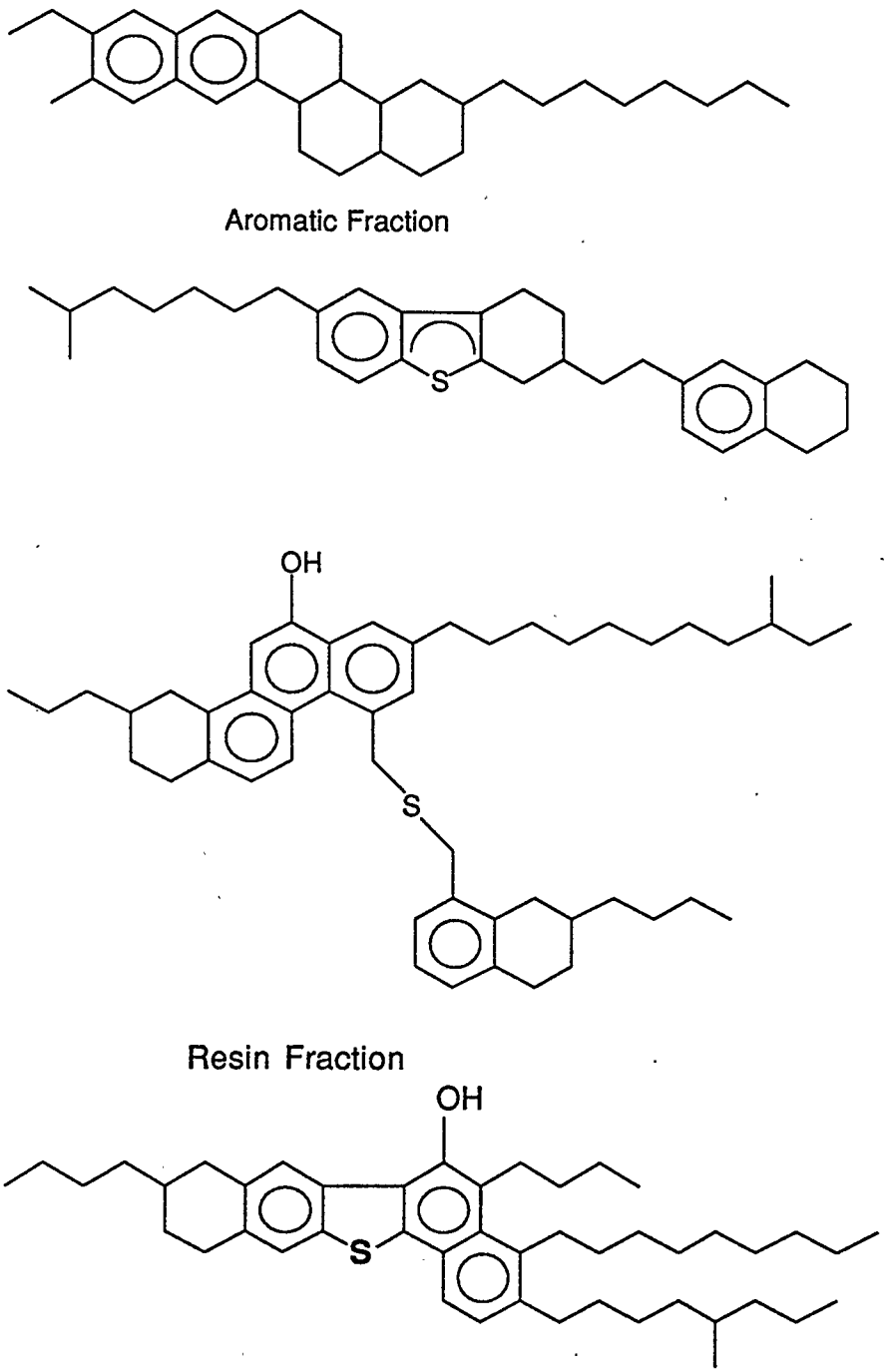


Figure 2. The average structures derived for the fractions of Athabasca bitumen from NMR data.

2.2.5 LC and HPLC Analyses of Athabasca Bitumen

Das et al.[25] studied the polynuclear aromatic fraction (separated using liquid chromatography) from Athabasca and 4 other bitumen samples using a combination of LC, HPLC and GC-MS. The list of PNA's (polynuclear aromatics) identified by GC-MS included: fluorene, phenanthrene, anthracene, pyrene, chrysene, benzofluorene, benzopyrene, picene, benzoperylene and some of their methyl derivatives. The authors found that the PNA content increased as the weight % of distillation residue above 350°C, was increased. They also found that the original bitumen contained significantly more PNA's than the syncrude obtained from the bitumen. Most of the work previously described involved deasphalted bitumen. The asphaltene (heptane insoluble, benzene soluble) fraction is a high molecular weight and is very resistant to upgrading and is known to be a particularly good coke precursor. Because of this, the asphaltene has attracted much more attention than the other bitumen fractions. Obviously, knowledge on the structural aspect of this fraction will help in understanding and hopefully aid in attempts to prevent coke formation.

2.3 Objectives and Strategy

One can see from the previous information that the upgraded coker gas oil is not an ideal replacement for conventional crude oil. The large amount of coke and aromaticity (in the diesel boiling range) formed during the coking process are highly undesirable. The Syncrude coker feed bitumen is obviously difficult to upgrade. A study of the mechanisms occuring during the coking process would be useful in order to understand and be able to improve this upgrading process.

In this work it was hoped that modelling the coking process on a lab scale and adding small amounts of compounds, of known chemical action, to the bitumen prior to coking and studying subsequent product distributions, on coking, would lead to a clearer understanding of the mechanisms involved in aromatics and coke formation. The upgraded coker gas oil would be separated into fractions according to boiling point, using a spinning band column distillation. The individual fractions would then be analyzed by NMR (using the global techniques mentioned to study the effects of specific additives on the carbon aromaticity, for example) and GC-MS for a study of individual components. In this way the result of perturbation of the coking (by the presence of the additive) could be studied and would lead to to a clearer understanding of the mechanisms important in this process.

2.3.2 Suitable Additives.

Various criteria were considered, in deciding which additives were worth coking with the bitumen, in an attempt to achieve the outlined goals. Suitable additives to study might include a basic site material (eg. CaO or MgO), $Ca(OH)_2$ was found by George [26] to increase CGO yields and also fix sulphur (from the bitumen) as inorganic sulphates which prevented high SO_2 emission usually associated with combustion of the coke resulting from coking. A free radical initiator and inhibitor, a hydrogen donor (discussed in chapter 4) and a super acid material were also considered to be suitable choices.

Bitumen contains high concentrations of sulphur, nitrogen, clay and metals which undoubtedly have an effect on the coking process. By synthetically enhancing their concentration, in the initial bitumen, one could probe their involvement in what is obviously a very complex reaction.

Nickel and vanadyl-porphyrins are found in the bitumen [27]. Addition of synthetic analogues, it was hoped would provide insight, into their involvement , if any, in the coking process. Also, nickel has considerable activity as a hydrogenation catalyst. Introducing a metal into the bitumen as a soluble porphine is a useful way of doing so and therefore Co, Ni and VO-TPP (tetraphenylporphine) were synthesized and used as additives. In the same way, nickel was also introduced as a bitumen soluble salt, i.e. the stearate.

2.4 Experimental

2.4.1 Construction of Model Coker

The first stage in this project was the building of a laboratory scale model coker (see Figure 3). This was built of 316 stainless steel in the hope that the inner surfaces would not provide an active surface which might affect results from coking runs and rapidly corrode because of the presence of SO_2 in the coking products. The coker consists of a pot (the height was 110mm, the inner diameter was 100mm) into which the bitumen was placed. The heating was provided by an arrangement of Nichrome wire embedded in a ceramic paste (1cm thickness) which provided insulation and protected the element. The length of Nichrome was calculated on the basis of amperage required for the desired heating rate. A special variac (20 Amp) was required to provide power to the heating element. Nitrogen (100ml/min) was continually flushed through the system in order that the cracked products could be distilled over before further reaction occurred. The liquid products were collected successively in an ice (0°C) and then a dry ice /acetone(-78°C) cooled receptacle.

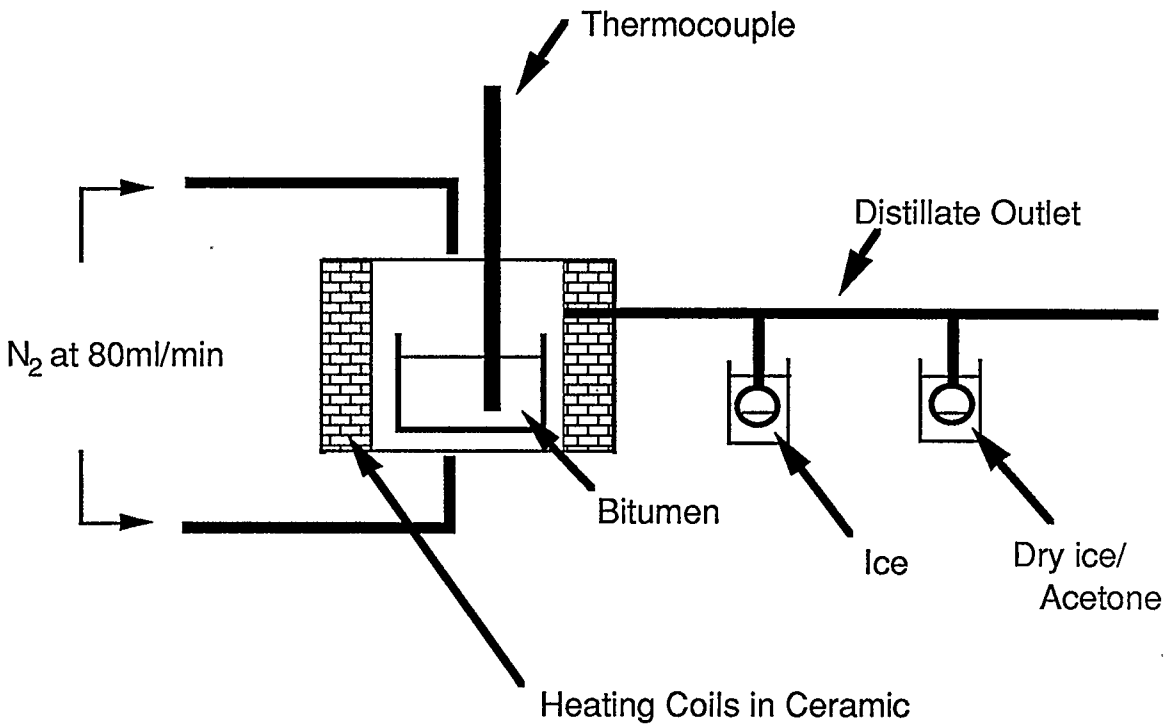


Figure 3. Schematic of lab scale coker.

2.4.2 Procedure

In a typical coking experiment bitumen (100g) was placed in the coker with an appropriate additive (1-33 wt %) already slurried into it. The bitumen was heated to 50°C to facilitate stirring with the additive, prior to coking. Following, is a list of additives and suppliers. The Syncrude coker feed bitumen was obtained from the Alberta Research Council (ARC). The nitrogen carrier gas and the power to the heater were switched on. The final coking temperature of 480°C took two hours to achieve. At this time the coker was switched off and the coker gas oil was recovered (and quantified) from the ice cooled receiver. The coke formed remained in the coker and was recovered and quantified.

Additive	Purity (%)	Supplier
Calcium carbonate	99+	Aldrich
Calcium hydroxide	98+	Aldrich
Magnesium oxide	98	Aldrich
Hexachloroethane	practical grade	M.C.B
Methyl cymanthrene	97	Aldrich
Aluminium trichloride	98	BDH
Zinc chloride	98	M.C.B
Vanadyl-TPP	(synthesized as in refs.[28-29] and purified by flash chromatography)	
Cobalt-TPP	same as vanadyl.	
Nickel-TPP	same as vanadyl.	
Nickel stearate	(Synthesized as in ref. [30])	
Nafion fluorinated ion exchange powder	unspecified	Aldrich

The next stage was fractional distillation of the resultant coker gas oil. The fractionation was carried out on a spinning band distillation column with a stainless steel band. The length of the column was 670mm and the inner diameter was 10mm. The reflux ratio employed was approximately 1:10. The fractions boiling below 175°C were distilled under water aspirator vacuum and the fractions boiling between 175°C and 425°C were distilled under vacuum-pump vacuum. The various fractions were then analysed using NMR and capillary GC-MS. The NMR used was a Varian XL 200. When obtaining quantitative ^{13}C NMR spectra special precautions were required to ensure that

nOe enhancement and the long relaxation times of aromatic (in particular, quaternary) carbons, did not cause errors. These were counteracted using a reverse gated-decoupling pulse sequence and a long inter-pulse delay of 20s. A minimum of 2000 scans were required for a reasonable signal/noise ratio, which could be achieved in an overnight run. The GC-MS used in these analyses consisted of a VG 70-70 (MS) with a Shimadzu GC-9A (GC). The column used was a 50m (SGE) capillary DB1 (non-polar).

2.5 Results and Discussion

2.5.1 Product Distributions on Coking

When the product distributions from the different coking runs were studied (Table 4) it was evident that the differences in most upgraded liquid yields were small. There is a possibility that the presence of both hexachloroethane and methyl cymanthrene may have slightly increased the yield of coker gas oil. What is very definite, though, is the fact that the presence of the Lewis acids ($AlCl_3$ or $ZnCl_2$) in large concentrations (>5%) led to increases in the amount of coke formed and corresponding decreases in the upgraded coker gas oil yields. This of course is an undesirable result, but interesting from a coke forming mechanism point of view. Strausz et al [31] reported that the presence of Lewis acids would encourage asphaltene degradation at low temperature (<150°C). At higher temperatures the dominant reactions were found to be polymerization, dehydrogenation and cracking to form gases. At 300°C, because of extensive interaction of $ZnCl_2$ with heteroatoms, the nitrogen, sulphur and oxygen content of the products decreased and the rate of conversion into lower molecular weight, heptane soluble, products increased. Considering the reactions that these additives are used to catalyze, it may be possible to explain the increased propensity for the

bitumen to form coke instead of coker gas oil.

Table 4. Product distribution on coking of bitumen in the presence of selected additives.

Additive	% Liquid Distillate	% Coke
None (Mk. 1 Coker)	78.6	16.3
Calcium carbonate (5%)	77.3	16.1
Hexachloroethane (5%)	82.2	13.1
Methyl cymanthrene (5%)	82.9	14.8
None (Mk. 2 Coker)	80.0	13.9
Aluminium trichloride (5%)	80.4	17.2
Aluminium trichloride (20%)	50.9	43.0*
Aluminium trichloride (33%)	50.3	48.3*
Zinc chloride (5%)	78.1	16.9
Zinc chloride (20%)	67.6	29.0*
Vanadyl-TPP (1%)	80.3	15.6
Cobalt-TPP (1%)	74.3	13.9
Nickel-TPP (4.2%)	76.3	18.9
Calcium hydroxide (15%)	80.8	14.3
Magnesium oxide (14%)	75.1	15.0
Nickel stearate (11.5%)	79.4	17.8
Nafion (11.1%)	78.5	21.6

*estimate, including subtraction of residual Lewis acid.

TPP=Tetraphenylporphyrin.

2.5.2 Distillation Characteristics of the Resultant CGO's

The Lewis acid runs have again provided the most interesting results in terms of modification of the volume of CGO distilling in a given boiling range (Table 5). The other additives resulted in small differences which could have been caused by errors made in the fractionation, e.g. due to changes in the vacuum. One of the original goals was to increase the proportion of liquid boiling at lower temperatures. In the $AlCl_3$ (33%) run, all of the coker gas oil distilled below 325°C. When the proportion of $AlCl_3$ was reduced to 20%, there was now 7% which boiled in the next highest range. Looking at the $ZnCl_2$ (20%) situation, it is evident that the distillation characteristics of the product coker gas oil were similar to the $AlCl_3$ (20%) run.

Table 5. Cumulative percentage volume distillate of coker gas oil in given boiling point ranges.

	Boiling Point Range (°C)				
Additive	20-175	175-325	325-375	375-425	425+
None (Coker Mk. 1)	6.1	33.9	53.6	82.5	100.0
Calcium carbonate (5%)	4.6	26.6	44.0	78.6	100.0
Hexachloroethane (5%)	8.0	33.5	55.8	73.1	100.0
Methyl cymanthrene (5%)	7.3	32.3	49.3	66.1	100.0
None (coker Mk. 2)*	8.1	37.2	54.4	72.7	100.0
Aluminium trichloride (5%)	6.3	30.1	52.9	73.0	100.0
Aluminium trichloride (20%)	44.2	93.4	100.0		
Aluminium trichloride (33%)	69.1	100.0			
Zinc chloride (5%)	5.4	33.0	56.8	60.8	100.0
Zinc chloride (20%)	9.8	40.2	63.1	100.0	
Vanadyl-TPP (1%)	8.3	25.8	49.4	68.1	100.0
Cobalt-TPP (1%)	5.1	28.0	47.4	66.7	100.0
Nickel-TPP (4.2%)	11.5	37.1	56.2	71.8	100.0
Calcium hydroxide (15%)	8.9	24.7	49.1	77.3	100.0
Magnesium oxide (14%)	8.4	34.8	59.3	79.8	100.0
Nickel stearate (11.5%)	7.3	39.4	53.9	69.4	100.0
Nafion (11.1%)	3.2	36.7	39.9	61.9	100.0

* At this stage an improved model coker was employed

Figure 4 illustrates the distillation characteristics of the Lewis acid runs compared with the control (no additive). One can see that the CGO from the Lewis acid runs were lower boiling but this was achieved at an unacceptable cost in terms of the loss of total yield of upgraded liquid product.

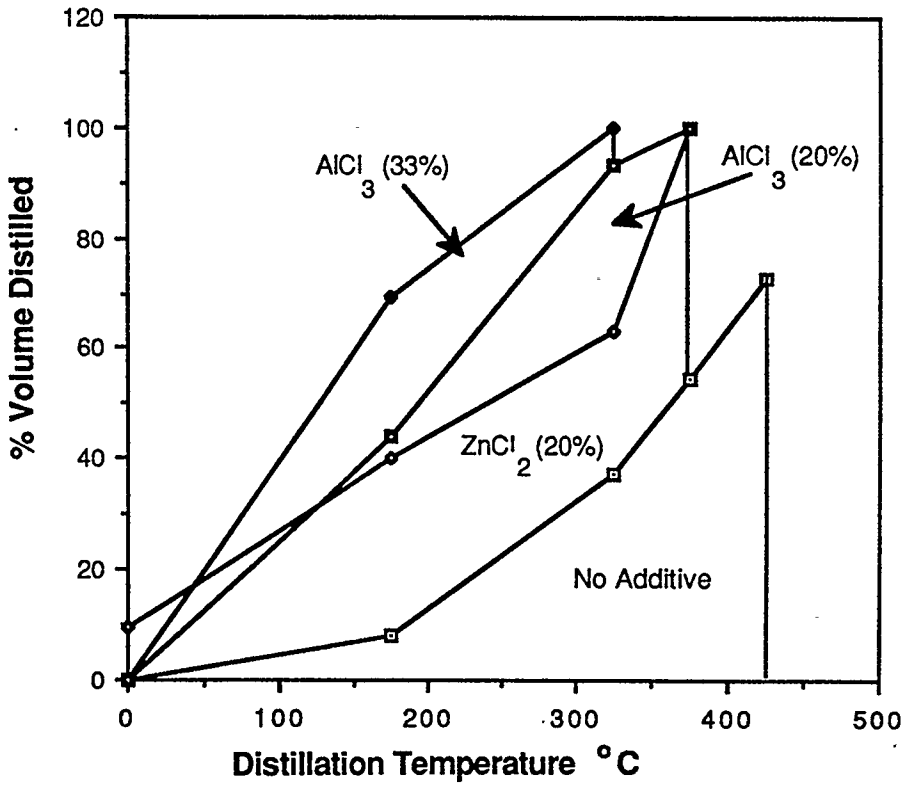


Figure 4. Volume CGO distilled at increasing temperatures for Lewis acids compared to control where no additive was used.

2.5.3 Analysis of CGO fractions using ^{13}C NMR

The next step was to analyse the fractions derived from the coker gas oils from the different coking runs. The ^{13}C NMR spectra of the fractions were

complex and the most useful way of interpreting the data was to compare the integrated area describing aromatic carbon with the total integrated area. This technique is superior to chromatographic separations used to estimate aromaticity since ^{13}C NMR will distinguish between aromatic and non-aromatic carbons of a compound such as tetralin, whereas the non-aromatic carbons would be misclassified based on a chromatographic separation.

Table 6 describes the results of these analyses. The lower the aromaticity, the better, especially in the diesel fraction (175-325°C).There is a relationship between the ^{13}C NMR derived aromaticity and the resultant cetane number [32-33] of the diesel fraction. Much lower aromatic carbon content is required in the diesel fraction if the standard of 40 (cetane number) required in Canada[1] is to be attained. For jet fuel a limit of 20% aromatic content is standard. Looking at the aromaticities of the fractions in the control run one can see that they increased steadily as the distillation temperature was increased. It is evident that again the small amounts of additives had little effect on the resultant aromaticities. Again the $AlCl_3$ runs were the most interesting. The aromaticity of the whole CGO for the $AlCl_3$ (20%) run was 18.1%, for the $AlCl_3$ (33%) 12.0%, compared with a figure of 30.6% for the control. The $ZnCl_2$ did not have a favourable effect on the aromatic content. Interestingly, its use caused significant increases in the carbon aromaticity of the diesel fraction and the whole coker gas oil. In fact it caused even higher aromaticity than the control coking run. Differences in other runs are smaller, if any. Care was exercised when studying the significance of small differences since some error in integration arises as a consequence of the phasing. Repeated calculation of the carbon aromaticity of a particular fraction indicated that Fac measurements were made with plus or minus 0.02 aromatic carbon points. One must also

remember that the fractionations had an associated error. It is possible to check

Table 6. ^{13}C NMR Fac measurements of the CGO fractions.

Additive	145-175	175-325	325-375	375-425	425+	Total Distil.
None (Mk 1)	0.19	0.22	0.27	0.31	---	0.27
$CaCO_3$ (5%)	0.21	0.19	0.27	0.31	0.40	0.35
HCE (5%)	0.23	0.18	0.30	0.34	0.39	0.33
MC (5%)	0.20	0.18	0.25	0.30	---	0.30
None (Mk 2)	---	0.26	0.29	0.30	0.34	0.31
$AlCl_3$ (5%)	---	0.27	0.29	---	0.36	0.31
$AlCl_3$ (20%)	0.17	0.25	---	na	na	0.18
$AlCl_3$ (33%)	0.11	0.09	na	na	na	0.12
Zinc chloride (5%)	---	0.25	0.28	---	---	0.29
Zinc chloride (20%)	---	0.35	0.34	0.35	0.34	0.37
Vanadyl-TPP (1%)	---	0.25	---	---	0.36	0.32
Cobalt-TPP (1%)	0.26	0.30	---	---	0.31	0.30
Nickel-TPP (4.2%)	---	0.33	0.30	0.35	0.36	0.39
$Ca(OH)_2$ (15%)	---	0.31	0.30	0.31	0.38	0.28
MgO (14%)	---	0.34	0.35	0.33	---	0.35
Ni stearate (11.5%)	---	0.33	0.26	0.36	0.36	0.34
Nafion (11.1%)	---	---	0.23	0.27	---	---

HCE=Hexachloroethane

MC=Methyl Cymanthrene

^{13}C aromaticity measurements by studying the ^{1}H NMR of the same fractions. The fractions from the Ni-TPP (tetraphenylporphine) run had higher carbon aromaticity compared to the control. This is also true of the MgO run. Further testing of these fractions using ^{1}H NMR and capillary GC-MS were required before being certain of the significance of these differences.

2.5.4.1 ^{1}H NMR Analysis

The spectra of these coker gas oil fractions were complex and therefore the most successful method for interpretation involved using a global analysis where assumptions are made based on the hydrogen environments found in chemical shift regions. Table 7 illustrates the cuts which were made. The signals within an assigned chemical shift region were then integrated and compared with those derived from different runs. A comparison could also be made of carbon (^{13}C) and proton (^{1}H) aromaticities (for a particular fraction) although one must remember that carbon aromaticity includes quaternary (carbons) whereas proton aromaticity does not take these into account.

2.5.4.2 Coker gas oil analysis

Initially, the whole bitumen was subjected to ^{1}H NMR analysis and compared to the coker gas oils derived on coking the bitumen with the various additives. The results of this analysis are illustrated in Table 8.

The integrations of the chemical shift ranges of the various H types are presented in Table 8 for the CGO's from various coking runs. It is striking that the values found in the starting bitumen were very similar to those of the coker gas oil where no additive was present. One knows from ^{13}C NMR analysis that aromatic carbon is created in the coking process.

Table 7. ^1H NMR chemical shift correlation chart.

Chemical Shift (ppm)		Assignment
6.0-9.3	H_{ar}	Protons attached to aromatic carbon
1.9-4.5	$H\alpha$	Protons attached to saturated α-carbon* or heteroatom
1.0-1.9	$H\beta$	Protons attached to a saturated β carbon(CH_3) or to a β,γ,δ (or more) carbon *(CH_2,CH)
0.5-1.0	$H\gamma$	Methylic protons on a γ (or more) carbon*

* With respect to an eventual aromatic ring

Obviously a large amount of aromatic carbon has been rejected, in the upgrading process, as coke. However, the upgraded coker gas oil still had about the same aromatic hydrogen content as the starting bitumen. Comparing the other hydrogen types, one can see (Table 8) that they were also very similar. This was significant in that although aromatic carbon is being rejected as coke, remembering that the presence of quaternary carbon is missed by ^1H NMR analyses, the aromaticity of the upgraded liquid is not improved. However, the upgraded coker gas oil is much less viscous than the starting bitumen and it has much lower boiling point characteristics.

Examination of the ^1H NMR analysis of the CGO (Table 8) showed interesting differences for the Lewis acid runs. Analysis of the upgraded coker gas oil from the $AlCl_3$ (20%) revealed that, compared to the control, there were

Table 8. ^1H NMR Analysis of H-type in Recovered Coker Gas Oils.

	Har	Hα	Hβ	Hγ
Whole Bitumen	0.07	0.17	0.50	0.26
Additive				
None (Mk. 1 Coker)	0.06	0.16	0.50	0.28
Calcium carbonate (5%)	0.07	0.17	0.50	0.26
Hexachloroethane (5%)	0.08	0.16	0.48	0.28
None (Mk. 2 Coker)	0.07	0.18	0.50	0.25
Aluminium trichloride (5%)	0.06	0.18	0.49	0.27
Aluminium trichloride (20%)	0.05	0.12	0.47	0.36
Aluminium trichloride (33%)	0.04	0.10	0.46	0.40
Zinc chloride (5%)	0.06	0.13	0.50	0.32
Zinc chloride (20%)	0.09	0.21	0.45	0.25
Vanadyl-TPP (1%)	0.10	0.16	0.46	0.29
Cobalt-TPP (1%)	0.07	0.13	0.49	0.31
Nickel-TPP (4.2%)	0.06	0.20	0.49	0.25
Calcium hydroxide (15%)	0.08	0.17	0.51	0.25
Magnesium oxide (14%)	0.06	0.17	0.49	0.28
Nickel stearate (11.5%)	0.08	0.15	0.50	0.28

TPP=Tetraphenylporphyrin.

lower aromatic, benzylic and increased Hγ protons. These same trends were found even more strongly in the $AlCl_3$ (33%) run. This suggested a reduction in the aromatic content of the fraction. Looking at the $ZnCl_2$ (20%) run, one finds that the trends were reversed, ie. there was now higher aromatic and benzylic and lower Hβ and Hγ protons, in the whole coker gas oil. Looking at other runs one can see differences in H-types for the VO-TPP and Co-TPP additives. Again these results need to be confirmed by capillary GC-MS analyses of the lower boiling fractions from these runs, to be sure that the differences are real and not arising from error in estimating the integrals of the different H-types.

2.5.4.3. Analysis of the CGO Derived Diesel Fractions

Examination of the diesel fractions of the same runs (Table 9) illustrated again the significant effect of the Lewis acid additives and to a lesser extent, in the $Ca(OH)_2$ and Ni-stearate runs. It was evident that the presence of $AlCl_3$ (33 wt %) caused a significant reduction in the aromatic and benzylic and increased the Hβ and Hγ proton content of the diesel fraction. The presence of $ZnCl_2$ (20 wt %) had caused the reverse, i.e. increased aromatic, benzylic and reduced Hβ and Hγ protons. The presence of $Ca(OH)_2$ appeared to have caused an increase in benzylic and a decrease in Hγ content of the diesel fraction. Ni-stearate seemed to have resulted in a slight increase in Hβ and slight decrease in Hγ protons.

Table 9. ^1H NMR Analysis of H-types in Diesel Fractions.

	Har	Hα	Hβ	Hγ
Whole Bitumen (uncoked)	0.07	0.17	0.50	0.26
Additive				
None (Mk. 1 Coker)	0.05	0.14	0.47	0.34
Calcium carbonate (5%)	0.04	0.14	0.50	0.33
Hexachloroethane (5%)	0.05	0.16	0.49	0.31
Methyl cymanthrene (5%)	0.03	0.17	0.48	0.32
None (Mk. 2 Coker)	0.05	0.16	0.48	0.32
Aluminium trichloride (5%)	0.06	0.18	0.45	0.32
Aluminium trichloride (20%)	0.07	0.11	0.46	0.37
Aluminium trichloride (33%)	0.02	0.05	0.49	0.44
Zinc chloride (5%)	0.05	0.20	0.48	0.27
Zinc chloride (20%)	0.09	0.23	0.41	0.27
Vanadyl-TPP (1%)	0.06	0.15	0.47	0.32
Cobalt-TPP (1%)	0.05	0.15	0.46	0.34
Nickel-TPP (4.2%)	0.05	0.17	0.49	0.29
Calcium hydroxide (15%)	0.04	0.22	0.48	0.26
Magnesium oxide (14%)	0.05	0.18	0.48	0.30
Nickel stearate (11.5%)	0.05	0.16	0.52	0.27
Nafion (11.1%)	0.05	0.18	0.49	0.28

TPP=Tetraphenylporphine

From the ^1H NMR data, it was possible to speculate on reactions which caused specific changes in integrations over the chemical shift regions (compared to equivalent fractions derived in the control). Figure 5 represents some of these reactions, thought to explain the data. (1) Dealkylation is characterized by the reduction in Hβ and Hγ protons. (2) Aromatization is characterized by loss of Hα and Hβ, and concomitant increase in the Har proton content and Fac. (3) Ring opening is characterized by a loss in Hα and a gain in Hγ protons.

Looking back to the observed NMR analyses of the whole CGO and diesel fractions it was evident that the presence of $AlCl_3$ caused the disappearance of aromatic species, characterized by decreased aromatic and benzylic with an accompanying increase in Hγ protons. The more $AlCl_3$ that was present, the lower was the aromaticity of the upgraded product. The presence of $ZnCl_2$ had the opposite effect, in that, now the aromatic, benzylic protons were increased and the Hβ and Hγ protons were decreased. This suggested that some aromatization (dehydrogenation) of previously hydroaromatic species had occurred.

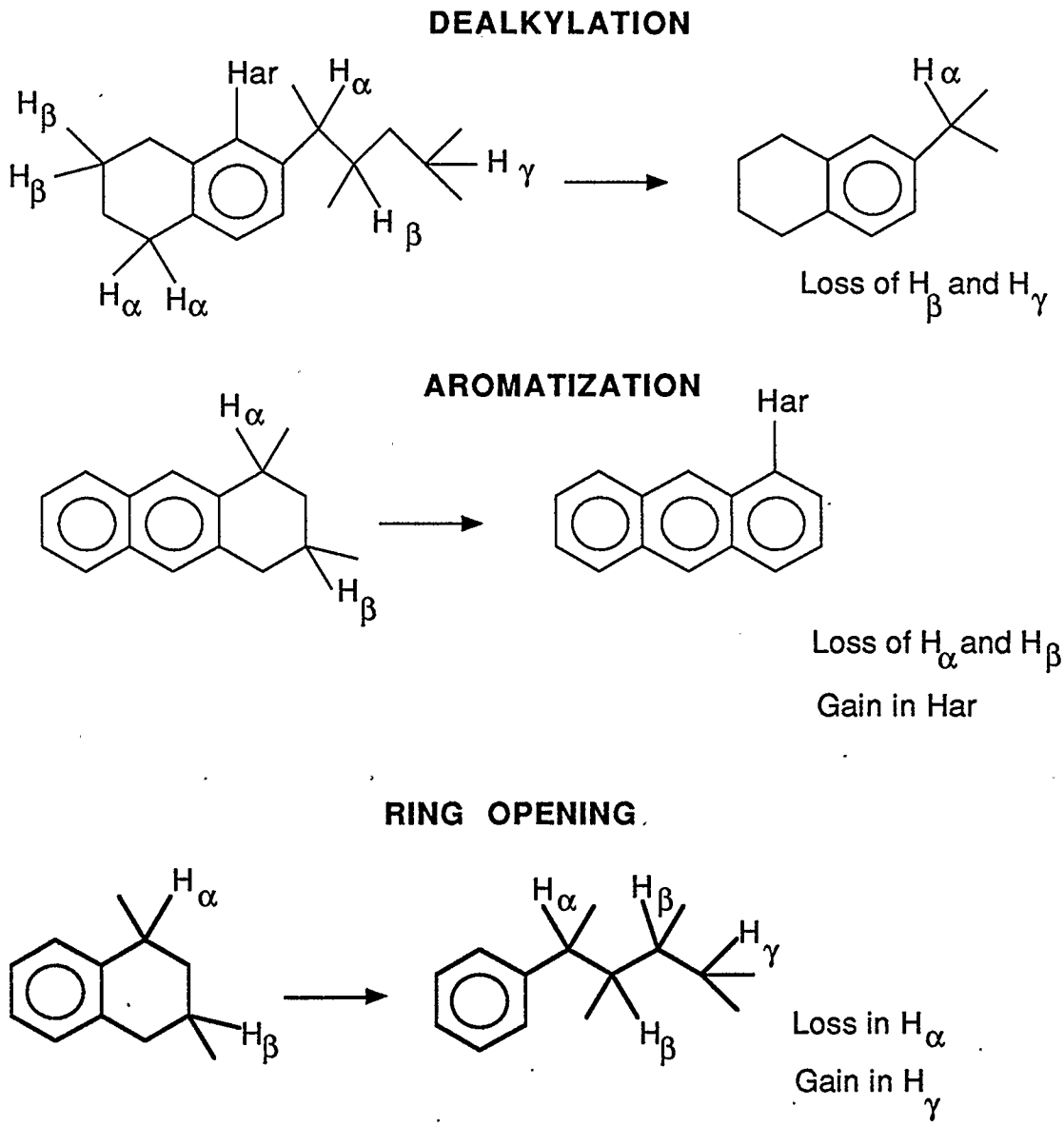


Figure 5. Reaction Types indicated by NMR analysis.

2.5.5 Capillary GC-MS Analysis

Analysis of the lower boiling fractions from the CGO's were carried out using capillary GC-MS to determine if various additives had any effect on the product distributions. Those analysed included the Lewis acid runs, as well as the VO-TPP, Co-TPP, Ni-TPP, $Ca(OH)_2$, MgO and Ni-stearate runs. The Lewis acid derived fractions were significantly modified. Analysis of the fractions from

the other runs failed to detect any major differences compared to the control, in terms of individual components present in the fractions. This was not considered as being conclusive evidence that the differences detected by NMR were unreal but they may have been too small to pick out in this mode of analysis.

Analysis of the low boiling fractions from the 5% $AlCl_3$ run revealed very little difference from the control fractions. When the additive concentration was increased to 33%, GC-MS analysis revealed that the CGO fractions had a very different constitution. The most obvious difference in the fractions from the Lewis acid runs, compared to the control, was the much increased complexity of the product distribution (see Fig 6 GC-MS TICs). The homologous series of 1-alkene/n-alkane (found in the control) were no longer present . This is illustrated in single ion chromatograms of masses 55 and 57 from the $AlCl_3$, $ZnCl_2$ and control fractions (Fig 7 and 8). At high $AlCl_3$ concentrations, the dominant species were now found to be substituted cyclohexanes, branched alkanes and substituted decalins. Interestingly, a number of substituted benzenes appeared in the 20% $AlCl_3$ run but these were lost when the additive concentration was increased to 33%. Again in the $ZnCl_2$ runs, at low concentration, little effect was seen in the product distribution. When the concentration was increased to 20%, the predominant species were now substituted benzenes (this is evident from SIC's of mass 77. Fig 9) and dihydroindenes. Less important components included substituted cyclohexanes and branched alkanes. In fraction 3 (225-275°C), substituted naphthalenes were also found to be an important feature.

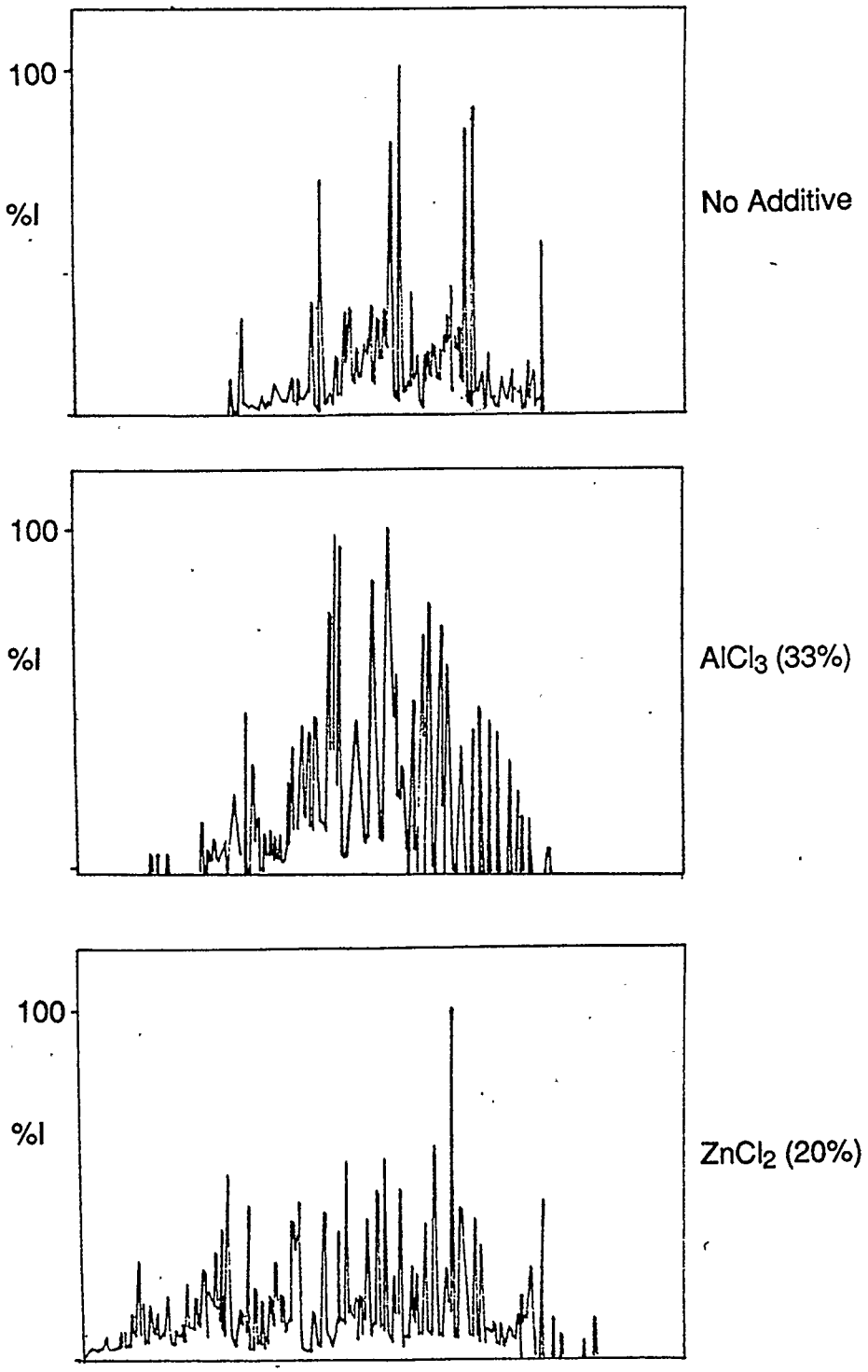


Figure 6. GC-MS TIC's for Lewis acid and control CGO's.

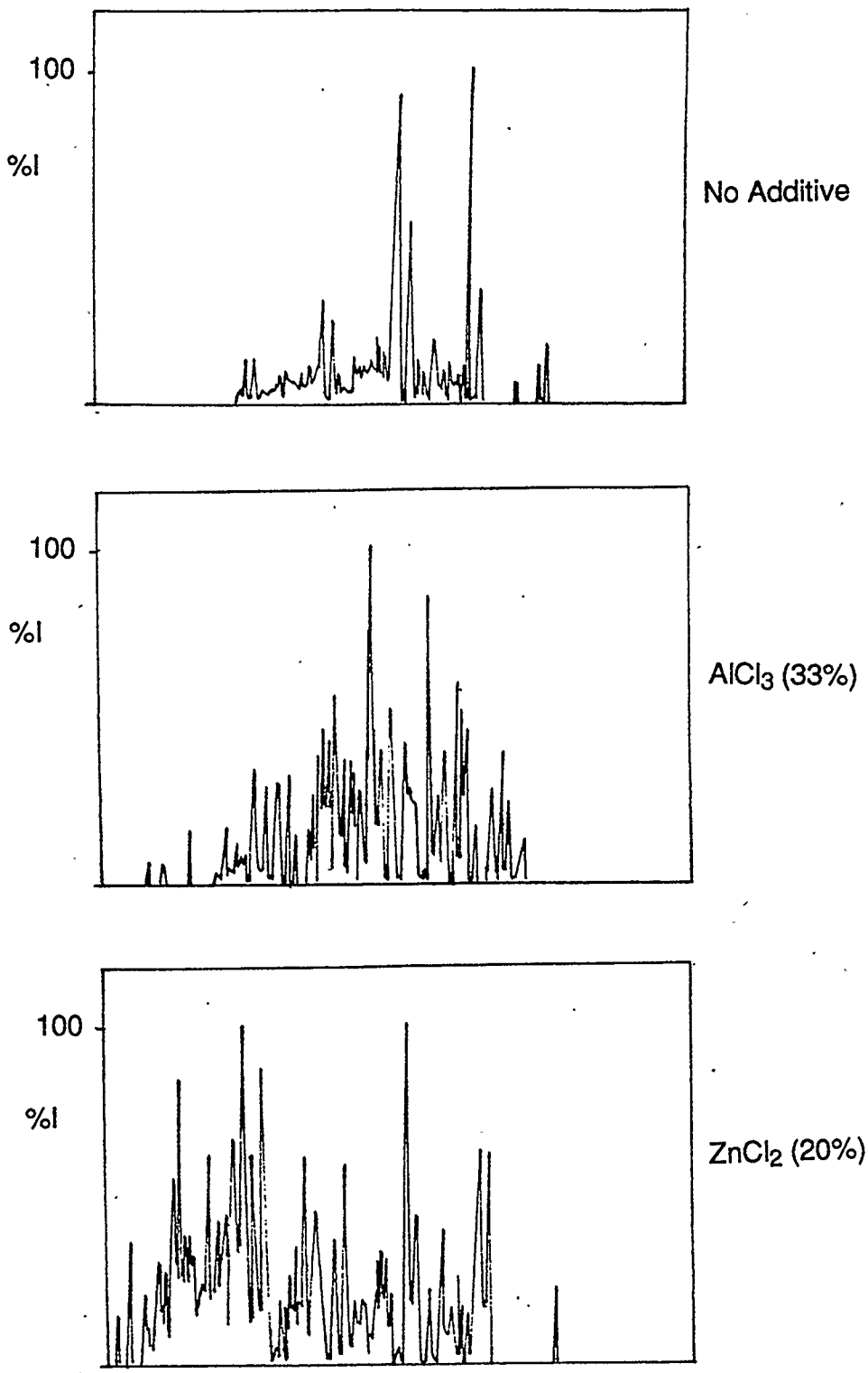


Figure 7. GC-MS SIC's (mass 55) for Lewis acid and control CGO's.

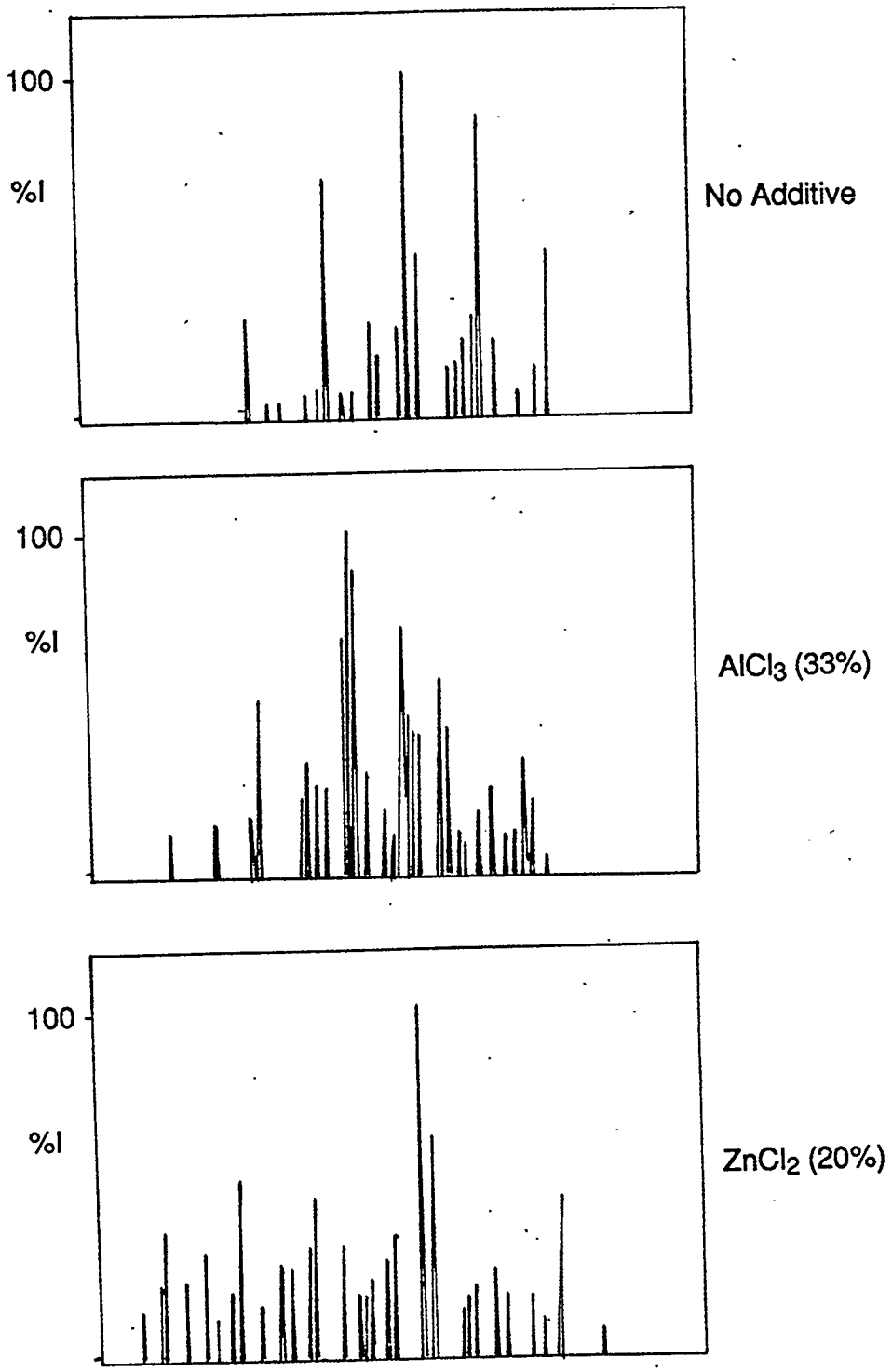


Figure 8. GC-MS SIC's (mass 57) for Lewis acid and control CGO's.

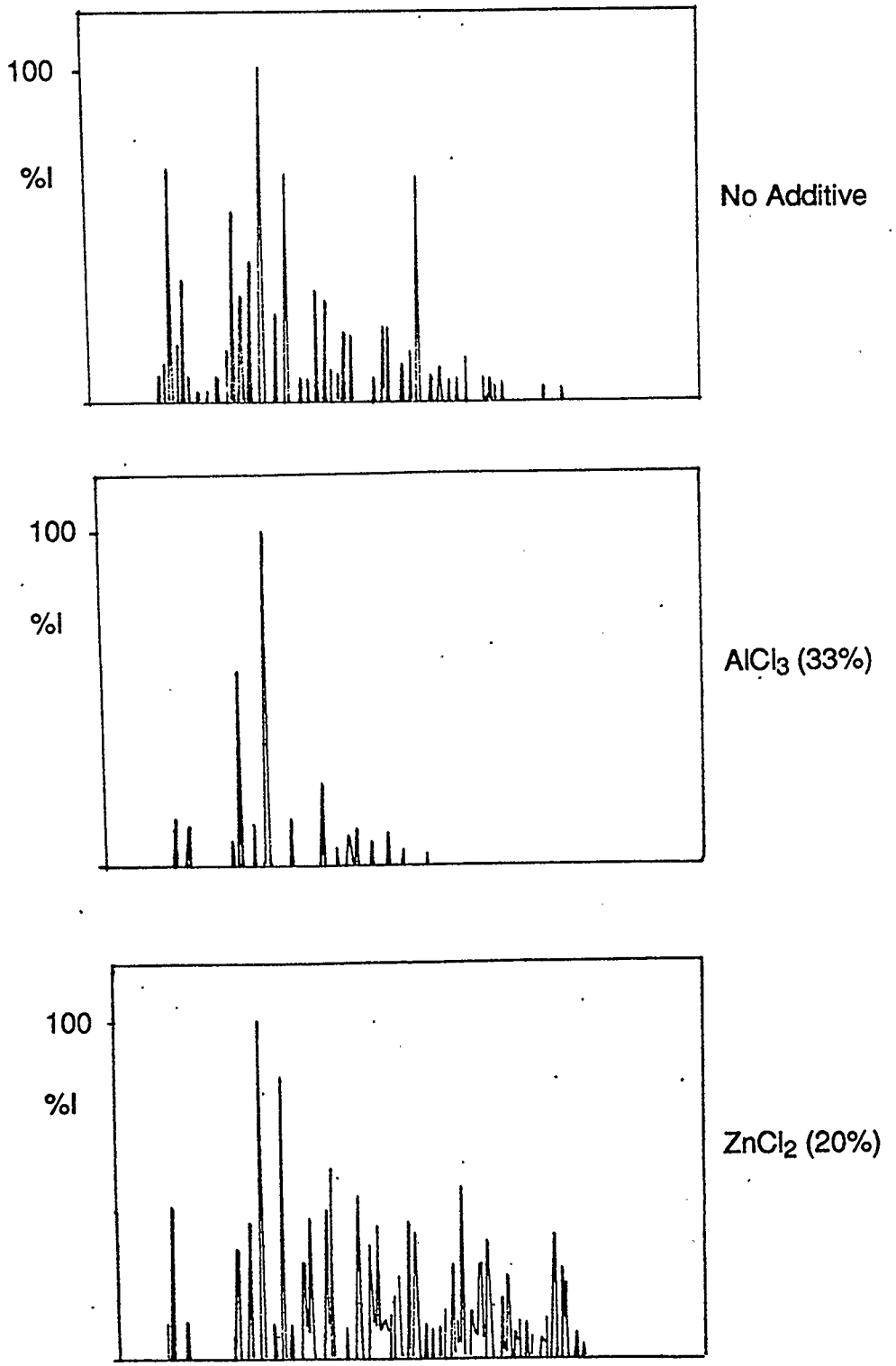


Figure 9. GC-MS SIC's (mass 77) for Lewis acid and control CGO's.

2.6 Further Discussion

It was evident that without an additive the average yield of coker gas oil (liquid product) was approximately 78-80% and the coke formed was approximately 14-16% of the starting weight of bitumen. The 6% which was unaccounted for was made up of low boiling gases which were not condensed at dry ice / acetone temperatures. These probably included H_2S, H_2, CO,CO_2,CH_4 and ethane. It is obvious that the presence of many of the additives, in small concentrations, had little or no effect on the product distribution (within the limits of experimental error). The most significant deviation occurred for the Lewis acid additives. Athabasca asphaltene is found to react with Lewis acids even below 100°C [31]. Both $AlCl_3$ and $ZnCl_2$ are known to catalyze coal liquefaction and solubilization [34-41]. In this work, the addition of large amounts of these compounds led to undesirable, increases in the coke formed and a concomittant decrease in the amount of coker gas oil collected. Considering the type of reactions which Lewis acids are known to catalyse, this result may not be surprising. In studies carried out by Bell et al. [42-43] it was found that $ZnCl_2$ and $AlCl_3$ catalysed the cleavage of aliphatic linkages between aromatic nuclei [43] but not the cleavage of direct aryl-aryl bonds between such nuclei. $AlCl_3$ was found to be significantly more active than $ZnCl_2$ but caused significant tar formation via Scholl condensation [42] which (Fig. 10) would account for the observed, increased coke formation and the reduction in aromaticity of the recovered coker gas oil as indicated in ^1H NMR analysis. The aromatic portion of the bitumen, which previously appeared in the upgraded CGO, has now been involved in $AlCl_3$ catalyzed coke forming reactions. This is further shown in the GC-MS analysis of the lower boiling fractions of the $AlCl_3$

runs where the disappearance of the substituted benzene compounds was found.

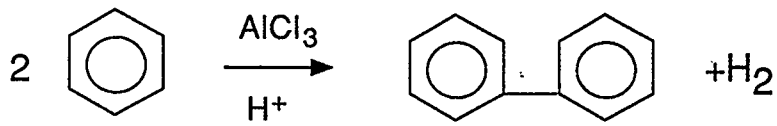


Figure 10. Friedel-Crafts or Scholl Arylation.

The Hγ proton content of the $AlCl_3$ derived fractions was found to.have increased, compared to the control (Tables.8 and 9). Again this was consistent with the loss of the aromatic content of the CGO due to $AlCl_3$ catalyzed condensation reactions. Aluminium trichloride ($AlCl_3$) is also known to catalyze ring closing reactions (Figure 11) [42-44]. This reaction would explain the loss of the 1-alkene/n-alkane series and the appearance of the substituted cyclohexanes and decalins. $AlCl_3$ also catalyzes cationic polymerization of alkenes [45] to form longer, but usually branched alkanes, which together with its tendency to catalyze alkane rearrangements [46], would explain both the high degree of complexity of the fractions derived from the $AlCl_3$ runs (from GC-MS analysis), and the presence of the branched alkanes.

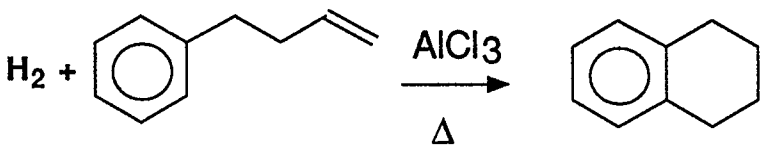


Figure 11. Ring closure catalyzed by $AlCl_3$.

The $ZnCl_2$ situation was quite different judging from the upgraded product analysis. The carbon aromaticities of both the whole coker gas oil and the diesel fraction were actually higher than in the control situation

(Tables 8 and 9). The ^1H NMR analysis further reinforced this conclusion and the results were exactly opposite those found for the $AlCl_3$ runs. In both fractions, the values of Har and Hα were higher and Hβ and Hγ protons were lower. The GC-MS analysis showed the presence of substituted benzenes, dihydroindenes and naphthalenes. These were the dehydrogenated equivalents of the components found in the analysis of the $AlCl_3$ runs. The dehydrogenating effect of $ZnCl_2$, has also been discussed by Strausz et al. [31], who found extensive dehydrogenation of hydroaromatic molecules. In the present work GC-MS analyses revealed that the series of 1-alkenes/n-alkanes, found in the control CGO, had disappeared when $ZnCl_2$ was used as an additive. It seems as if the same broad types of coke forming reactions had occurred in the $ZnCl_2$ runs with the addition of the dehydrogenation causing the highly aromatic character of the upgraded product fractions.

2.7 Conclusions

The large decrease in yield of CGO with it's attendent low aromatic character suggested that the aromatic compounds present in the upgraded bitumen were the main coke forming agents. Both the NMR and GC-MS analysis confirmed that the reactions important in the coke formation, in the presence of the Lewis acids, involved ring closing, arylation and dehydrogenation reactions (especially in the case of $ZnCl_2$). Extensive alkane rearrangement (via carbonium ions) led to a complex mixture of branched alkanes being formed. GC-MS analysis pointed to the presence of aromatics and alkenes as prime coke forming precursors.

With regard to the original objectives of this work, one can see that small amounts of slurried additives had little or no effect on the resultant CGO

composition. From the observed results it appeared that the coking process was basically a thermal one and only when large amounts of Lewis acids were added, which resulted in a change of mechanistic pathway (from mainly radical to carbonium ion), was it possible to perturb the system enough to notice any major difference in the upgraded product distribution. This approach did give new insight into coke formation, via a carbonium ion pathway.

Obviously, a different approach is required to probe the thermal mechanisms important in the coking process. A probe is needed which will involve itself in the upgrading process, be observable, and yet not perturb the system, mechanistically. A new approach to this problem is addressed in the next chapter.

Chapter 3

d_{10}-pyrene as a Mechanistic Probe in the Coking Process

3.1 Introduction

Coking of bitumen involves old technology but there have been only a few reports concerning the organic reaction mechanisms which occur during the coking [47]. It is, however, generally conceded that there has been a considerable average molecular weight reduction through presumed "cracking reactions".

The previous chapter reported attempts to study coking mechanisms by adding compounds of known chemical action, thus perturbing the system, and studying the effect on the upgraded product. It is impossible to follow the reactant (Syncrude coker feed bitumen) through to products (gases, CGO and coke), during the course of the coking process, because of the complexity of the bitumen. One needs to add some chemical species to the bitumen, prior to coking, and follow it through the upgrading process, in order to learn more about coking mechanisms.

Before discussing a suitable probe, it is important that the reader is aware of the species found in the bitumen and the ways in which they are known to react when pyrolyzed.

Polynuclear aromatic compounds are known to be important constituents in bitumen. The varieties of these compounds found in bitumen include; fluorene, phenanthrene, anthracene, pyrene, chrysene, benzofluorene, benzopyrene, picene, benzoperylene and some of their methyl derivatives [25].

3.1.2 Pyrolysis of Polynuclear Aromatic Compounds

Aromatic compounds derive their unusual stability from the delocalization of π-electrons among the ring molecular framework. For aromatic molecules to react, their delocalization energy must be overcome.

Since this delocalization energy is often large, overcoming the initial destabilization is the rate determining process. This means that the reactivity of aromatic compounds should be related inversely to their delocalization energies. This relationship was found to hold in the reactivity towards a methyl radical [48] of a series of aromatic hydrocarbons.

Polynuclear aromatic compounds can be transformed thermally into carbonaceous residues during pyrolyses. The chemistry involved in the transformations is complex and involves: bond cleavage, polymerization, molecular rearrangement and H-transfer reactions. Treatment of the aromatic compound at 350-500°C leads to a complex pitch mixture. Further thermolysis at >500°C leads to the formation of a true coke. The pyrolysis of anthracene has been studied extensively [49-51]. The initiation mechanism is not well understood. One possibility is the formation of the anthryl radical by a disproportionation reaction as shown in Figure 12

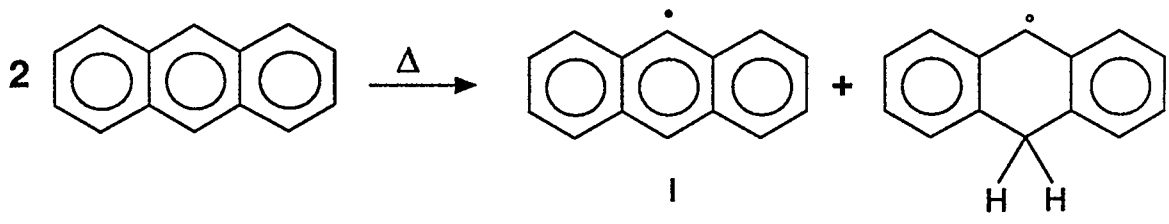


Figure 12 Formation of the Anthryl Radical by a Disproportionation Reaction.

This reaction would be expected to proceed slowly because of the instability of radical I. When the products of pyrolysis of anthracene were

analyzed it was found that dimers (which are not only the 9,9'- but the 2,9-dimer and many others) were found as well as dihydroanthracene. Polymerization was the dominant reaction occuring in the pyrolysis of aromatic hydrocarbons. Analysis of the products of the pyrolysis of anthracene at 440°C by gel permeation chromatography (GPC) showed the presence of dimers, trimers, tetramers and higher oligomers [52] of up to 10 anthracene units. This result was confirmed by FDMS (Field desorption MS) analyses [53]. The complexity of this pitch was similar to those extracted from a coal or petroleum source.

This oligomerization process could certainly be one way of explaining coke formation. A second modification involves initial oligomerization of the anthryl radicals and formation of a stable odd-alternate radicals in the second stage condensation process through loss of a hydrogen atom as shown in Figure 13. By this mechanism, low molecular fragments are stabilized by the released hydrogen atoms and at the same time higher molecular weight is being generated through these condensation reactions.

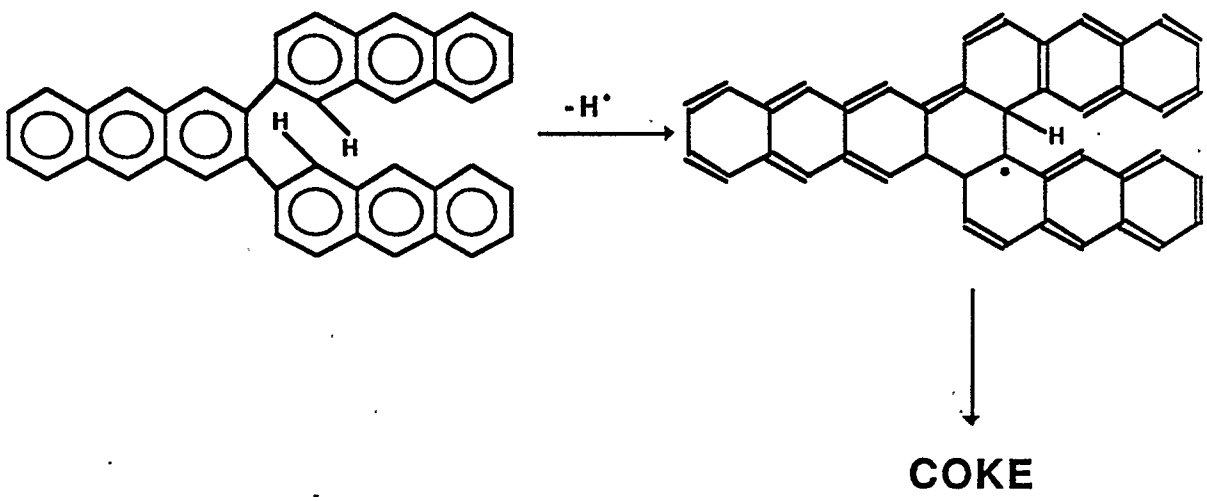


Figure 13. Possible mechanism for formation of stable π radicals during polymerization of anthracene.

Pyrene was found to dimerize at 500°C and can form extensive sheets at higher temperatures. In all of these cases dehydrogenative condensation was found to have occurred [54]. Naphthalene was more stable than anthracene and required a higher pyrolysis temperature to form the pitch and coke [55].

3.1.3 Polynuclear Aromatic Compounds as H-Shuttles

Pyrene and various other polynuclear aromatic compounds were found to be useful coal liquefaction solvents [56-60]. Derbyshire et al. [56] found that coal conversions of up to 90% were obtained using pyrene as the liquefaction solvent. In a hydrogen atmosphere, enhanced liquefaction yields were achieved. Analyses of the pyrene-coal reaction products revealed the presence of hydro- and alkylated pyrenes. Obviously, the high boiling liquefaction solvent did more than act as a physical solvent but was also involved in H-shuttling reactions stabilizing reactive fragments which would otherwise engage in regressive polymerization reactions. Kwon et al. [55] compared anthracene and phenanthrene as coal liquefaction solvents and found anthracene to be a more suitable because of it's greater H-shuttling ability, i.e. it formed the dihydro-species with more ease than phenanthrene.

Deuterium isotopic labels have been successfully used to follow coal upgrading reactions [61-64]. The label is usually introduced as deuterium gas or as a D-donor (d_{12}-tetralin). The label incorporation is then followed into the products of the upgrading process, using ^2H NMR. Knowing that aromatic compounds can act as H-shuttles it seemed reasonable that a deuterated equivalent could be added to the bitumen and coked. The extent and mechanisms of the shuttle reactions could then be followed by examination of the upgraded material using ^2H NMR.

3.2 Objectives

With the object of development of additives which might decrease the amount of coke formation, it was decided to study in more detail, some of the organic reactions taking place during thermal coking. It was hoped that addition of a suitable deuterium probe to the bitumen would allow a better understanding of the mechanisms important in the coking process.

3.3 Stategy

It was decided that a small amount of d-10 pyrene should be added to the bitumen which would be coked. It was hoped that the pyrene would involve itself in the coking process (as a H/D-shuttle) and the environment of the label could be discovered in the product coker gas oil fractions using ^{2}H NMR. It was also anticipated that recovery of residual, exchanged, pyrene and MS analysis would reveal the level of exchange which happened at the coking temperature (see Figure 14). Analysis of the recovered pyrene by ^{1}H NMR would show any selectivity in the exchange of protons into the pyrene.

The rationale behind this experiment is multifold:

1. Pyrene has a boiling point which is high enough so that it remains dissolved in the bitumen well into the coking temperature range.

2. Pyrene has the potential to serve as a hydrogen donor but only if it is first reduced, i.e. it would obviously not initiate hydrogen donor processes but is capable of serving as a convenient "detector" for such reactions (hydrogen shuttling). It is known to greatly enhance coal conversion in this capacity [65]. The presence of dihydropyrene (1.9% weight of the original pyrene) has been detected in the pyrolysis of Monterey coal in the presence of pyrene, under hydrogen pressure at 400°C for 1 hour [65]. If pyrene does become involved in coke formation then deuterium, liberated in the condensation process, would be

free to stabilize radical fragments. This mechanism of stabilization could then be studied using ^2H NMR to follow the incorporation.

3. If indeed (deuterium) donor reactions do occur, then the recovered pyrene can be analyzed for proton content. Since there are initially three different types of (deuterons) in pyrene, any preferential exchange involving these different sites will hopefully provide specific mechanistic information as to the type and specificity of reactions occuring during the coking.

4. If deuterium donor reactions do occur, the resulting deuterium content in the coker gas oil fractions can easily be investigated on a "global" basis by ^2H NMR spectroscopy or by MS for the individual components.

5. Some of these deuterium atoms transferred to the coker gas oil may be irreversibly incorporated, whilst others may be back exchangable if one re-exposed the gas oil to ordinary h_{10}-pyrene under conditions similar to those used in the original coking reaction. Such exchange reactions would provide information on the kinds of reactive intermediates which are produced either reversibly or irreversibly during the coking process.

3.4 Experimental

Syncrude coker feed bitumen (25g) with 0.4g d_{10}-pyrene (obtained from MSD at 98% isotopic purity and used without further purification) slurried into it (the bitumen was at 50°C to make stirring possible), were placed into the lab scale coker (described in chapter 2) and the power was switched on. Heat-up, from room temperature to the final coking temperature of around 480°C, took 2 hours to achieve. Once the coking reaction was complete, coker gas oil (20.3g) was collected and subsequently fractionated on a spinning band distillation column in the same manner as previously described in chapter 2. The yield of coke was also quantified (4.8g). The coker gas oil fractions were

subjected to ^2H NMR analysis to examine deuterium incorporation into the different boiling ranges. The residual d-pyrene was then collected (mainly from fraction 5) and analyzed using direct probe MS, in order to be able quantify the amount of exchange occuring during the coking reaction. The recovered pyrene was finally analyzed using ^1H NMR, in order to study the selectivity of any exchange from the d-10 pyrene. This experiment was then repeated to be sure of reproducibility.

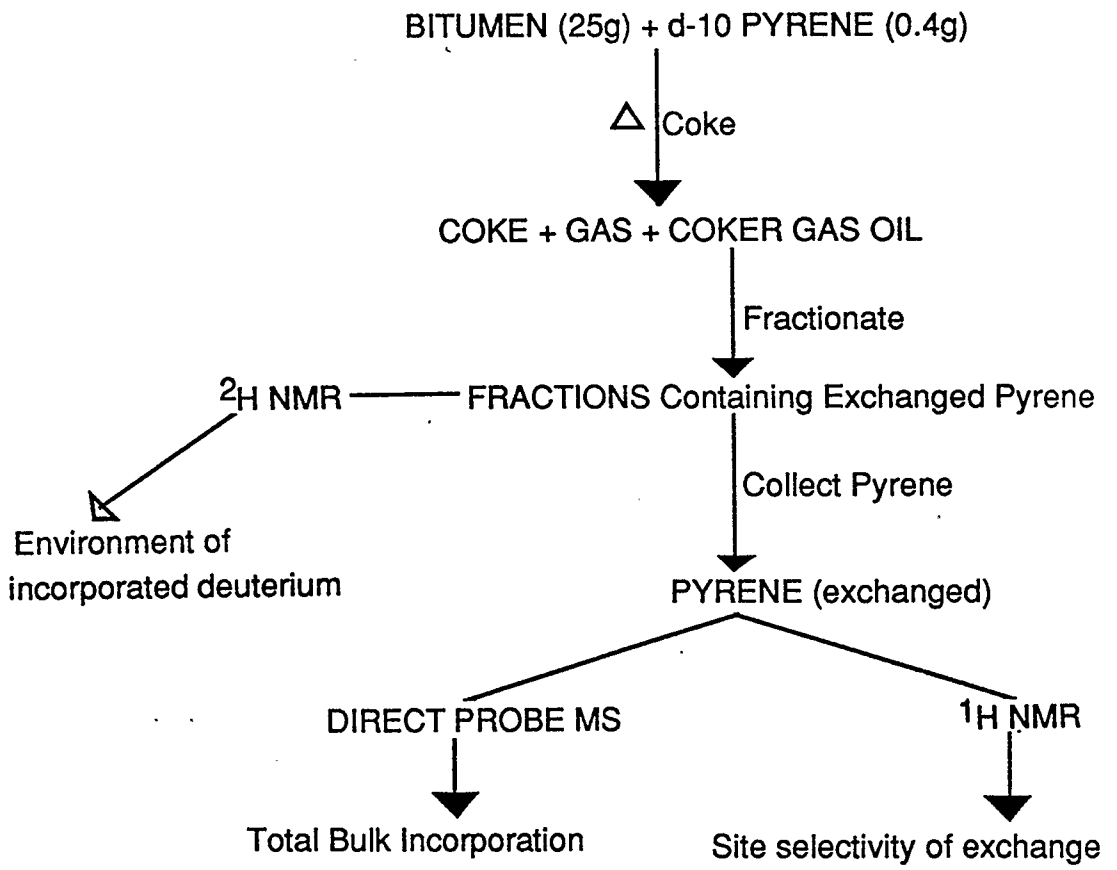


Figure 14. Schematic of d-pyrene experiment.

3.5 Results and Discussion

3.5.1 ^{1}H and ^{2}H NMR Analyses of Recovered CGO Fractions

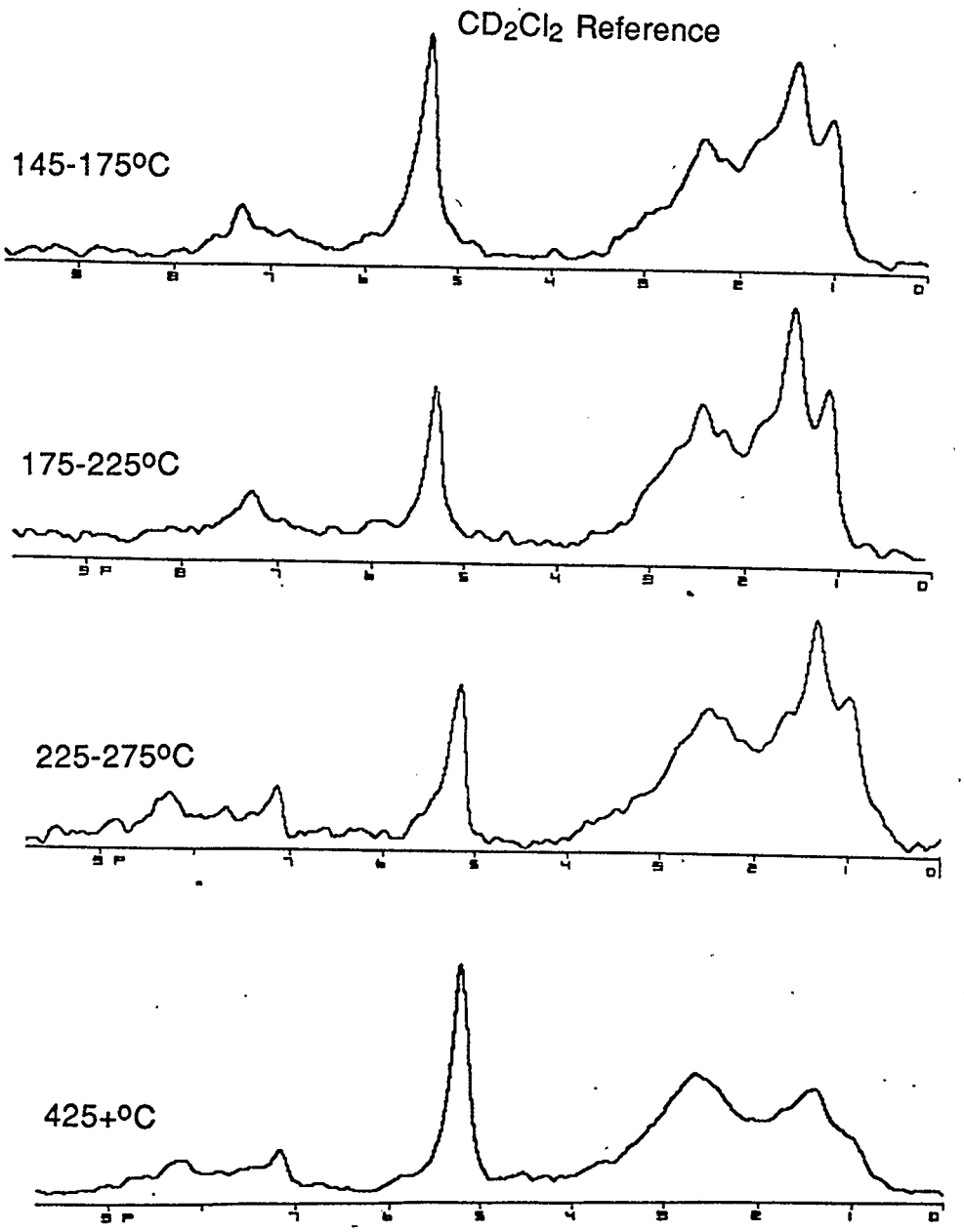


Figure 15. ^{2}H NMR of the recovered CGO fractions.

Figure 15 illustrates the ^2H NMR spectra obtained for the different boiling fractions. The fraction containing the majority of the recovered d-pyrene (fraction 5, 325-375°C) is not shown because it was completely dominated by a ^2H peak for the recovered d-pyrene. Pyrene was recovered (purified by sublimation and recrystallization) in near quantitative yield (both by actual recovery and estimates based on quantitative GC measurements) suggesting that the pyrene was not involved in coke formation and was therefore acting as a true shuttling agent. There was also no evidence for dimerization or hydrogenation of the pyrene. In Figure 16 the global data from the spectra are compared for earlier and later boiling fractions. Immediately obvious, is the fact that deuterium incorporation was extensive and had occurred in all possible environments.

Table 10. Global H/D type analysis of the coker gas oil fractions from coking experiment.

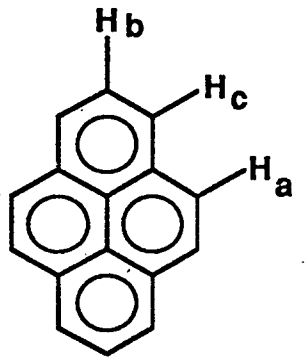
B.P. Range of Fraction (°C)	Aliphatic (0.-1.9ppm)		Benzylic (1.9-3.2ppm)		Aromatic (6.0-10.0ppm)	
	^2H	^1H	^2H	^1H	^2H	^1H
145-175	0.57	0.84	0.34	0.14	0.09	0.02
175-225	0.53	0.80	0.38	0.14	0.09	0.06
225-275	0.50	0.78	0.35	0.16	0.15	0.06
>425	0.37	0.77	0.47	0.17	0.16	0.07

3 deuterium NMR regions were assigned:

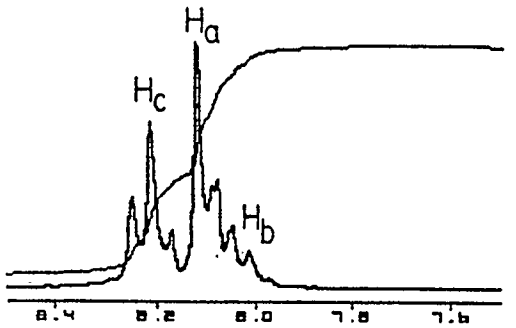
1. aromatic (6-10ppm)
2. benzylic, allylic etc.(1.9-3.2ppm)
3. aliphatic (0.5-1.9ppm)

The latter division is arbitrarily set and represents only a qualitative measure of the corresponding hydrogen/deuterium types. For comparison purposes (Table 10), the corresponding measurements for ^1H NMR analyses of coker gas oil fractions, produced in work reported in chapter 2 are shown. A comparison of the two sets of data gives one some idea of those degraded molecules which have interacted at some point with pyrene (or dihydropyrenes) in contrast to species which may have formed in other ways. It is interesting to note the way the chemical environments available for exchange varied as the boiling-point of the fraction increased. The aliphatic region decreased whilst the aromatic and benzylic regions increased. These trends were also followed when studying the deuterium incorporation. By comparing the fractions of deuterium / hydrogen types in Table 10 it was evident that deuterium has found its way into more benzylic sites than expected on a purely statistical basis.

3.5.2 ^{1}H NMR Analysis of Recovered d-Pyrene



Pure h_{10}-pyrene



Recovered (originally d_{10}-pyrene)

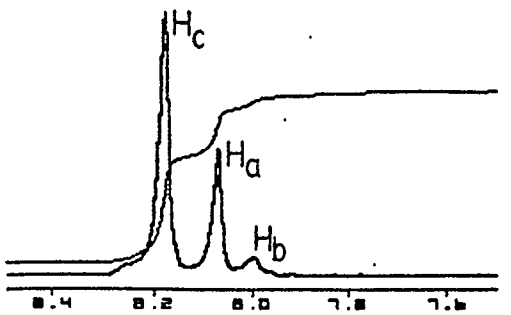


Figure 16. ^{1}H NMR of recovered pyrene compared to pure d-10 pyrene.

The ^1H NMR spectrum of the recovered pyrene was compared in Figure 16 to that of the pure h-10 pyrene. It was immediately obvious that a selective H-D substitution had occurred and that the ring positions most exchanged by protons were in environment **c** followed by **a** and least substitution in position **b** (according to Fig 16 where the different environments in pyrene are labelled). This selectivity can be explained if one considers the energies of the radicals produced on addition of a hydrogen atom to the d-10 pyrene molecule. Theoretical calculations carried out by Herndon [66-67] suggested that the most stable radical was formed by addition to position **c** followed by **a** and lastly **b**. These calculations were based initially on the premise that the enthalpies of radical addition to polyaromatics could be calculated from the number of Kekule structures of the molecule and it's radical. This premise was confirmed by SCF-MO calculations [68]. A similar relevant result was found in the reaction of d_8-naphthalene with an Illinois No.6 coal, by King et al. [62]. The recovered naphthalene was found to have exchanged more at the 1 position than the 2. This result would be expected on the basis of radical stability, on addition of a hydrogen atom to d-naphthalene.

3.5.3 MS Analysis of Recovered d-Pyrene

The total amount of proton exchange could be calculated from a direct probe MS (Figure 17) of the recovered pyrene. The most intense peak in the molecular-ion envelope was still the original d-10 species and an approximate averaging of the various peaks gave an overall proton incorporation of 6-9%. Assuming that this deuterium had all gone into the coker gas oil fractions, the total deuterium content of the latter was small. The presence of the residual pyrene in certain coker gas oil fractions (275-425°C) made a direct D/H

determination difficult.

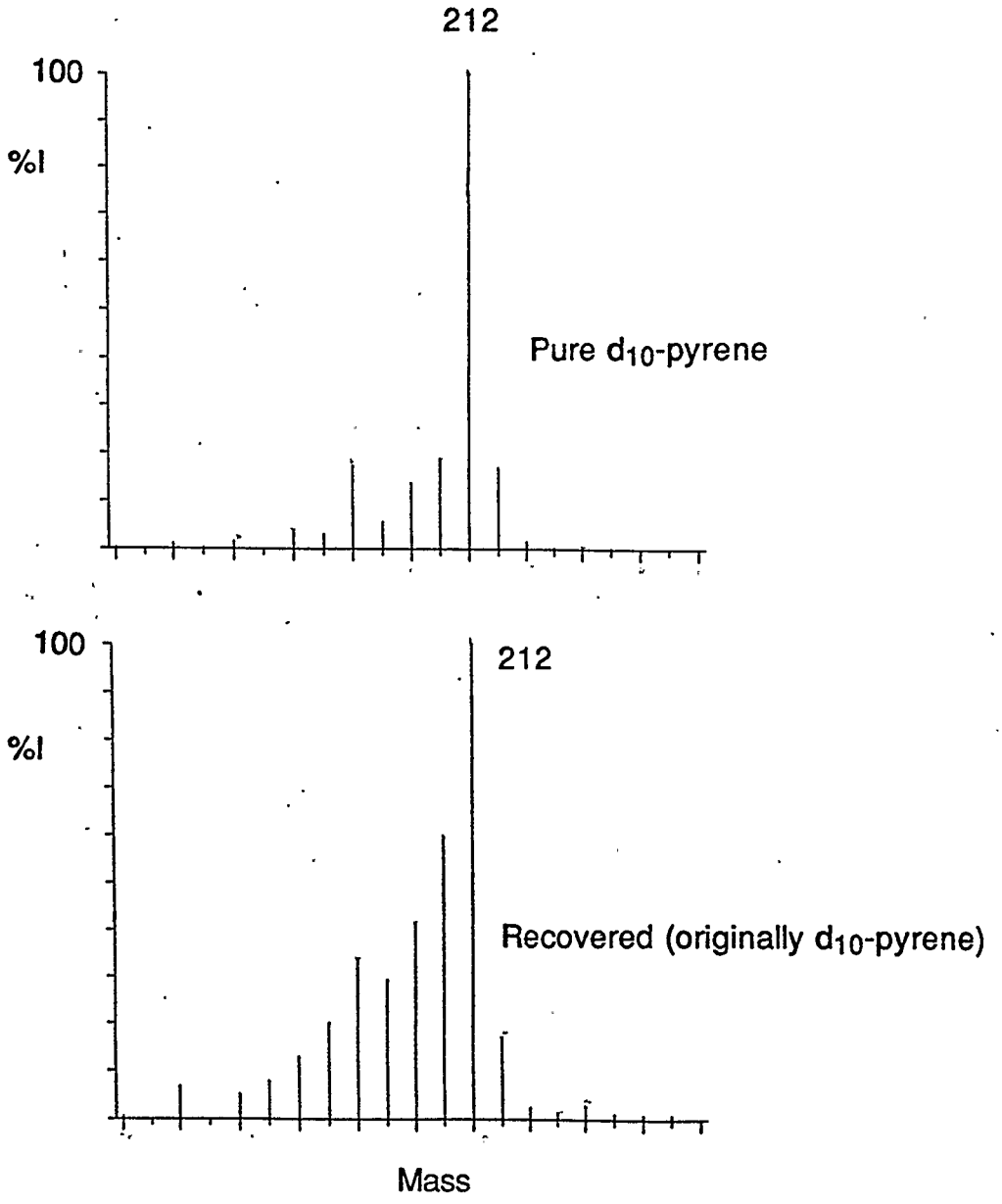


Fig 17. Direct probe MS analysis of the recovered pyrene.

The fact that the deuterium incorporation into the coker gas oil was small and found in so many different environments indicated that hydrogen mobility was very extensive during coking, although the Figure 17 data also showed that one does not have a complete equilibrium situation in the hydrogen / deuterium mobility.

3.6 Further Experimentation

In order to assess whether the observed deuterium incorporation was reversible, a further experiment was carried out in which a high boiling (375-410°C) coker gas oil fraction (obtained from the distillation of the recovered exchanged coker gas oil) was heated to approximately 450°C for an hour in a tube bomb (described in chapter 4), in the presence of h-10 pyrene (obtained from Aldrich at 99% purity and sublimed before use). The pyrene (originally h-10) was then recovered and monitored for deuterium content using ^2H NMR. The spectra from this experiment are shown in Figure 18.

It was evident that the exchange from the d-pyrene was low (from MS analysis) and only slightly above natural abundance levels. Comparison of the spectrum of natural abundance deuterium in h-pyrene with that from the recovered (originally h-10) pyrene, showed that some deuterium from the CGO fraction had been back exchanged. This indicated that there was indeed a reversible element of the whole deuterium incorporation. The next step was to obtain and compare the ^2H NMR of the fraction (after back exchange with h-pyrene) to that already studied (before back exchange). This analysis showed that the D type involved in the reversible exchange was the benzylic / allylic portion, i.e. the spectrum of the recovered coker gas oil fraction was depleted in

benzylic deuterium. The deuterium exchanged into the recovered (initially h_{-10}) pyrene, again with selectivity already described.

3.6.2. ^2H NMR Analysis of Recovered, exchanged, h-pyrene

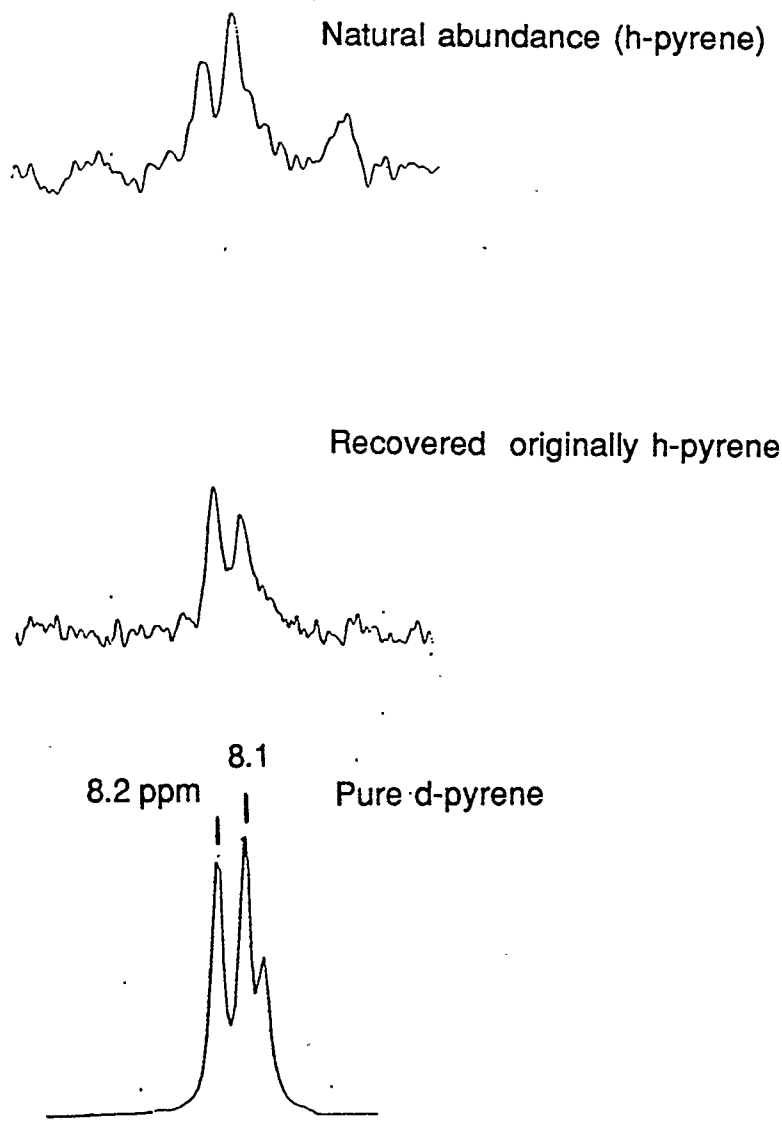


Figure 18. ^2H NMR analysis of pyrene recovered from back exchange reaction compared to pure d-10 and natural abundance deuterium in h-pyrene.

3.7 Model Exchange of h-pyrene and d-tetralin

In order to determine if the observed selectivity of exchange into the labelled pyrene was directed by the presence of the bitumen, it was decided that a series of model exchange reactions should be carried out between a suitable D-donor and h_{-10} pyrene at temperatures around that experienced in the coking experiment. One hoped to see the same selectivity in the exchange of deuterium into the pyrene, as was noted in the bitumen experiment. One also wanted to explore the temperature dependence of the selectivity. These model exchange reactions were carried out in tube bombs at the temperatures shown in Figure 19 for a period of an hour.

3.7.2. Direct Probe MS Analysis of the Recovered h-Pyrene

Once the pyrolyses were complete, the exchanged pyrene was recovered and analysed by direct probe MS in order to discover the extent of substitution of deuterium into the h-pyrene. The results of this analysis is shown in Figure 19.

From the MS data (Figure 19) it was evident that the extent of exchange varied with the exchange reaction temperature. At 400°C the extent of exchange amounted to 17% of the available sites in the recovered pyrene. At 450°C, not surprisingly, the extent of exchange had increased substantially, to 55% of the available sites. It must be remembered that the proportion of the 3 different available sites. 40% are H**c**, 40% are H**b** and 20% are H**a.** Therefore it was known even before ^{1}H NMR analysis that the site selectivity at 500°C would be lower because of the high degree of overall exchange.

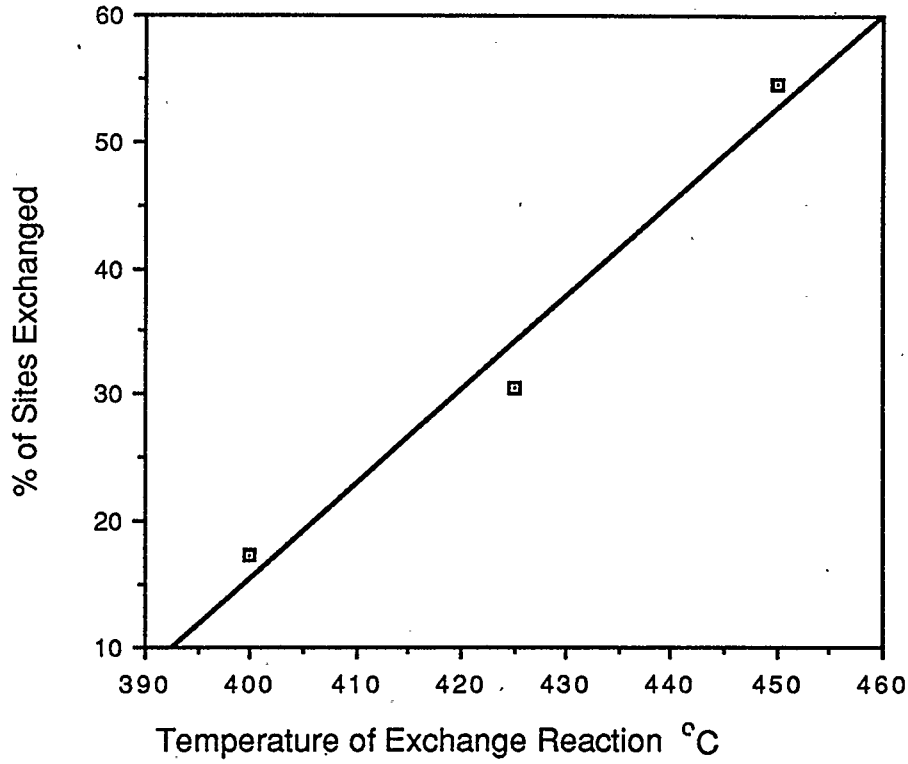


Figure 19. Direct probe MS analysis of the recovered, exchanged (originally h-10) pyrene, illustrating the extent of exchange occuring at various temperatures.

3.7.3 ^{1}H NMR Analysis of the Recovered Pyrene

The next step was the analysis of the recovered pyrene, using ^{1}H NMR in order to learn the site selectivity of the exchanged deuterium. Results of this analysis are illustrated in Figure 20.

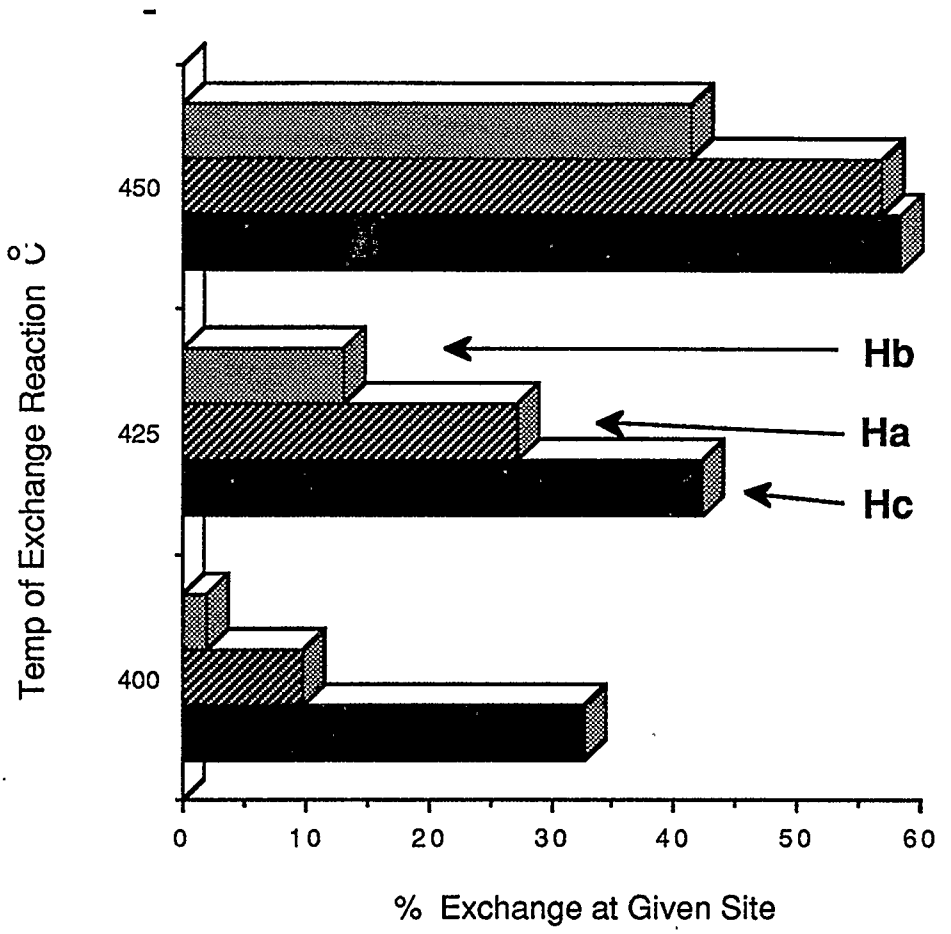


Figure 20. Selectivity of exchanged h-pyrene in the model exchange reactions.

Looking at the results of the ^1H NMR analysis, it is evident that at 400°C the site selectivity was high and that the preferred site of exchange was Hc followed by Ha and lastly Hb. This matched exactly the order seen in the bitumen/d-$_{10}$ pyrene coking experiment. As the temperature of the model exchange reaction was increased, the selectivity quickly diminished. At 450°C the selectivity was found to be very low.

3.7.4 Condensation of Pyrene

An interesting result which was not anticipated (under these pyrolysis conditions) was the discovery, by MS analysis, of a dimer of pyrene, recovered from the model reaction mixture, at 450°C (Fig 21). This was not completely surprising considering what was said about oligomerization on pyrolysis of various pure polynuclear aromatic hydrocarbons [53, 69], however, it must be remembered that in this situation there were H-donor species available from the bitumen, which could partially hydrogenate the pyrene molecules to give pyrenyl radicals which could then couple in a termination step of an overall free radical chain process.

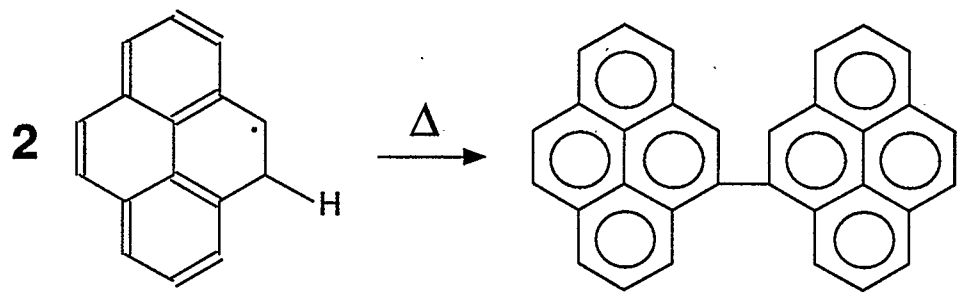


Figure 21. Dimer of Pyrene formed on pyrolysis of pyrene in back exchange reaction.

3.8 Further Discussion

In studying bitumen, one is dealing with a very complex mixture of compounds, and mechanistic studies must deal with broad classes of reactions. Based on the results already outlined, the following two categories are envisaged:

(1) Reversible H-donor reactions (Figure 22), e.g.

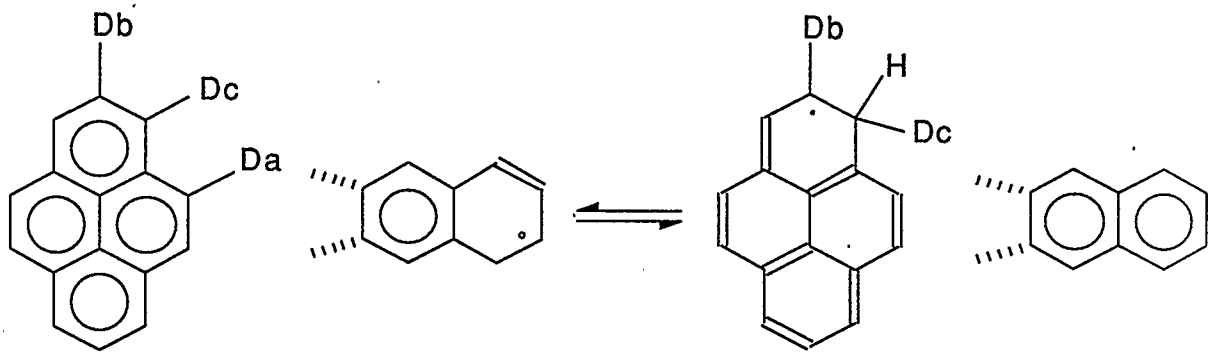


Figure 22. Possible mechanism for reversible H-donor reactions.

where the dihydronaphthalene radical is used only for illustrative purposes to represent possible naturally occuring, bitumen derived, hydrogen donor fragments (stabilized radical), present in the bitumen. The dihydropyrenyl radical could in principle, then reversibly react with a variety of naturally occuring aromatic compounds. This type of reaction would explain the reversible element observed in the back reaction with h_{10}-pyrene.

(2) Irreversible quenching of reactive radicals, again by a bitumen derived fragment (Figure 23).

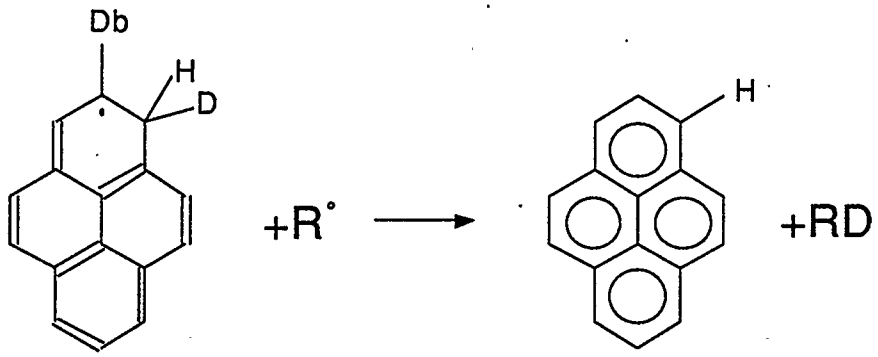


Figure 23. Mechanism of irreversible quenching of reactive radicals.

There are several ways in which reactive radicals could be envisioned to form. Side-chain cleavage from an aromatic radical (Figure 24) was one such route. Subsequent reaction of the alkyl radical, formed on dealkylation, with the d-pyrene would also go some way to explain the irreversible exchange found.

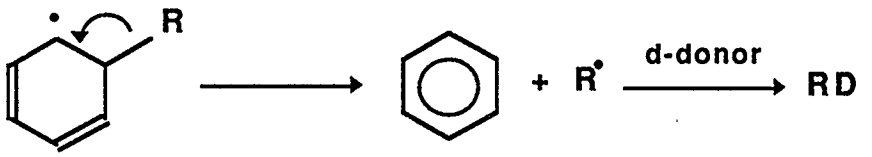


Figure 23. Mechanism of irreversible quenching of reactive radicals.

3.9 Conclusions

The use of a deuterated polynuclear aromatic as a mechanistic probe turned out to be a fortuitous choice. The small amount of pyrene added acted as a detector and did not perturb the system, i.e. did not involve itself in coke formation. Clearly, from the variety of exchange it can be concluded that the reservoir of hydrogen available in the bitumen itself is extensive (in terms of it's ability to stabilize reactive fragments arising in situations discussed previously) and very mobile (judging from the variety of environments in which deuterium was found to have incorporated itself). Although a polynuclear aromatic species can involve itself in the upgrading process, it cannot be considered as a net hydrogen donor but it has the ability to shuttle (with great ease at coking temperatures) hydrogen, from hydrogen rich to hydrogen depleted regions of the bitumen. From the selectivity of H/D exchange it appears that the stabilization reactions occur as free radical processes.

Two types of H-D exchange were found. Substitution into the alkane environment was not reversible and presumably occurred as an irreversible process during coking (possibly due to dealkylation). However, benzylic

substitution was back exchangeable and seems characteristic of reversible processes.

The thermal nature of the coking process (characterized by radical mechanisms) explains the lack of success in perturbing the system (work reported in chapter 2) with small amounts of additives. The reactions important in causing the observed irreversible exchange appear to be dealkylation reactions where the cleaved, reactive, alkyl radical removes deuterium in a stabilization step.

It has also been found that radical coupling of aromatic fragments is a significant process under coking conditions. The mechanistic implications of this potential coke forming reaction have been discussed (this chapter-3.1.2).

Chapter 4

H-Donor Upgrading of Bitumen Asphaltene

4.1 Introduction

It has already been reported in Chapter 2 that coking of bitumen leads to production of large quantities of coke. Efforts have been made in this work (reported in chapters 2 and 3) to study the mechanisms of coke forming reactions. It has long been known that a particular sub-fraction of the whole bitumen, i.e. asphaltene (heptane insoluble, benzene soluble), has a particular propensity for forming coke. With this in mind, a study of the thermal/upgrading reactions of the asphaltene was thought to be a useful, more focussed attempt to study the mechanism of coke formation. Asphaltene (derived from bitumen) is a high molecular weight fraction which is extremely complex and a discussion of what is known of its' structure and reactivity is essential to aquaint the reader with the nature of the problem faced in upgrading this material.

In practical terms, upgrading amounts to increasing the H:C ratio of the bitumen. This is achieved in the coking process by rejecting carbon as coke. Obviously this is a wasteful process since the high sulphur content of the coke prevents it being used as a fuel because of environmental considerations. The reader must be made aware that other upgrading strategies exist, all with different advantages and disadvantages. Hydrogen addition can be achieved by hydrocracking, where the bitumen to be upgraded is heated under hydrogen pressure in the presence of some dual purpose (hydrogenation/cracking) catalyst. Some technology exists for this process, including LC-Fining [70] (Syncrude) and H-Oil (Husky) [71]. The disadvantage of this type of process is the use of expensive H_2 gas and catalysts which have limited lifetimes because of coke fouling and deactivation due to vanadium, nickel and other trace metals in

the bitumen. Coking removes a large proportion of sulphur, nitrogen, nickel and vanadium (which are captured in the coke formed). In hydrocracking these very undesirable components find their way into the upgraded product streams or in catalyst deactivation schemes, etc.

Another possible route to addition of hydrogen (in upgrading) is the use of hydrogen donors. There are several processes which have been run on a pilot plant scale, involving H-donors. One of these is the Gulf DRB [72] process . Another has been developed by Exxon and is known as the Exxon donor solvent (EDS) Process Development Project [73], which is a coal liquefaction project [74]. In an industrial situation the H-donor solvent is generated downstream and is usually a mixture of compounds from a distillation cut. The Gulf process utilizes a middle distillate cut, which on depletion is recycled after rehydrogenation under hydrogen pressure. During the start-up of these processes, the H-donor comes from an external source. Some easily available H-donor solvents are creosote and anthracene oils (from coal). These industrial H-donors are complex mixtures of hydroaromatic compounds which have the ability to transfer hydrogen from their saturated structure to form unsaturated products and at the same time, enrich the hydrogen content of the species being upgraded. Again this technology has been around for a long time (since the thirties) and a review of the different H-donors available and how they work will follow.

One must realise that extensive H-donor capability exists in the whole bitumen. In the coking process, presumably, the compounds found in the maltene fraction (relatively hydrogen rich) would donate hydrogen to the higher molecular weight species found in the asphaltene fraction. In this present work the maltene H-donor will be replaced with a pure H-donor so there is obviously some relevance between this and previous studies (reported in chaps.2 and 3).

Background Discussion

4.2 Characterization of Asphaltene

4.2.1 Definition

The term "asphaltene" describes a solubility class. The asphaltene fraction is defined as being soluble in benzene and insoluble in pentane or another straight chain alkane. The soluble part is termed the "maltene" fraction (from an upgrading point of view, this is a more valuable fraction). Experiments have been carried out where different n-alkanes are used to precipitate the asphaltene [25, 75-77]. The asphaltenes generated by the varying solvents are very different, e.g. the heptane asphaltene (which has become the standard) is more aromatic in character and higher in heteroatom content than the equivalent pentane-derived material [78].

4.2.2 Petroleum Asphaltene Molecular Weights

Many different investigations have been carried out to determine the molecular weights of asphaltenes. The reported values vary enormously according to which technique is used in the determination. In one relevant study [79] vapour phase osmometry was employed and the calculated molecular weights varied from 2300 to 12500, depending on the solvent used. This large variation was thought to be due to the tendency of asphaltene molecules to associate even in dilute solutions of non-polar solvents. The precise nature of this association is still not clearly understood but hydrogen-bonding and charge-transfer complexation have been suggested [80-81].

4.2.3 Structure of Asphaltenes

Yen [82] has described petroleum derived asphaltene as being unisotropic in structure and as a mesomorphic liquid where many individually oriented clusters are randomly suspended. The individual clusters were found to be somewhat ordered, in that the planar aromatic portions of the asphaltene tended to stack themselves in layers. X-ray diffraction revealed that 5 or 6 layers is the average level of association. The attraction leading to layering was thought to involve a π–π interaction between the aromatic portions of the asphaltene. Figure 24 illustrates the macromolecular structure of asphaltene according to Yen's [83] interpretation of X-ray analyses.

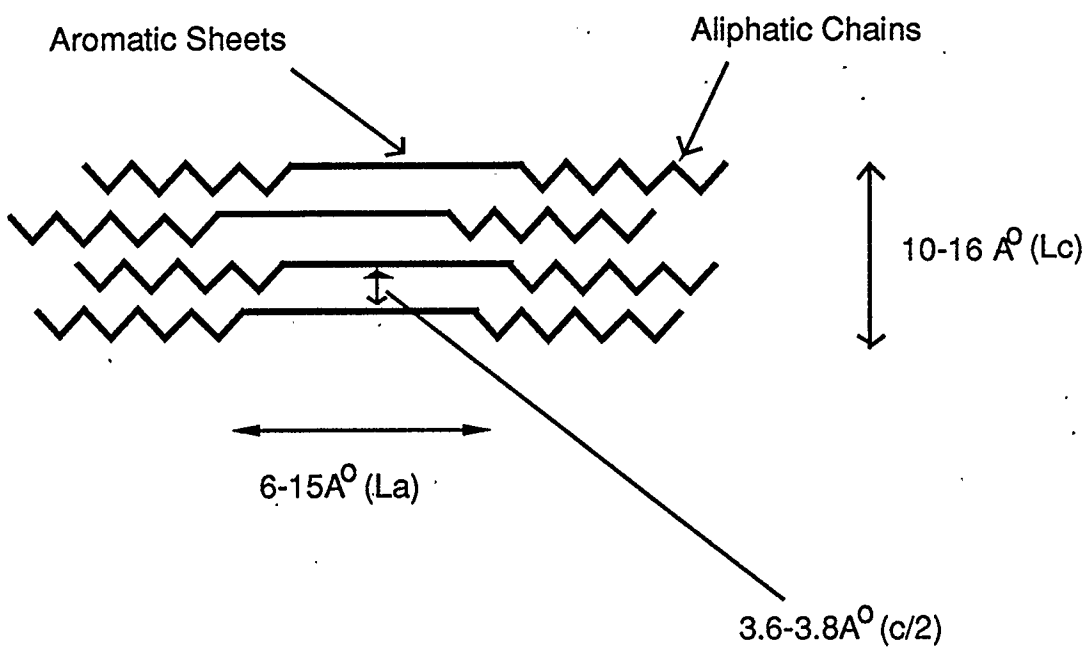
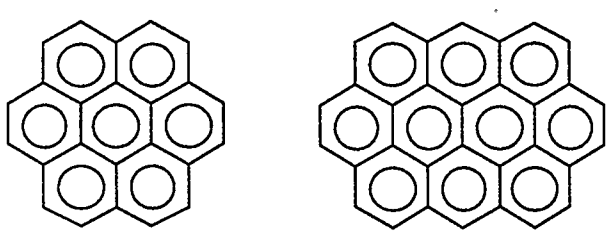


Figure 24. Representation of Asphaltene from X-ray data.

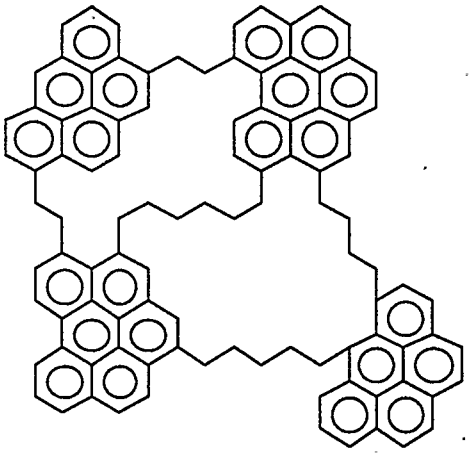
4.2.4 NMR Analysis of Asphaltenes

Using both ^{13}C and ^{1}H NMR it is possible to learn much about the structure of asphaltenes. This technique essentially identifies and quantifies hydrogen or carbon atoms according to their chemical and physical environments. Making approximations concerning the chemical shift, it is possible to estimate the fraction of protons (^{1}H) which are in an aromatic or naphthenic or methylene environment. Using this type of analysis coupled with molecular weight information and elemental analysis it is possible to formulate average structures of the asphaltene.

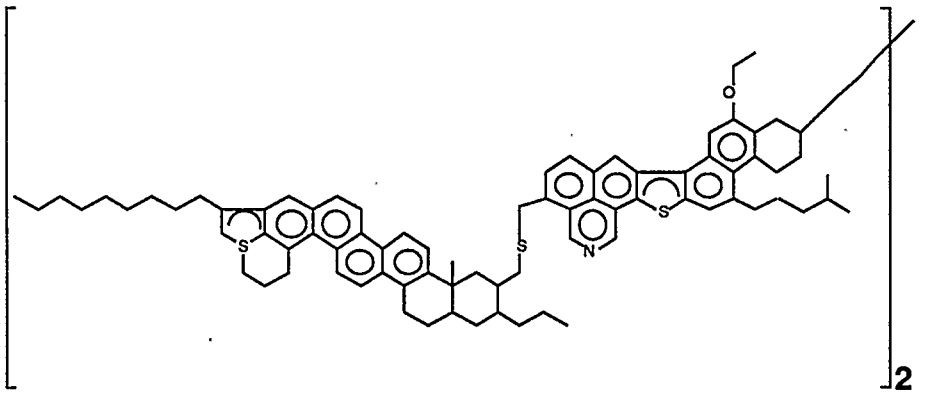
Many such studies have been made [80-81,84-89]. The results of these studies suggest that the asphaltene can be considered as a large central polynuclear aromatic system with some incorporated heteroatoms (nitrogen, oxygen and sulphur), attached alkyl chains and hydroaromatic ring systems [79]. Average structures have been suggested on the basis of the NMR studies and for Athabasca asphaltene the speculated structures include (a) large polynuclear aromatic systems [86], (b) smaller, but linked polynuclear aromatic systems [87], (c) linear polymeric polynuclear aromatic systems [88] and (d) a sulphur-polymer system [89].



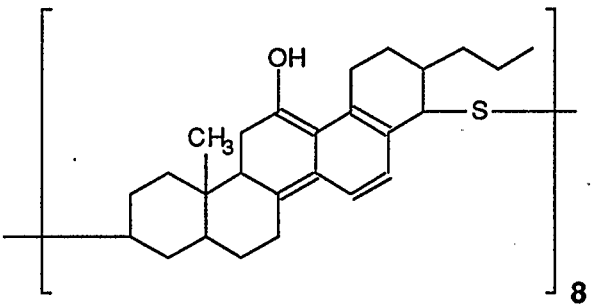
(a) Large polynuclear aromatic system.



(b) Smaller polynuclear aromatic systems.



(c) Linear polymeric polynuclear aromatic systems.



(d) Sulphur-type polymer system

Figure 25. Possible structures for asphaltene derived from NMR analyses.

4.2.5 Pyrolyses of Asphaltenes

A common method of studying asphaltenes structurally, involves pyrolysis and then the study of specific degradation products isolated in the maltene (heptane soluble fraction) , by GC-MS or direct study of the products by pyroprobe GC-MS. Thermolysis of Alberta oil sands asphaltenes at 300-450°C is known to liberate a homologous series of n-alkanes [90-93]. In one relevant study Speight et al. [94] reported pyrolyzing Athabasca asphaltene and analyzing the products using GC-MS. Using selected ion monitoring a series of n-alkanes were found (nC_9-nC_{21}), a series of alkylbezenes, alkylnaphthalenes, benzothiophenes and dibenzothiophenes. Similar results were reported by Steedman et al [95-96] using pyrolysis-GC analysis of condensible products from Athabasca asphaltene at 350, 500 and 800°C.

Pyrolysis of Athabasca asphaltenes has been found to involve loss of alkyl sidechains and other saturated moieties from the aromatic core. Some of the heteroatoms are also lost. The loss of sidechains will reduce the solubility, whilst loss of the heteroatoms will increase the solubility in a non-polar solvent. Lowering the molecular weight generally increases and aromatic condensation decreases solubility [97]. This means that recovered asphaltenes from a pyrolysis reaction can be products of deep structural alteration as opposed to unreacted asphaltenes.

4.3 H-Donors

It has long been recognized that H-donors could be employed to improve on upgrading of petroleum and bitumen asphaltene [98-99]. The use of H-donors is so far limited to pilot plant studies but has great potential for an upgrading process in industry. The source of H-donors used in these industrial processes

are complex mixtures of hydroaromatic compounds. Obviously, to simplify the study of this upgrading strategy, especially in a laboratory situation, single hydroaromatic compounds are used to simulate the industrial mixtures.

4.3.2 Experimental Comparison of Different H-donors

A large amount of recent research has shown the importance of H-donors and H-transfer agents in the dissolution of coal [57,100-109]. It was demonstrated by Neavel [106] that the presence of a H-donor significantly enhanced coal conversion, even at very short reaction times. In a study of the reaction of tetralin with Athabasca bitumen asphaltene [98] it was found that pyrolysis of the asphaltene in the presence of tetralin at 437°C led to a 76% conversion with only 1.6% coke formed.

In a similar study, Kamiya et al. [107] reacted a bituminous coal at 400°C and a brown coal at 350°C with various H-donors and found that three ring donors were more efficient at transferring hydrogen than tetralin. Interestingly, when the liquefaction temperature was increased to 450°C, tetralin appeared to be the most efficient donor. It was found that the conversion of coal increased with increasing activity of the donor and almost proportionally to the amount of hydrogen donor consumed.

In another relevant study, Sato et al [108] studied the liquefaction of Taiheiyo and Yallourn coals at 430-450°C (in an autoclave under hydrogen pressure) and found that tetralin and its methyl derivatives were useful H-donors especially in comparison to decalin. Based on hydrogen consumption, the order of the donors was found to be; 1-MT>2-MT>5-MT>6-MT>tetralin>1-MN>trans decalin
(MN=methylnaphthalene and MT=methyltetralin)

4.3.3 Mechanism of H-transfer from H-donor solvents

In a study by Curran et al. [101], the kinetics of transfer of hydrogen from tetralin were studied. A Pittsbugh coal was reacted with tetralin at 325-450°C and residence times from 2.5 minutes to 2 hours, in a sealed autoclave. Maximum H-transfer amounted to 2.2-2.6 %weight .

According to Curran et al. [101] the hydrogen transfer process was a purely thermal reaction and attempts to accelerate the reaction by the addition of catalysts (hydrocracking or hydrogenation) are unsuccessful. Contrary to this view it was found that the presence of certain S-containing compounds (benzenethiol and diphenyldisulphide are particularly useful) in H-donor reactions with coal [110] led to increased liquefaction yields as well as enhancing the rates of hydrogen atom transfer reactions of tetralin. The presence of H_2S was known to enhance H-shuttling reactions [111]. In model cracking studies H_2S was found to accelerate cleavage of various types of bonds likely to be important in coal structures [112-114]. The ability of H_2S and other S-compounds to be involved in H-shuttling and bond cleavage reactions was believed to be due to free radical chain mechanisms involving SH radicals as intermediates [111-115].

4.4 Objectives

Given the preceeding information on the structure of asphaltene and the use of H-donors in upgrading, the following specific objectives were decided upon in the present study of coke formation and asphaltene degradation in the presence of H-donors:

(1) To optimize the useful (non coke forming) degradation of bitumen asphaltene.

(2) To study mechanisms of degradation with / without H-donors present.

(3) To investigate and compare some different H-donors in their ability to usefully degrade bitumen asphaltene.

4.5 Strategy

It was hoped that the outlined objectives might be achieved by conducting tube-bomb pyrolyses of the bitumen asphaltene in the presence of selected H-donors / non-donors. The use of the closed tube-bomb is required since most H-donors have normal boiling points in the range (200-300°C) whereas H-donor reactions require temperatures of approximately 400°C. By analyzing the product distribution, after pyrolysis, one would gain meaningful information concerning the ability of a particular H-donor to degrade asphaltene into more useful products (maltene) . This would involve using capillary GC-MS to characterize as many products as possible. The recovered asphaltenes would also be analyzed using ^{1}H and ^{13}C NMR to give an idea of the structural changes which had occurred to the virgin asphaltene during different pyrolyses, i.e. different donors / non-donors, using different donor loadings, different temperatures and duration of pyrolyses. Finally, by analyzing the recovered H-donor solvent, using capillary GC, one would be able to estimate the net amount of H transferred in a given reaction by comparing the ratio of residual donor to that of the dehydrogenated product formed on H-donation (e.g. in the case of tetralin, the product being naphthalene).

4.6 Experimental

4.6.1 Preparation of Bitumen Asphaltene

As previously mentioned, the bitumen was obtained from Syncrude and was coker feed (bitumen extracted from the tar sands). Bitumen (100g) was dissolved in 100ml of toluene. To this was added 8L of heptane. The mixture

was stirred (using magnetic stirring bar) for 24 hours and then the precipitated asphaltene was filtered off. The approximate yield of asphaltene was 10g. The asphaltene was rinsed with clean heptane until colourless (the heptane), on passing through the bed of asphaltene. The asphaltene was then dried for 24 hours at reduced pressure (11-15mm Hg) at 80°C. The prepared asphaltene was then used without further treatment.

4.6.2 Pyrolysis Procedure and Product Fraction Analyses

In a typical pyrolysis, a sample of asphaltene (600mg) was placed in the tube-bomb (316 stainless steel-the length of the bomb was 160mm, the internal diameter was 8mm and the approximate volume was $8cm^3$) with the appropriate additive and heated in a muffle furnace (the temperature was monitored by an internal thermocouple) for a predetermined amount of time (usually an hour). The bomb was then removed from the furnace and rapidly quenched in cold water and left to cool for a further 5 minutes. It was opened and filled with n-heptane and left for 15 minutes. The heptane soluble material (maltene) was filtered off into a small flask and the bomb was refilled with heptane. This was repeated 4 times in all. The bomb (minus the maltenes) was filled with pyridine and left overnight. The pyridine was then poured off and filtered. This was repeated 4 times in all. The pyridine was evaporated off and the remaining pyridine soluble material (asphaltene and preasphaltene) was dried as before and weighed. The pyridine insoluble material (coke) remaining was removed from the bomb (mechanically), dried and weighed. Next, the already recovered pyridine soluble material was refluxed in benzene ($30cm^3$) for an hour. The preasphaltene (pyridine soluble-benzene insoluble) material was filtered off leaving the asphaltene (benzene soluble) solution. The benzene was then evaporated off and both fractions were then dried in a vacuum oven

(60°C) and quantified. Figure 26 illustrates this extraction scheme.

The recovered donor solvent (found in the maltene) was subjected to GC analyses in order to determine the extent of H-donation. The remaining maltene was then analyzed using capillary GC-MS to elicit information on its' composition (individual components). The recovered asphaltene was studied using ^{1}H and ^{13}C NMR in order to learn about the degradation which had occurred compared to the virgin sample.

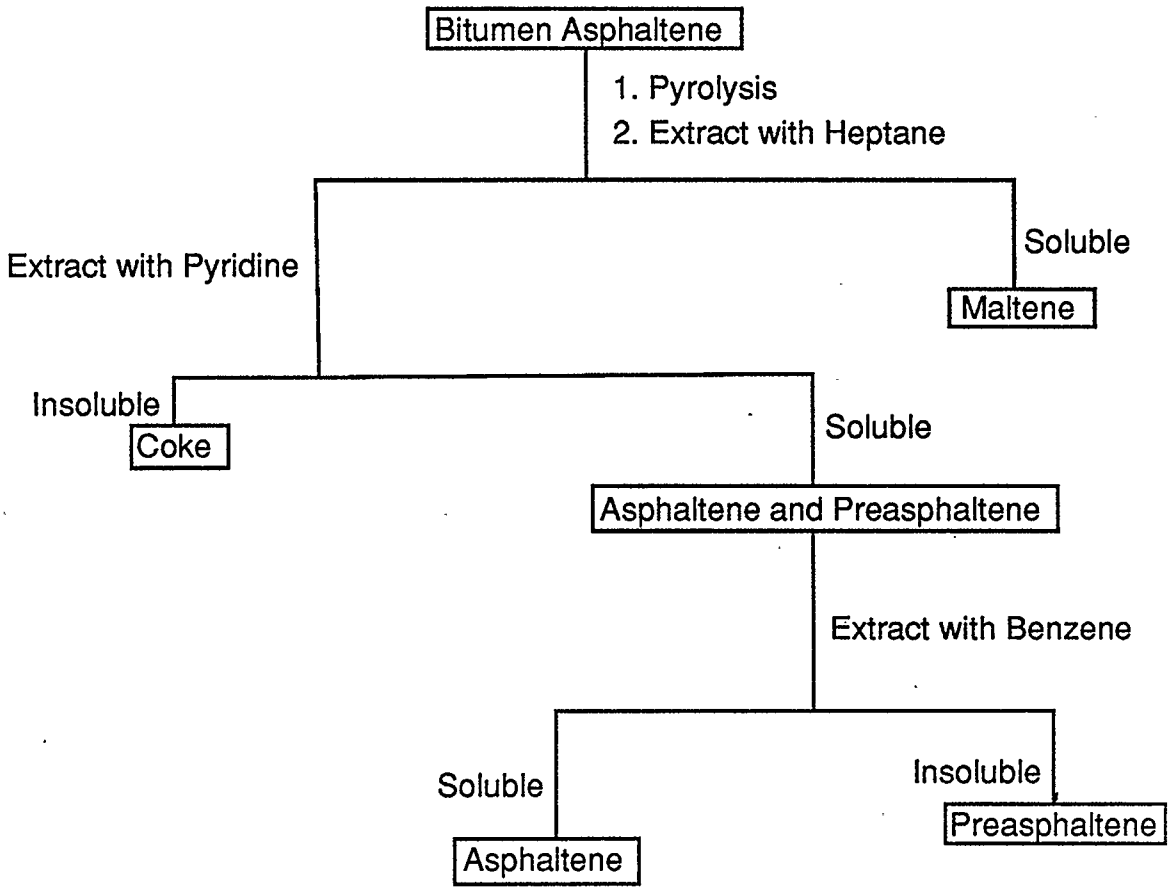


Figure 26. Schematic of pyrolysis product separation.

4.7 Results and Discussion

4.7.1 Reaction of Various H-Donors with Asphaltene

Figures 27-30 show the distributions of various fractions found in pyrolyses carried out with different H-donors. These included a control, where no additive was used and 1-methylnaphthalene (which can act as a reaction vehicle without any net capability as a H-donor) in the pyrolysis of the asphaltene. Two H-donors were used, tetralin (tetrahydronaphthalene) and 1,2-dihydronaphthalene. All of the pyrolyses described, involved an asphaltene loading of 600mg and a donor solvent loading of 1.2g. The duration of these pyrolyses was 1 hour. The temperature of the pyrolyses varied between 400 and 500°C.

As already described in Fig. 26 the pyrolysis products were separated into coke, a pyridine soluble, benzene soluble fraction (asphaltene), a pyridine soluble, benzene insoluble (preasphaltene) material and heptane soluble maltene. This left a small amount of product gases which were not studied in this work, unaccounted for. To a first approximation the recovered asphaltene was considered material which was not much altered from its virgin state. This turned out to be a poor approximation when considering later data describing structural features of the recovered asphaltene.

4.7.1.2 Study of Recovered Asphaltene

Fig. 27 illustrates the percent of recovered asphaltene obtained after pyrolysis at different temperatures and in different solvents. The most obvious feature is that at low temperature most of the products were recovered as an asphaltene fraction. One would expect the amount of asphaltene recovered to decrease as the pyrolysis temperature was increased since the energy

available for bond breaking was increased. Another noticeable feature is that the presence of the hydrogen donors increased the proportion of products recovered as asphaltene. This may be due to stabilization of reactive fragments which otherwise would combine in coke forming reactions.

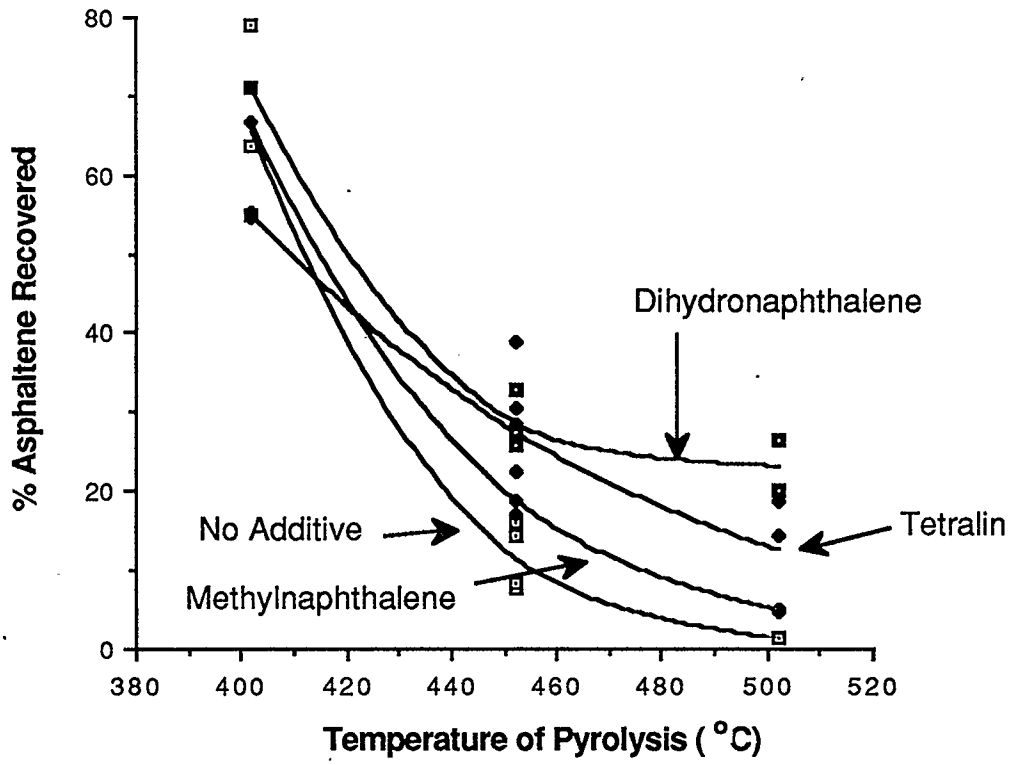


Figure 27. Percentage starting weight of asphaltene recovered as asphaltene on pyrolysis.

4.7.1.3 Study of Recovered Preasphaltenes

Figure 28 illustrates the proportion of products recovered as preasphaltene in asphaltene pyrolyses, in the presence of various solvents.

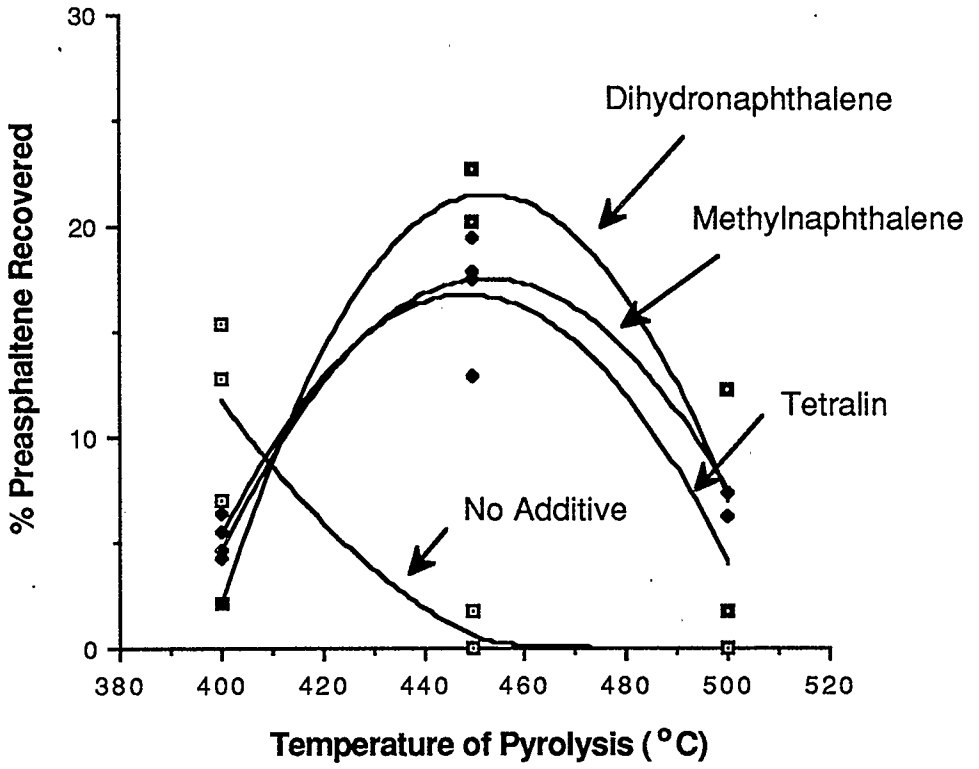


Figure 28. Percentage starting weight of (initially asphaltene) preasphaltene recovered on pyrolysis.

One can see that when no solvent was used, preasphaltene was recovered at 400°C. At higher temperature only coke was recovered (Fig 29) as well as a small amount of maltene. Preasphaltene is considered to be intermediate between asphaltene and coke and therefore the existence of stabilizing mechanisms, e.g. as provided by H-donors, preventing coke formation and might be expected to result in an increased yield of preasphaltene. Clearly the ability of the solvent to prevent coke formation, based on preasphaltene yield, was at a maximum at 450°C. Interestingly, the presence of methylnaphthalene, which is not a net H-donor, but which might

have been involved in shuttle reactions, caused the same behaviour as the presence of tetralin and dihydronaphthalene (which are true H-donors), in terms of preasphaltene production. At 500°C, even in the presence of H-donors, the amount of preasphaltene formed was small and to a large extent replaced by coke formation (Fig 29). It seems reasonable that the H-donor loading of 2:1 (donor to asphaltene) may have been inadequate to prevent coke formation at this temperature (too little donor hydrogen).

4.7.1.4 Study of Recovered Coke

Figure 29 illustrates the proportion of coke recovered after the pyrolyses. It was evident that without solvents being present, the amount of coke formed increased rapidly as the temperature increased and reached a maximum yield at 450°C. Surprisingly, the presence of the non-donor, methylnaphthalene, was quite successful in reducing coke formation, although not as good as the donor solvents. The H-donors were obviously very successful in reducing coke formation at 450°C and to a lesser extent at 500°C. Again at 500°C, it appeared as if the ability of the donor to stabilize reactive fragments from forming coke, was somewhat reduced, possibly because the amount of donatable hydrogen was insufficient.

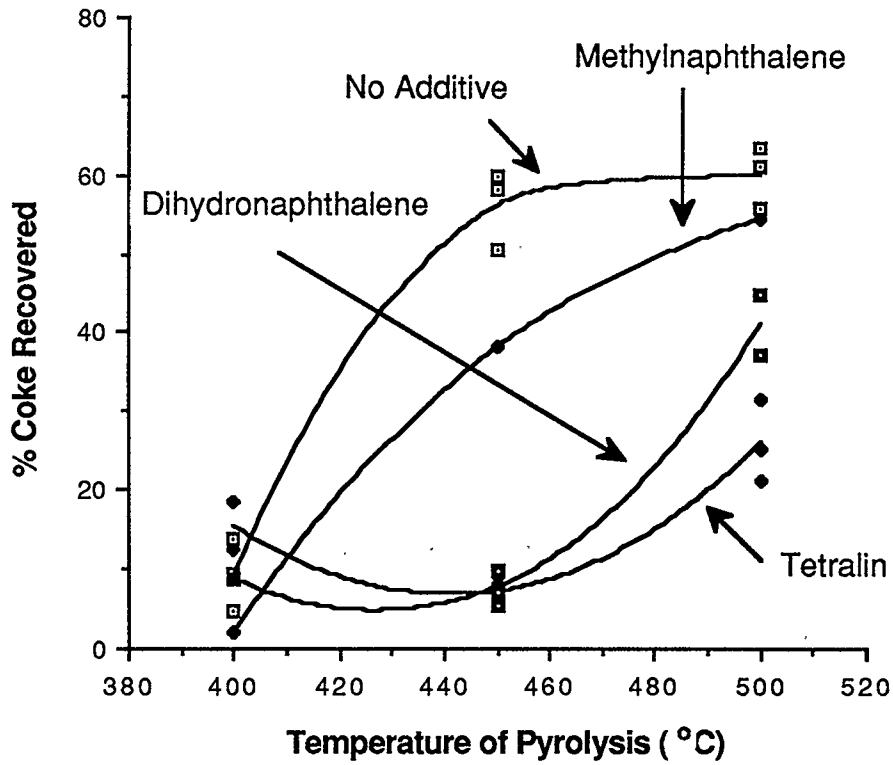


Figure 29. Proportion of starting asphaltene recovered as coke in the pyrolyses of asphaltene at different temperatures with various additives.

4.7.1.5 Recovered Maltene/Conversion

In this work useful upgrading of the asphaltene amounted to prevention of coke formation and increasing the proportion of material recovered as low molecular weight maltene. Figure 30 illustrates the success in achieving this aim. One can see that tetralin had consistently led to the highest conversion over the whole temperature range. Dihydronaphthalene was successful at 450°C but less so at 500°C, in its ability to convert asphaltene to maltene. This again might have been due to H-donor depletion, remembering that the same

loading (mass) was used for both tetralin and dihydronaphthalene, although tetralin had twice the donor potential of dihydronaphthalene.

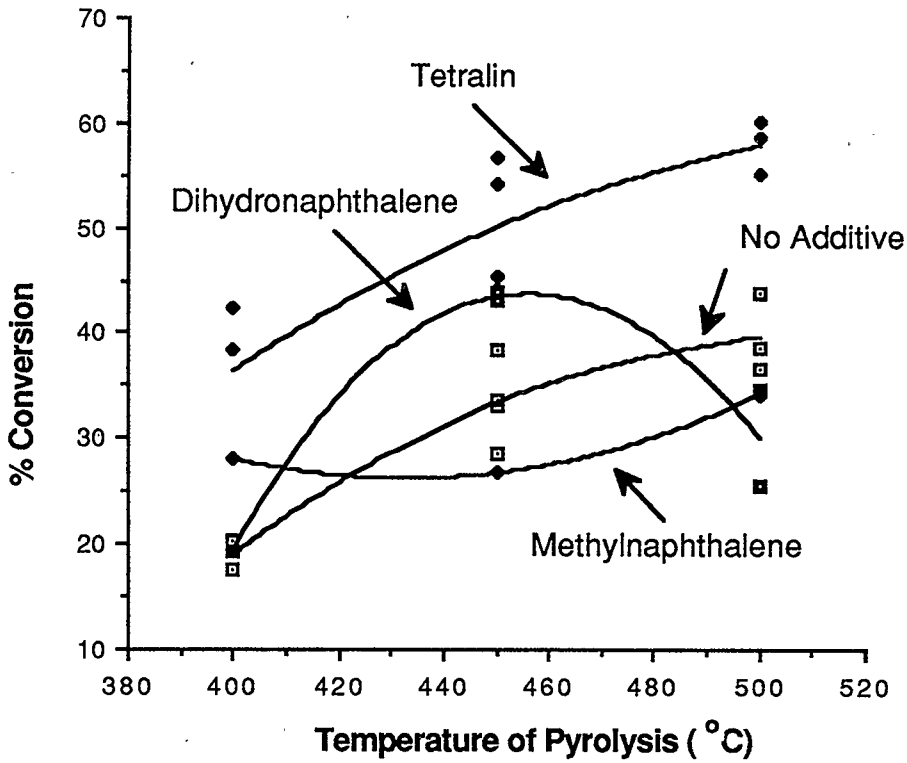


Figure 30. The proportion of material (starting weight of asphaltene) which is not recovered as asphaltene, preasphaltene or coke, mostly maltene.

4.7.2 NMR Analyses of the Recovered Asphaltene

4.7.2.1 Carbon Aromaticity

The product distributions (recovered on pyrolyses) have been discussed. The next step was to study these fractions, in particular the asphaltene, using NMR to give an idea of the structural changes, compared to the virgin material, which occurred during pyrolyses. The ^{13}C NMR spectra were extremely complex and single resonances were impossible to differentiate. The simplest way to treat this data was to compare the integration over the aromatic chemical shift region with that of the total aromatic and aliphatic regions. This gave a very useful idea of the degree of degradation which had been experienced by the asphaltene in a particular pyrolysis, e.g. an increased aromaticity might describe a tendency for dealkylation and aromatization. It was hoped that by comparing the GC and ^{13}C NMR information one might learn more about degradation under different conditions.

Figure 31 illustrates the carbon aromaticity of the recovered asphaltenes. No asphaltene was recovered in the situation where no solvent was used at 500°C so data does not exist for this case. One can see that the carbon aromaticity increased uniformly as the temperature of pyrolysis increased, regardless of the solvent employed. It appeared that the presence of the H-donors did decrease the formation of aromatic carbons to a small degree. The fact that the aromatic carbon content of the recovered asphaltenes varied so much (0.57-0.85) suggested that the structure of these asphaltenes, recovered at various temperatures, were very different from the initial asphaltene. Speculation as to the structure of these recovered asphaltenes will be discussed after ^{1}H NMR analysis of the same fractions has been introduced.

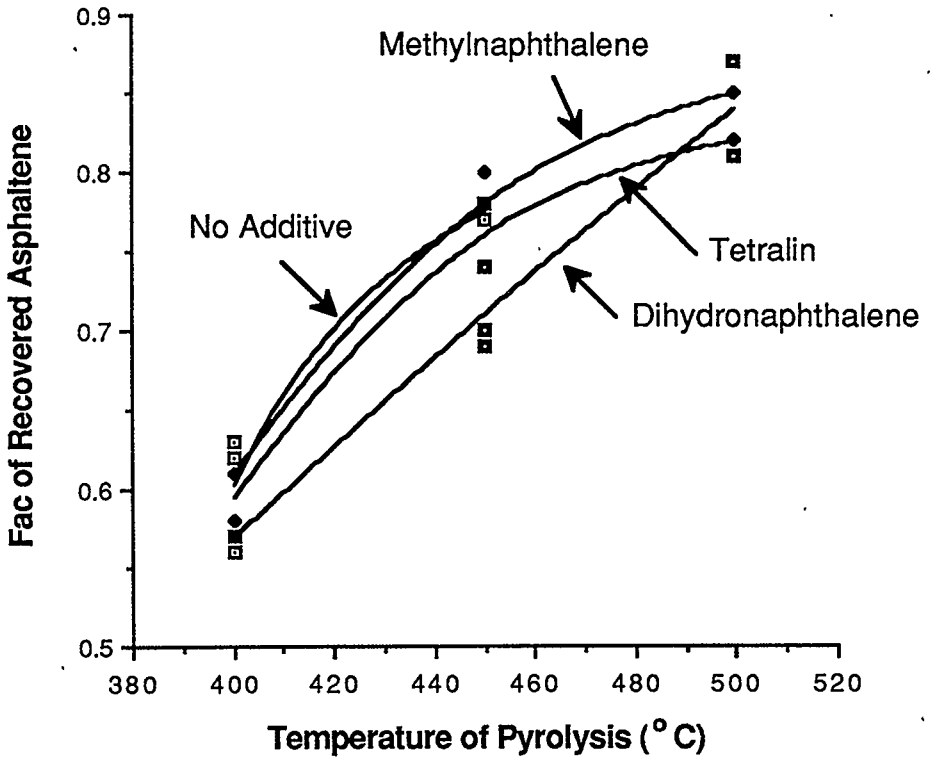


Figure 31. Carbon aromaticity of the recovered asphaltene from the asphaltene pyrolysis at different temperatures with various additives.

4.7.2.2 ^{1}H NMR Analysis of Recovered Asphaltene

The asphaltene recovered from the pyrolyses products was analysed using ^{1}H NMR and compared to virgin sample. The spectra were extremely complex and the most successful method for interpretation involved a global analysis where approximations were made based on chemical shift assignments (previously discussed in chapter 2). The signals within an assigned chemical shift region were integrated and were then compared with those derived from different runs.

Table 11. ^1H NMR analysis of H types present in asphaltene recovered from pyrolyses in the presence of different solvents (donor loading was 1.2g, duration of pyrolyses was 1 hour).

Run	Add	Temp(°C)	Hγ	Hβ	Hα	Har
		Virgin asphaltene	.139	.468	.258	.135
39	None	400	.185	.531	.183	.095
37	THN	400	.154	.548	.202	.090
38	DHN	400	.169	.479	.197	.128
161	MN	400	.160	.400	.250	.190
33	None	450	.074	.389	.264	.255
45	THN	450	.106	.407	.241	.234
44	DHN	450	.113	.394	.222	.262
89	MN	450	.090	.330	.310	.260
31	THN	500	.054	.279	.241	.408
32	DHN	500	.038	.208	.223	.510
113	MN	500	.060	.180	.260	.510

MN=1-Methylnaphthalene, THN=Tetralin, DHN=Dihydronaphthalene.

Comparison of the ^1H NMR data (Table 11) revealed that the largest variations in H-types, from the various recovered asphaltenes, existed at the different pyrolyses temperatures rather than with different solvents. Looking at Table 11 one can see the effect of the solvents on the hydrogen environments

in the recovered asphaltene. This structural infomation was then compared to that obtained from the virgin asphaltene and it was possible to speculate on the reaction types which have occurred on thermolysis.

At low temperature (400°C), not surprisingly, the recovered asphaltene was least altered, compared to the virgin asphaltene. In fact the integrated hydrogen values were very similar, indicating that at this temperature the structural integrity of the original asphaltene had remained fairly intact, although some measured degradation (to maltene) had in fact occurred. At 400°C, some interesting differences were evident when comparing MN with the others (Table 11). One can see that the MN derived asphaltene was significantly more aromatic and that the average chain length of the attached aliphatic groups was reduced (this is indicated by the lower value for Hβ–seeFig.32)

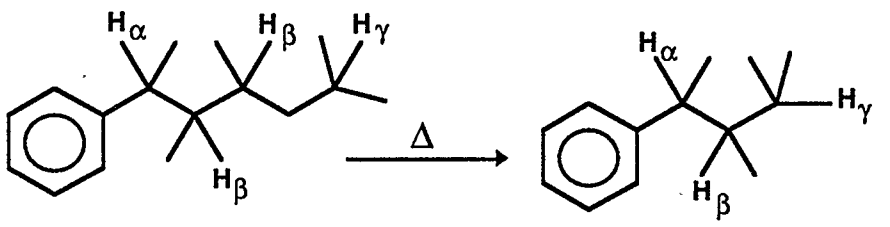


Figure 32. Reduction of Hβ through dealkylation.

Also for MN the value for Hα was higher, indicating that dealkylation had been important under these conditions (not α-cleavage). Comparing the asphaltenes recovered at 400°C to the virgin asphaltene, one found that the pyrolyzed asphaltenes had lower Hα and higher Hβ and Hγ (except MN).

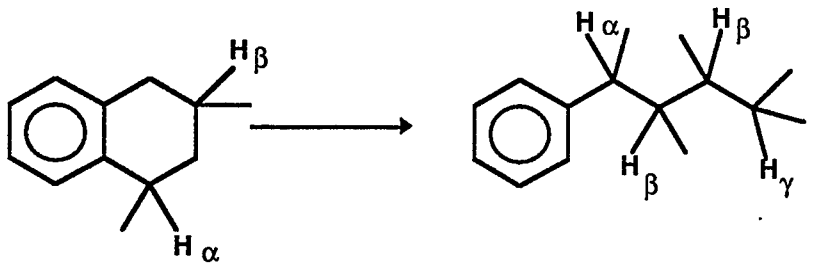


Figure 33. Ring opening leading to reduced Hα and increased Hγ.

This suggested that some ring opening (see Fig.33) may have occurred. At 450°C there was an even more pronounced difference, when comparing the virgin asphaltene to the recovered asphaltenes. Significant increases in the aromaticity of the asphaltenes were evident, with corresponding decreases in Hβ and Hγ (Hα had remained about the same), indicating that dealkylation had been important in transforming the virgin asphaltene. The least change was noted for Hα, which indicated that the amount of hydrogens α to an aromatic ring had remained fairly stable. Aromatization and condensation reactions had probably occurred but corresponding losses in Hα might well have been offset by H-transfer reactions leading to the creation of hydroaromatic molecules (converting Hγ to Hα). Again comparing MN to the others, one could see evidence of lower Hβ and slightly higher Hα values. This again pointed to increased dealkylation.

As the temperature was increased from 450 to 500°C, the virgin asphaltene structure was still further changed (increased aromaticity and decreased Hβ and Hγ) by more of the same type of degradation as already mentioned. The changes in asphaltene with increasing temperature of pyrolysis is further illustrated in Figure 34 which shows the ^{1}H NMR analysis of the asphaltenes recovered from the runs that involved tetralin.

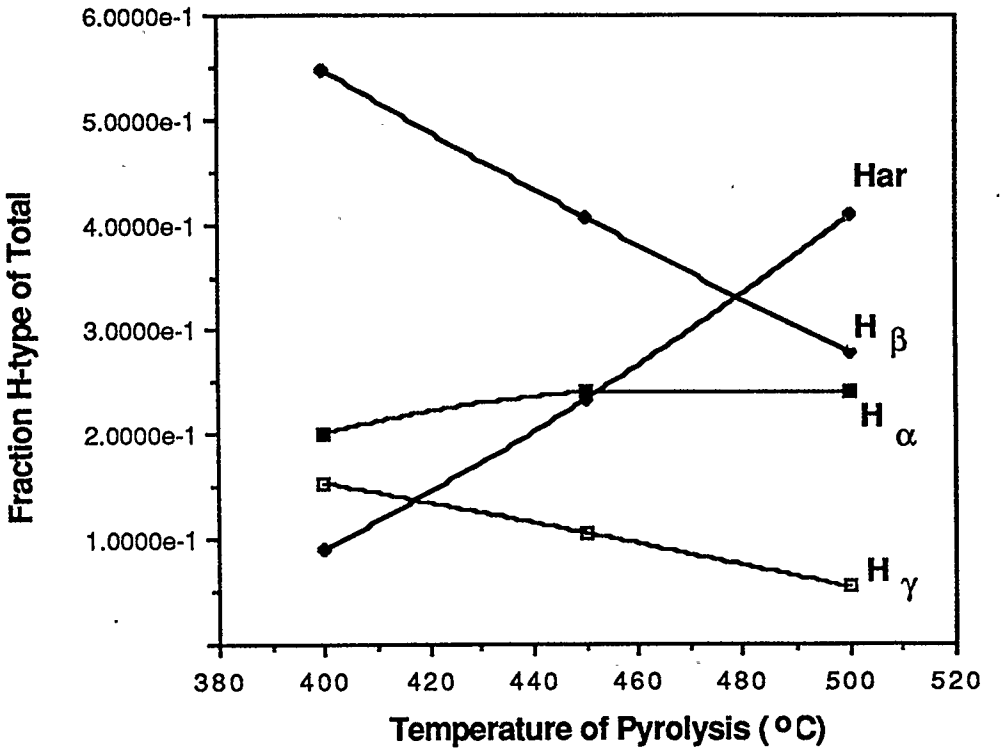


Figure 34. Variation of H-types as the temperature of pyrolysis (Donor is tetralin. Loading 1.2g) is varied, in recovered asphaltene.

One notable feature is the fact that Hα increased only slightly between 400 and 450°C and levelled out between 450 and 500°C. This may have suggested that β-cleavage was the important dealkylation mechanism leaving methyl groups attached to aromatic nuclei.

Careful integration of the chain methylene resonance (1.3ppm) and comparison to that of the methylic signal (0.9ppm) revealed that the average chain length of the alkyl groups associated with the virgin asphaltene was approximately 10 carbons long (remembering that the methylic carbons have 3 hydrogens and the methylene carbons have 2).

4.7.3 Extent of H-Transfer from Donor Solvent

The next step involved analysis of the recovered H-donors to find out how efficient they were at the various pyrolyses temperatures and how they compared to each other in their ability to transfer hydrogen. The DHN and THN runs have already been described. At this stage two additional donors were also studied, i.e. DHP (9,10-Dihydrophenanthrene) and DHA (9,10-Dihydroanthracene) and the results were compared with DHN and THN. The results of the GC analysis of the recovered H-donors are shown in Table 12. The ratio of the donor compared to the dehydrogenated donor was found and then the amount of H transferred was calculated. This did not mean that all of the hydrogen used was transferred to the upgraded products. Some H_2 gas may also have been formed. A modification to this calculation had to be made in the cases of DHN (which disproportionates into tetralin and naphthalene) and DHA (which disproportionates into tetrahydroanthracene and anthracene).

In order that one would be able to compare different runs (with small differences in the asphaltene and donor loadings) it was decided that a suitable form for the derived quantity would be mg of H_2 expressed (from the donor) per gram of asphaltene originally present. In examination of the results one has to remember that the loading of H-donor was not the same in terms of the total amount of hydrogen available for transfer. To clarify this situation, the potential hydrogen available for transfer was noted as well as the percentage of the potential utilized.

Table 12. GC analysis of the recovered donor solvent. Hydrogen donated in terms of hydrogen expressed in mg/g asphaltene.

Run no.	H-Donor	Temp.(°C)	H_2 Exp. *	Donor Potential *	% Utilization
105	DHP	350	1.2	10.4	11.5
142	DHA	350	0	10.2	8.8
37	THN	400	1.6	28.9	5.5
38	DHN	400	1.4	14.0	10.0
140	DHP	400	4.4	8.1	54.3
92	DHA	400	0	10.6	0
45	THN	450	9.1	27.5	33.1
44	DHN	450	5.9	13.4	44.0
106	DHP	450	8.3	8.5	97.6
67	DHA	450	2.8	10.9	25.7
60	THN	500	26.2	28.5	91.9
32	DHN	500	11.6	11.6	100.0
116	DHP	500	10.5	10.6	99.1
117	DHA	500	6.0	10.7	56.1

* mg hydrogen expressed per gram initial weight of asphaltene expressed from the donor.

Figure 35 represents the absolute amount of transferred hydrogen at different temperatures using the various H-donors. One has to remember that if the donor loading was too low then the true ability of the donor to transfer hydrogen was not fully recognized in this analysis. In other words, the reference point being the situation where there was infinite dilution of the asphaltene in

the H-donor solvent. This was the case for DHP and DHN at 500°C.

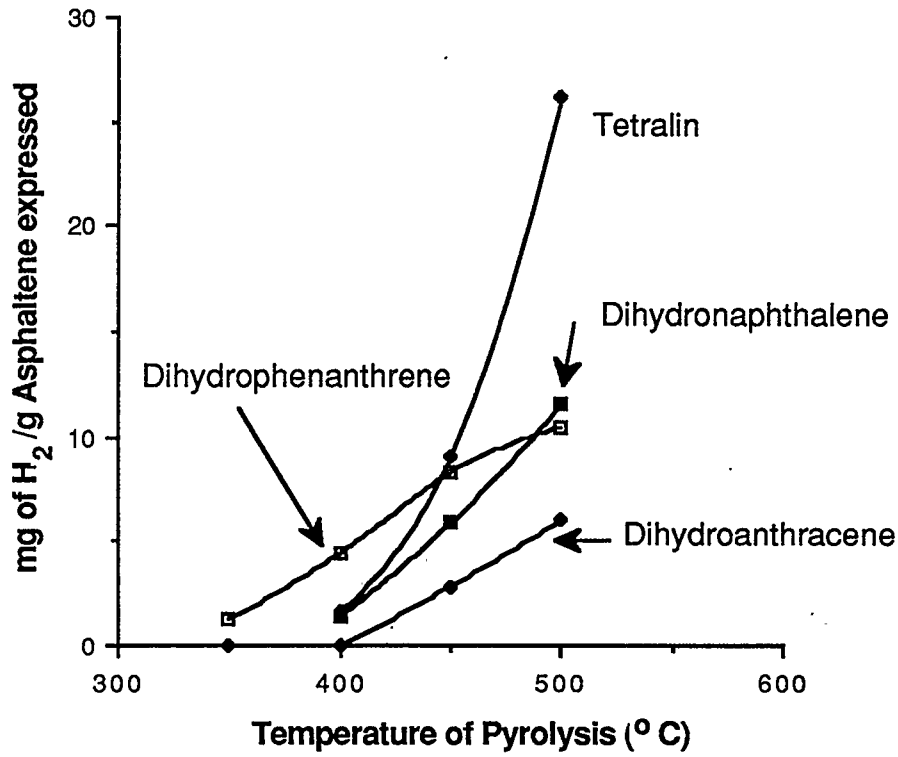


Figure 35. mg of H_2 / g initial weight of asphaltene expressed from H-donor. Calculated by analysis of recovered H-donor.

Looking at Figure 35 one can see that DHP had the ability to donate hydrogen at lower temperatures than the other donors. DHA and DHN may have been somewhat hindered by their tendency to disproportionate and the resulting THN and THA (tetrahydroanthracene) were worse H-donors than DHN and DHA, respectively. At temperatures above 450°C, tetralin became the best donor. At 500°C tetralin, DHN and DHP had almost donated their full potential (although their potential was lower).

To further state the problem of insufficient donor loading and percentage

utilization of the available donor potential, Figure 36 compares these quantities. One can see how the different donors compare and how DHP was particularly good at even low temperatures although its' full donor potential was depleted at 450°C. DHN and THN behaved less well and DHA was particularly poor (disproportionation tied up hydrogen as THA, which is a poor donor). From this analyses (Fig.36) it is obvious that donor depletion was a significant factor in the determination of the hydrogen transferred. At 500°C, DHP, DHN and tetralin had all reached their maximum potentials as H-donors.

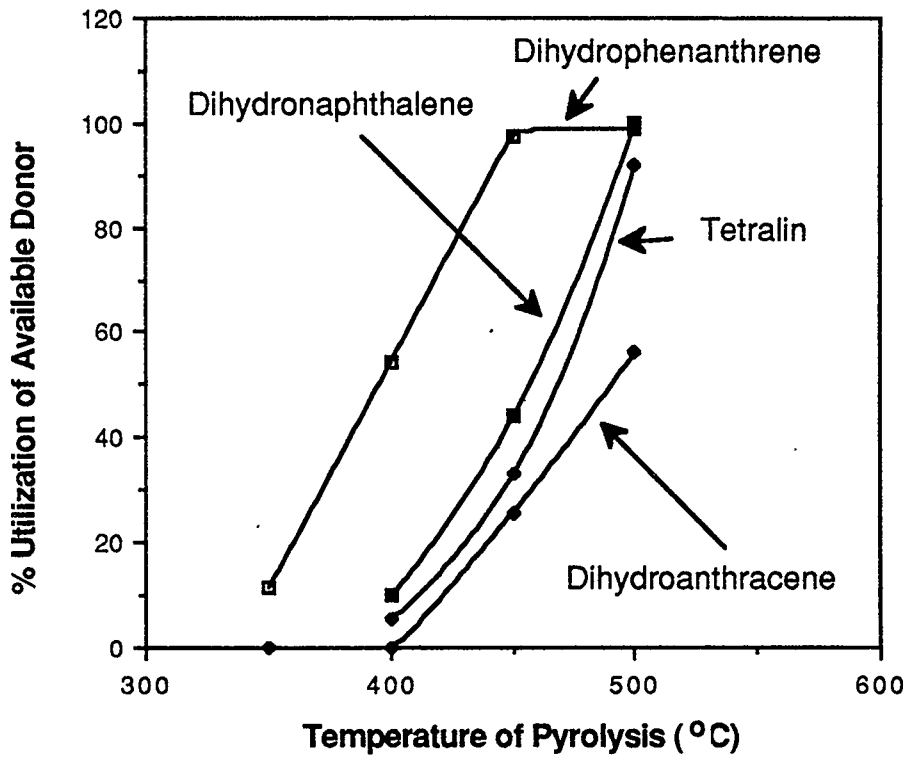


Figure 36. Comparison of the percentage of the available hydrogen transferred at increasing temperature.

4.7.4 Capillary GC-MS Analyses of the Recovered Maltenes

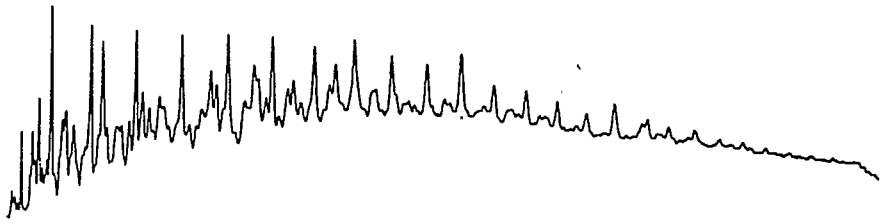
Analysis of the maltene fractions derived from pyrolyses (involving standard donor loading and duration) revealed that the components (of the maltene) depended more on temperature of pyrolysis than on whether donor/no donor was present. At 400°C (no donor present) the predominant species were a homologous series of n-alkanes (nC_8-nC_{30}). Decane was present in the highest concentration (Fig. 37). The only other components detected were small concentrations of branched alkanes. The same basic pattern was evident for the tetralin and dihydronaphthalene runs although the selectivity for n-alkanes as opposed to branched, was lower (Fig. 38 of the relevant SIC's of mass 57). At longer retention times, small concentrations of substituted naphthalenes were also detected.

When the pyrolysis temperature was raised to 450°C the series of n-alkanes were still predominant although less so than at 400°C. In the maltene derived from the no donor run (450°C), the branched alkanes were less in evidence than was the case at 400°C. Among the new compounds detected were substituted benzenes, dihydroindenes, benzothiophenes and naphthalenes. The minor components detected in the H-donor derived maltenes were similar to those found in the no donor run (450°C).

When the temperature was increased to 500°C the predominance of the previously described n-alkanes had disappeared. They were, however, still present in less significant concentrations. In all runs at 500°C the major predominating species were now found to be substituted benzenes. Also detected were small concentrations of substituted thiophenes, dihydroindenes, benzothiophenes and naphthalenes. Again comparing the relevant SIC's of mass 55 (Fig. 39) it was evident that there were a large number of components in the no donor run which contained the fragment mass 55. This can be

compared to the dihydronaphthalene case where this fragment was almost nonexistent.

No Additive, 400°C, 1 hour.



No Additive, 450°C, 1 hour.

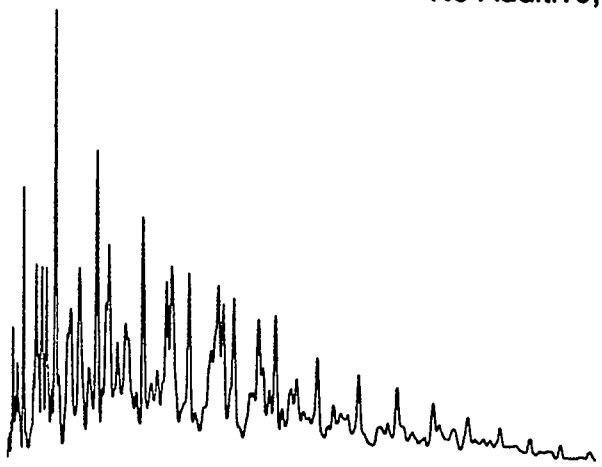
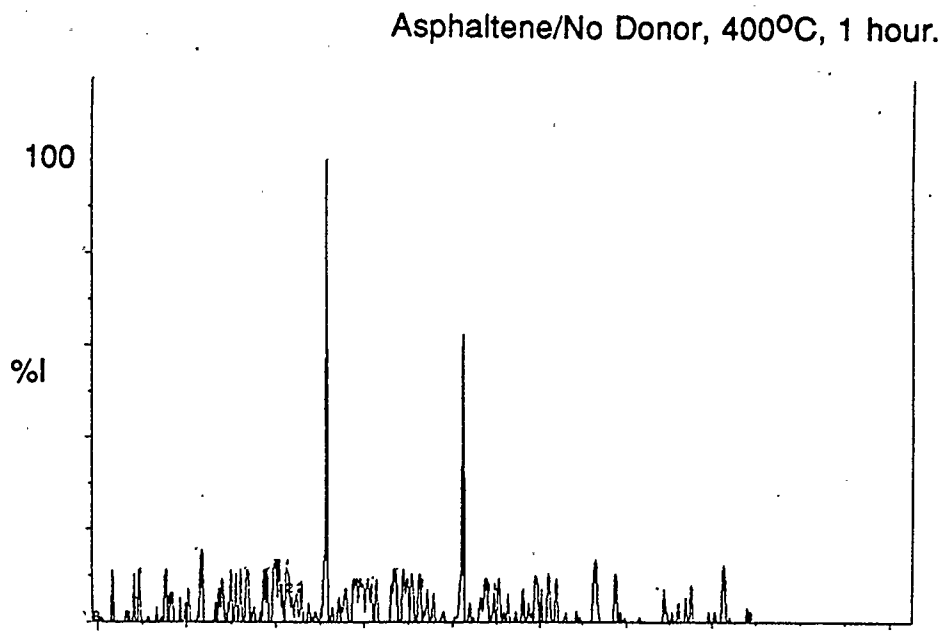


Figure 37. GC analyses of recovered maltenes.



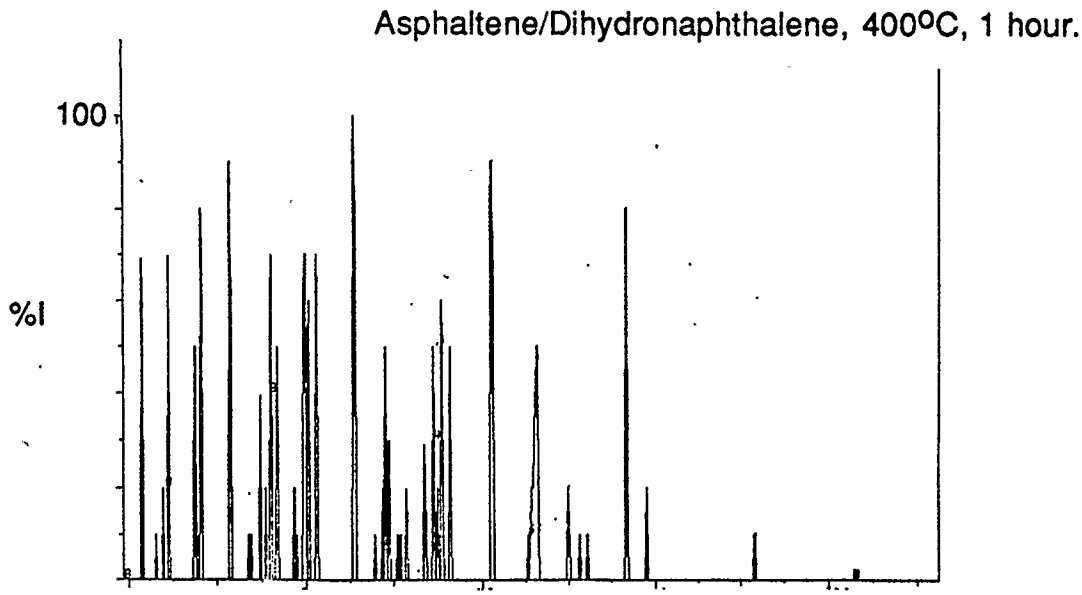


Figure 38. GC-MS single ion chromatograms (mass 57).

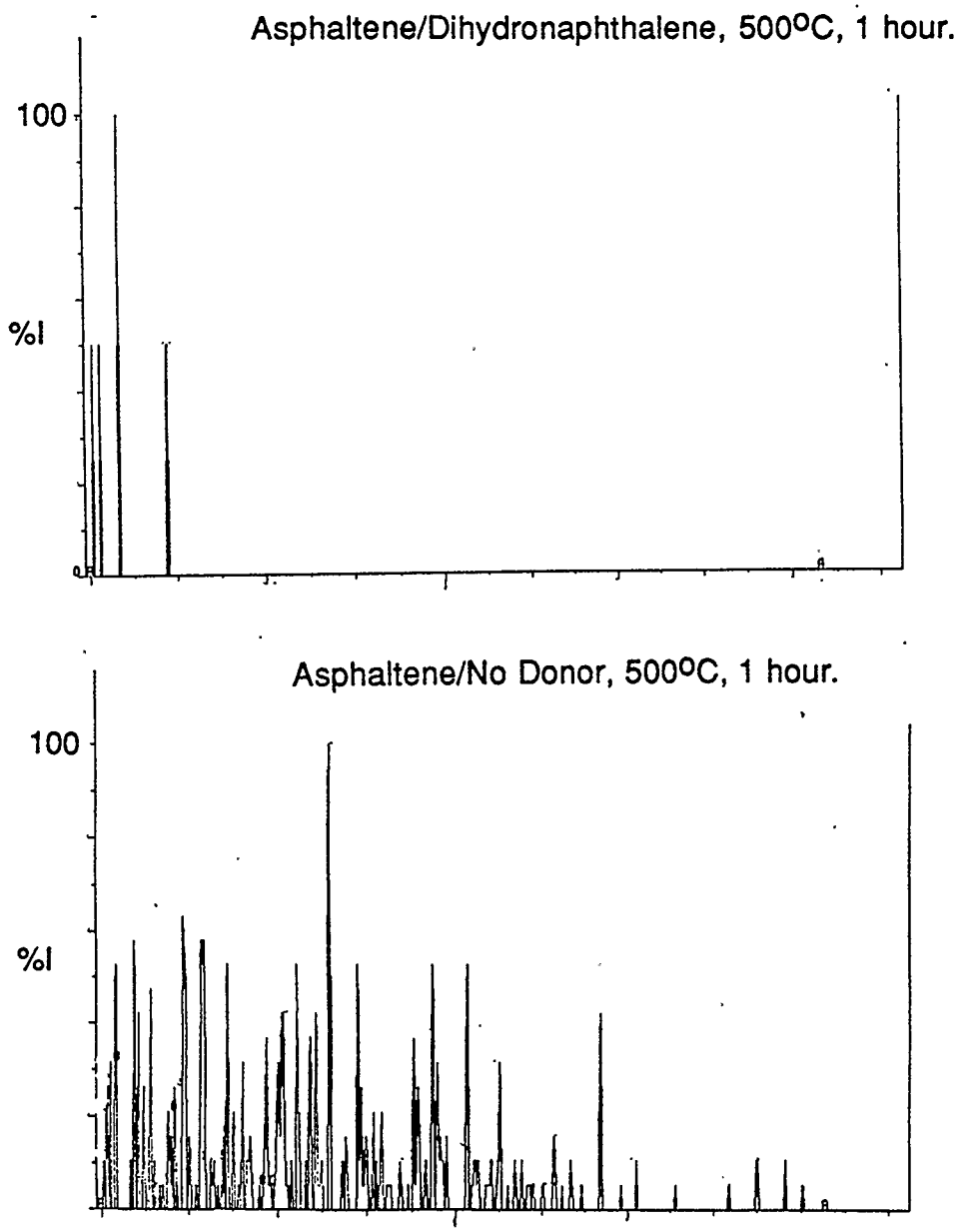


Figure 39. GC-MS single ion chromatograms (mass 55).

4.7.5 GC Quantification of Alkane fraction in recovered maltenes

The GC-MS analysis of the recovered maltenes from asphaltene pyrolyses under various conditions has already been discussed. It has been demonstrated that under moderate thermolysis, the recovered maltene was dominated by a series of n-alkanes. As far as degradation of asphaltene was concerned, alkanes were considered a desirable product in the pyrolyses (certainly when considering aromaticity of the diesel fraction). Different pyrolysis conditions have been discussed in terms of efficiency of conversion of initial asphaltene. It was thought that it would now be useful to compare different pyrolyses in terms of the total production of alkanes. This was possible by quantitative GC using nC_{14} or nC_{25} as a reference spike.

Table 13 illustrates the alkane yields for some different maltenes derived at various pyrolysis temperatures (all 1 hour) using different solvents. At low temperature (400°C), because of the limited thermal activity occurring at this temperature, one can see that the type of solvent did not make much impact on the alkane yield or on the overall conversion in the pyrolyses. At 450°C the most striking feature was the large difference between the alkane yield derived from the tetralin compared to the other donor / non-donor, pyrolyses. The alkane yield was twice that of any of the others and the overall conversion was much higher, also. There did not seem to be a correlation between the amount of alkane and the subsequent conversion in the other donor solvent pyrolyses eg. DHN gave a low n-alkane yield (10.1mg from an original asphaltene loading of 600mg) and yet the maltene/conversion was relatively high (44.1%).

Table 13. Quantification of total alkane fraction derived from maltene from asphaltene pyrolyses in the presence of different additives.

Additive	Temp. (°C)	Wt. of Alk fr(mg)	% Conversion
None	400	6.9	17.5
THN	400	6.3	23.1
DHN	400	6.6	19.4
MN	400	4.5	28.1
None	450	18.6	38.3
THN	450	40.5	59.7
DHN	450	10.1	44.1
MN	450	25.0	26.5
DHP	450	11.5	34.2
DHA	450	17.9	*

* Not calculated.

(Donor:Asphaltene loading 2:1, 1h pyrolyses)

4.8 Effect of Increased donor loading and duration of pyrolyses

After the previous examination of pyrolyses with different solvents it seemed logical to concentrate on tetralin, since it was found to be so efficient at supressing coke formation. One also wished to discover the effects of longer reaction time and if this would lead to more or less useful degradation, or if there was a strictly defined limit to how far the aphaltene could be usefully degraded at a given pyrolysis temperature. One also wanted to study the effect

of a higher donor loading at the higher temperatures where previous data pointed to donor depletion.

4.8.2 Product Distribution

Table 14 demonstrates the results of these new pyrolyses with regard to product distribution. Looking at this table, it is evident from run 56, where the H-donor loading was increased, that the conversion of the asphaltene was increased when compared to the value for conversion in run 124 (when the standard loading was used). The coke formation was approximately the same. The carbon aromaticity (of the recovered asphaltene) had decreased on increasing the donor loading. Run 66 revealed that with the increased load and now increased time of pyrolysis, an even greater conversion of the initial asphaltene and a significant increase in the aromaticity of the recovered asphaltene was observed. Under these relatively severe conditions only 23.5% of the original weight of the virgin asphaltene remained as high molecular weight, recovered asphaltene, preasphaltene or coke .

Previously, it was found that at 500°C, with the standard donor loading that coke formation increased because of donor exhaustion. Looking at run 61 (Table 14) one can see that the increased loading did indeed decrease the coke formation from 54.7 to 9.1%. The conversion had correspondingly increased from 34.2 to 77.2% of the initial starting weight of the asphaltene. Only 22.8% of the starting weight of asphaltene was recovered as high molecular weight material. This appeared to be the limit in the effort to usefully degrade the asphaltene. The carbon aromaticity of the recovered asphaltenes was almost the same, compared to run 122. Increasing the time of pyrolysis (run 62) led to a reduction in the conversion and an increase in the amount of pyridine solubles recovered. Obviously, this recovered asphaltene and

preasphaltene did not consist of unreacted material but had arisen from regressive combination occurring due to the longer reaction time. It might also be that under these severe conditions the donor was either exhausted or degraded. The aromaticity of the recovered asphaltene was also significantly increased from 0.83 to 0.90, indicating the increased severity of the reaction conditions.

Table 14. Product distribution and carbon aromaticity (recovered asphaltene) on asphaltene pyrolysis in the presence of tetralin at different donor loads and different times of pyrolysis.

Run	Temp(°C)	Load(g)	% Pyr Sol	% Coke	%Conversion	Fac
124	T450	1.2	46.8	9.0	44.2	0.79
56	T450	3.0	30.4	8.4	61.4	0.74
66	T450	3.0(4h)	11.8	11.7	76.5	0.83
122	T500	1.2	11.1	54.7	34.2	0.82
61	T500	3.0	13.7	9.1	77.2	0.83
62	T500	3.0(4h)	30.8	12.4	56.8	0.90

4.8.3 ^{1}H NMR Analysis of Recovered Asphaltenes

Table 15 illustrates the results of the ^{1}H NMR analysis of the recovered asphaltenes in the situation where the loading of the H-donor and also the time of pyrolysis were increased .

Table 15. ^{1}H NMR global analysis of recovered asphaltenes from pyrolyses involving increased donor loading (tetralin) and duration.

Run	Temp(°C)	Load(g)	Time(h)	Hγ	Hβ	Hα	Har
Virgin asphaltene				0.139	0.468	0.258	0.135
45	450	1.2	1.0	0.106	0.407	0.241	0.234
56	450	3.0	1.0	0.171	0.377	0.191	0.226
66	450	3.0	4.0	0.053	0.216	0.143	0.588
31	500	1.2	1.0	0.054	0.279	0.241	0.408
47	500	3.0	1.0	0.078	0.347	0.213	0.362
48	500	3.0	4.0	0.023	0.125	0.105	0.725

As was suspected, the increased loading did have a great effect and led to significantly increased Hγ and decreased Hβ and Hα (run 56). This might reasonably be explained by ring opening and to a lesser extent, dealkylation reactions. As the time of pyrolysis was also increased (run 66), one can see a large reversal in the trend for Har and Hγ, and again significant decreases in Hβ and Hα, suggesting that dealkylation and aromatization were the important reactions occurring. The H-aromaticity was now found to be 0.588 (run 66) compared to 0.135 for the virgin asphaltene, illustrating just how different the structures were.

At 500°C the conditions were even more severe and the changes in the asphaltene structure more deep-seated. It is evident that the same general trends applied to the recovered asphaltene. As the donor loading was increased (run 47) one can see how the formation of aromatic hydrogen was

reduced, which was not surprising considering the added availability of hydrogen which would be expected to inhibit aromatization reactions. The decrease in Hβ (compared to virgin asphaltene) was moderated, again suggesting a reduction in the amount of dealkylation and the possibility of ring opening, which had occurred. One has to remember that in the degradation of the asphaltene, the hydrogen types present in the recovered asphaltene are being studied, i.e. the alkyl fragments have become maltene and once attachment is lost with the aromatic core of the virgin asphaltene, the proportion of aromatic hydrogen in the recovered material would be higher even if no new aromatic hydrogen had been produced in the pyrolyses. Again as the time of pyrolysis was increased (run 48) the effects of the increased loading were somewhat reversed. Under these extreme conditions of pyrolysis, the structural changes were large and in these series of recovered asphaltenes the observed Har ranged between 0.230-0.725. The Hγ ranged between 0.171 and 0.023 which indicated that the amount of remaining alkyl chains (longer than 2 carbons) attached to aromatic nuclei were small, under these extreme conditions (run 48) . The fact that the change in the aromatic hydrogen was so much larger than the corresponding decrease in Hγ, suggests that the widespread dealkylation was certainly associated with a large production of new aromatic hydrogen, but that aromatization reactions were also important. Under the extreme conditions of degradation (run 48) Hβ, Hα and Hγ were all low in the recovered asphaltene and therefore one knows that the majority of substituent groups associated with the virgin asphaltene and the less degraded asphaltenes were lost (aromatized or cracked into lower molecular weight maltene products).

4.8.4 Extent of H-Transfer from Recovered Donor Solvent

Table 16 displays the results of the GC analysis of pyrolyses involving tetralin under conditions where the loading and duration of pyrolysis were varied.

Table 16. GC analysis of the recovered tetralin for the increased loading and time runs.

Run	Temp(°C)	Load	mg of H_2/ g Asphalt.	Potential Donatable	% Utilization
124	450	1.2	9.1	27.5	33.1
56	450	3.0	13.7	67.3	20.3
66	450	3.0(4h)	43.1	67.9	63.5
122	500	1.2	26.2	28.5	91.9
61	500	3.0	44.0	73.1	60.2
62	500	3.0(4h)	67.3	67.6	99.6

Comparing this information with conversion data (Table 14) it was evident that an increase in conversion was experienced when the donor loading was increased (run 56) yet there was only a small increase in the amount of hydrogen expressed from the donor (Table 16). When the duration of pyrolysis was also increased (run 66) there was a sharp increase in the hydrogen expressed as well as the conversion (Table 14). Also important, was the fact that even with the extended duration of pyrolysis, the donor was not exhausted (63.5% of the available hydrogen has been expressed).

At 500°C (run 122) one can see that although a large quantity of hydrogen was expressed from the donor, there was still a very large amount of coke formed (54.7%, Table 14). It is evident that under these pyrolysis conditions the donor potential was almost exhausted. One can see that when the loading was increased (run 61) there was a large jump in the amount of hydrogen expressed (from 26.2 to 44.0 mg H_2/g of initial asphaltene) and a very significant decrease in the coke formed (from 54.7 to 9.1%). Increasing the duration of the pyrolysis (run 62) did increase the amount of hydrogen expressed (from 44.0 to 67.3 mg H_2/g of initial asphaltene) and used all of the potential H-donor, but this was found not to contribute usefully since the conversion decreased, the coke formed increased slightly and the amount of pyridine soluble material recovered, increased significantly (Table 14).

4.8.5 Quantification of the Recovered Alkanes in the Maltene

The next step was to quantify the n-alkanes present in the maltene, using GC. Table 17 illustrates the results of this study. Looking at the increased loading run (450°C) one finds that the yield of the alkane series, in the maltene, had actually decreased (from 40.5mg to 22.1) although the conversion (previously reported) had remained almost constant. This suggests that the added donor inhibited dealkylation. When the duration of pyrolysis was increased, the yield of alkanes decreased even further (to 15.1mg) although the conversion increased (from 58.8 to 70.6%). At 500°C, under all conditions, the alkane yield was found to be zero or very small, although in the case of the increased loading and increased loading/increased duration run, the conversions were high (58.6 and 77.2% respectively). Obviously, under these conditions other components dominated the product distribution.

Table 17. Quantification of alkane fraction derived from maltene on asphaltene pyrolyses in the presence of tetralin for various lengths of time.

Add.	Load(g)	Time(h)	Temp(°C)	Wt of Alkanes(mg)	% Conversion
THN	1.2	1.0	450	40.5	59.7
THN	3.0	1.0	450	22.1	58.8
THN	3.0	4.0	450	15.1	70.6
THN	1.2	1.0	500	1.9	20.7
THN	3.0	1.0	500	0	58.6
THN	3.0	4.0	500	7.7	77.2

4.9 Large Variations in Duration of Pyrolyses-Constant Donor Loading

The previous pyrolyses reflect an attempt to optimize conversion of asphaltene under practical conditions. In this present work, much longer (less practical) durations of pyrolyses were employed to study (more from a mechanistic point of view) the extremes of conditions. Shorter durations (more practical) were also studied in order to examine, fully, the importance of contact time in the conversion of asphaltene.

4.9.2 Product Distribution

Table 18 illustrates the results of these experiments, in terms of product distribution. The standard donor loading of 2:1 (donor to asphaltene) was used.

Table 18. Product distribution on asphaltene pyrolyses with different temperatures and duration of pyrolyses.

Run	Temp (°C)	Time(h)	% Pyr Sol.	% Coke	% Conversion
172	400	1.0	57.5	18.4	42.5
93	400	24.0	28.6	16.3	55.1
188	400	65.0	13.4	30.4	56.2
97	450	0.25	82.9	3.0	14.1
95	450	0.5	57.1	6.6	36.3
124	450	1.0	46.8	9.0	44.2
160	450	24.0	5.4	37.5	57.2
102	500	0.25	50.5	28.9	20.6
103	500	0.5	22.5	17.5	60.0
122	500	1.0	9.9	31.6	58.6

From Table 18 one can see that at low temperature (400°C), the increased duration of pyrolysis did indeed drastically decrease the amount of pyridine soluble material recovered, with a small increase in conversion. This was also true at 450°C although now a corresponding undesirable increase in coke formation was observed. When the time of pyrolysis was reduced, the amount of degradation/cracking was correspondingly reduced. At 450°C and 15 minutes pyrolysis, very little happened to the initial asphaltene. Increasing the duration to 24 hours increased the conversion to 57.2% but with an undesirable increase in coke formed (compared to the 1 hour pyrolysis).

Under the more extreme thermal conditions at 500°C, even for 15 minutes, significant degradation had occurred. It was evident that at 500°C, 30 minutes was the optimum pyrolysis time (at the 2:1 loading) since this resulted in maximum conversion. Increasing the pyrolysis time to an hour only decreased the proportion of recovered pyridine soluble material with corresponding increases in coke formation and no increase in conversion. From these analyses it is evident that increasing the duration did cause more of the initial asphaltene to react but if the reaction was left too long, with insufficient stabilizing mechanisms available, e.g.from H-donors, then coke was formed in increasing amounts.

4.9.3 Extent of H-Transfer from Donor Solvent

The next step was to examine the donor utilization (GC) and conversion. The results are displayed in Table 19. It was evident from run 93 that a high proportion of the donor potential was exhausted even at low temperature with a long contact time, and the conversion was correspondingly high. The donor utilization was increased further at 65 hour duration although the conversion remained the same. At 450°C (run 97) the donor utilization and conversion was found to be very low. When the duration of the pyrolysis was increased to 0.5h the donor utilization increased slightly and there was a large increase in the conversion but still significantly less than for run 45 (1h). Even at 500°C, at short contact time (run 102), the donor utilization was found to be minimal. A maximum conversion was achieved at 0.5h (run 103) with moderate donor utilization. When the contact time was further increased to 1h, although the donor utilization increased, there was no corresponding increase in the conversion. Comparing the hydrogen expressed in runs 103 (0.5h, 500°C) and

60 (1h, 500°C), it was clear that using more of the donor potential did not guarantee a higher conversion.

Table 19. Donor utilization (asphaltene pyrolyses) with variable time and constant (2:1) donor loading (tetralin).

Run	Temp.(C)	Time(hrs)	$mgH_2/gAsp^*$	Donor Potential	%Conversion
37	400	1.0	1.7	28.7	42.5
93	400	24.0	19.0	29.6	55.1
188	400	65.0	23.0	29.2	56.2
97	450	0.25	0.1	30.6	14.1
95	450	0.5	3.5	29.1	36.3
45	450	1.0	9.1	27.5	44.2
102	500	0.25	0.9	29.3	20.6
103	500	0.5	15.2	28.0	60.0
60	500	1.0	26.2	28.5	58.6

* mg of H2 expressed from the donor solvent per gram of initial asphaltene.

4.9.4 Alkane Quantification

Looking at Table 20 and comparing the quantified n-alkane fraction recovered in the maltene fractions, one can see that large values were found for the long, low temperature runs (93 and 188). The shorter, higher temperature (450 and 500°C) runs yielded low values for the respective alkane fractions. One has to remember that GC-MS analysis showed that the low alkane yield for

the high temperature runs were due to reforming reactions, yielding benzenes as opposed to alkanes, rather than to insufficient reaction times. From Table 19 data it was apparent that the high temperature reforming was not a function of H-donor depletion. It was evident that optimum conversion, with respect to alkanes in the recovered maltene, occurred at 400°C, long contact times and at 450°C at shorter contact times (1h).

Table 20. Alkane quantification (from recovered malteneand) and ^{13}C aromaticity (of recovered asphaltene) for variable time runs (tetralin).

Run	Temp.(C)	Time(hrs)	Fac	Wt Alkanes (mg)
37	400	1.0	0.58	6.9
93	400	24.0	0.92	54.4
188	400	65.0	0.95	51.3
97	450	0.25	0.55	0.8
95	450	0.5	0.64	3.5
45	450	1.0	0.74	40.5
102	500	0.25	0.57	1.9
103	500	0.5	0.76	2.1
60	500	1.0	0.82	1.9

4.9.5 Degradation of the Recovered Asphaltene

Table 20 shows the results of ^{13}C NMR analyses of the recovered asphaltenes. One might expect a correlation between the aromaticity of the asphaltene and the subsequent yield of alkanes (in the maltene), i.e. the more alkyl groups cleaved from the aromatic nuclei of the asphaltene, the more

aromatic the recovered asphaltene would expected to be. Looking at the carbon aromaticity of the recovered asphaltene run 188 (65h,400°C), compared to that for run 37 (1h 400°C) , it is evident that deep-seated degradation of the virgin asphaltene had occurred and that the recovered asphaltenes (from the more extreme pyrolyses conditions) were very different, structurally from the virgin asphaltene. It is interesting that the long duration, low temperature runs (93 and 108) also caused very highly aromatic, very degraded, recovered asphaltenes.

4.10 Effects of Promoters in the H-donor/Asphaltene Reaction

After learning how the reaction conditions (duration and temperature) affected the ability of a donor to transfer hydrogen to the asphaltene, one wondered if the H-donation was a purely thermal reaction or if the rate of H-transfer could be influenced by the addition of a promoter. To this end, pyrolyses were carried out at the standard loading and duration (2:1, 1 hour) using tetralin and either a small amount (50mg) of a metal carbonyl (possible hydrogenation-dehydrogenation catalyst) or a sulphur compound (radical initiator in the amounts shown in Table 21.

4.10.2 Product Distribution

Table 21. Product distribution of pyrolysis of asphaltene in the presence of tetralin / sulphur initiator.

Temp (°C)	Add.	% PSBS	% PSBI	% Coke	% Conversion	Fac
300	T	78.0	0	4.1	17.9	0.52
300	T+1(0.1g)	78.9	6.2	9.7	5.3	0.57
300	T+1(0.3g)	62.0	1.2	31.3	5.5	0.55
300	T+2(0.3g)	82.4	3.4	10.5	3.7	0.55
300	T+3(0.3g)	76.6	3.8	16.3	3.3	0.56
400	T	53.3	4.2	18.4	24.1	0.59
400	T+2(0.1g)	59.9	6.1	3.3	30.8	0.58
400	T+3(0.1g)	60.0	0	8.0	31.9	0.60
450	T	26.2	12.9	6.7	45.8	0.74
450	T+1(0.1g)	20.6	15.8	11.5	52.1	0.82
450	T+2(0.1g)	13.2	27.4	4.3	55.1	0.78
450	T+3(0.1g)	17.8	14.9	4.5	62.8	0.74

1=PhSH PSBS=Asphaltene

2=PhSSPh PSBI=Preasphaltene

3=$PhCH_2SPh$ T=Tetralin

Looking at Table 21 it appears that the addition of the indicated sulphur radical initiators had little or no effect on the product distribution. There was an increase in coke formation at 300°C (runs with PhSH, 0.3g and $PhCH_2SPh$,

0.3g) compared to the control, where tetralin was present alone . This result might have been expected (confirmed in section 4.11) as a result of adding an initiator to the tetralin/asphaltene mixture, during pyrolysis. Stimulation of H-transfer from the H-donor might also have been expected which would effectively counter the added asphaltene radical formation.

4.10.3 Extent of H-Transfer from the H-Donor

The next step was to ascertain if these sulphur additives had had any influence on the donor utilization. The results of the GC analysis are displayed in Table 22.

Comparing the control runs where only the tetralin was present to those with the sulphur additives, it appeared as if the presence of the additives did increase the amount of donor potential utilized under most of the conditions tested. This agreed with observations by Stock et al. [110] in H-donor coal liquefaction studies. Also, in work carried out by Potgieter [116], different catalysts were tested for their propensity to dehydrogenate the H-donor, i.e. tetralin. It was found that stannous chloride was not an ideal catalyst for hydrogenation of coal since it caused tetralin to be hydrogenated to decalin, which is not an effective H-donor. CoO_2-KO was found to be more effective in dehydrogenating tetralin and the rate of dehydrogenation of tetralin was found to be directly related to the rate of coal hydrogenation.

Contrary to this, in a study by Curran et al. [101], the kinetics of transfer of hydrogen from tetralin were studied. A Pittsbugh coal was reacted with tetralin at 325-450°C and residence times from 2.5 minutes to 2 hours, in a sealed autoclave. Maximum H-transfer amounted to 2.2-2.6 %weight. The hydrogen transfer process was suggested to be purely a thermal reaction and attempts to accelerate the reaction by the addition of catalysts (hydrocracking or

hydrogenation) were unsuccessful. Also the reaction (coal conversion) was found not to depend on the nature of the H-donor solvent, i.e. as long as mobile hydrogen atoms were available for transfer.

Table 22. GC analysis of recovered donor solvent from runs where tetralin and a S-additive were employed.

Run	Additive	Temp (°C)	mgH2/gAsp* Expressed	mgH2/gAsp* Potential of Donor	% Utilization
78	T	300	0	29.5	0
79	T+2(0.3g)	300	1.6	28.4	5.6
80	T+3(0.3g)	300	0.83	29.8	2.8
84	T+1(0.1g)	300	0	29.6	0
85	T+1(0.3g)	300	0	28.7	0
37	T	400	1.6	28.9	5.5
72	T+2(0.1g)	400	2.7	28.1	9.6
73	T+3(0.1g)	400	2.4	27.5	8.7
45	T	450	9.1	27.5	33.1
70	T+2(0.1g)	450	12.7	29.6	42.9
71	T+3(0.1g)	450	10.8	29.0	37.2
86	T+1(0.1g)	450	11.0	29.0	37.9

* mg of H_2 expressed from H-donor per gram of original asphaltene.

4.10.4 Metal Carbonyl Additives

Next, runs involving the addition of metal carbonyls were studied. Table 23 illustrates the product distribution of the runs carried out compared with a control. All pyrolyses were carried out under the standard loading of tetralin:asphaltene (2:1) for 1 hour at 450°C.

Table 23. Product distribution, GC and ^{13}C NMR (of the recovered asphaltene) analysis of the tetralin/metal carbonyl pyrolysis runs.

Additive	% PSBS	% PSBI	% Coke	% Conversion	Fac	mg H_2/g Asp*
None	26.2	12.9	6.7	45.8	0.74	9.1
$Fe(CO)_5$	20.6	13.1	11.1	55.2	0.76	7.3
$Co_2(CO)_8$	23.9	10.6	13.6	52.0	0.81	9.8
$Cr(CO)_6$	19.7	7.3	13.2	59.8	0.75	12.8
$Mo(CO)_6$	17.5	4.9	17.2	57.3	0.80	13.8
$W(CO)_6$	25.3	3.1	10.6	61.0	0.78	11.1

* mg of H_2 expressed from H-donor per gram of original asphaltene.

Looking at Table 23 it is evident that there are small differences in the product distributions of the metal carbonyl runs, compared to the control. The addition of the metal compound appears to have caused the formation of more coke and increased the conversion. Looking at the GC results (remembering that the donor potential amounts to around 18 mg of H_2/g Asphaltene) one can see the differences in the hydrogen used. The presence of Cr, Mo and W appear to have increased the hydrogen expressed from the donor to a small degree. Interesting, the presence of the iron catalysts appears to have impeded

expression of hydrogen from the donor. The carbon aromaticities of the recovered asphaltenes were slightly higher than the control situation where the donor was alone present, indicating that more degradation of the virgin asphaltene has occurred.

4.11 Reaction of Bitumen Asphaltene with Radical Initiator

Previously (this chapter), thermal degradation of bitumen or coal was described as occurring by free radical mechanisms. The presence of a H-donor was thought to transfer hydrogen to reactive radical fragments which prevented regressive combination and eventual coke formation. One has to remember that a large amount of hydrogen donor capability resides within the asphaltene structure itself. In the absence of a suitable H-donor these radical fragments could combine in radical termination steps to form higher molecular weight material and eventually, coke.

In this next series of experiments, bitumen asphaltene was pyrolyzed in the presence of sulphur radical initiators to see if, as might be expected, coke formation would be increased. Table 24 illustrates the results of this study, in terms of the observed product distribution in these pyrolyses.

Looking at Table 24 it was evident that at 300°C the addition of the indicated sulphur radical initiators caused larger amounts of higher molecular weight material to be formed. The carbon aromaticities of the recovered asphaltenes from these runs were also significantly higher (indicating increased degradation/aromatization). At 400°C the effects of the initiators was even more evident. The recovered pyridine soluble material was lower with corresponding increases in the amount of coke formed (compared to the control). Again the carbon aromaticities of the recovered asphaltenes, from the runs where initiators were present, were much higher than the control. At 450°C the

differences in the product distributions were small, presumably because even without the initiators being present, almost all of the initial asphaltene had formed coke. Obviously, the H-donor functionality, inherent in the asphaltene itself, were insufficient to stabilize the reactive radicals formed under these higher temperature conditions. The recovered asphaltenes from runs with the initiators present, again had much higher carbon aromaticities than the control (0.98-0.99 as compared to 0.78 for the control).

Table 24. Product distribution and carbon aromaticity (recovered asphaltene) of pyrolyses involving bitumen asphaltene and sulphur radical initiators.

Temp (°C)	Additive	% PSBS	% PSBI	% Coke	% Conversion	Fac
300	None	54.6	2.2	5.2	38.0	0.50
300	2 (0.1g)	54.7	5.9	42.4*	0	0.58
300	3 (0.3g)	74.7	15.9	8.6	0.7	0.55
300 (2h)	2 (0.3g)	37.1	2.6	27.9*	32.4	0.61
400	None	53.5	15.4	13.6	11.5	0.60
400	2 (0.3g)	25.3	21.1	38.4	15.3	0.72
400	3 (0.3g)	32.6	16.6	49.2	1.5	0.70
450	None	12.9	0	58.4	28.7	0.78
450	1 (0.3g)	6.0	5.2	52.5	36.3	0.98
450	2 (0.3g)	11.6	0	63.5	24.9	0.99

1=PhSH 2=PhSSPh 3=$PhCH_2SPh$

* Under low temperature pyrolyses separation of coke from PS is difficult.

The presence of the sulphur radical initiators obviously caused extensive additional regressive condensation (formation of coke) compared to the control situations where only asphaltene was present. This presented itself in the form of reduced amounts of recovered pyridine soluble material as well as dramatic increases in the amount of coke formed and most obviously in the carbon aromaticities of the recovered asphaltenes.

4.12 Concluding Discussion

It has been demonstrated that H-donors are very successful in reducing coke formation during the pyrolysis of bitumen asphaltene. Interestingly, 1-methylnaphthalene was also found to have significant ability in reducing coke formation even though it had no net H-donor capability. Tetralin was found to be a particularly useful donor over the range of temperatures tested. 9,10-dihydrophenanthrene was the best H-donor at lower pyrolysis temperatures (in terms of ability to donate hydrogen). The thermal degradation of asphaltene (in the presence of H-donors) was characterized by dealkylation, aromatization, condensation, and at low temperature, ring opening reactions.

Examination of the virgin asphaltene using ^1H NMR revealed that the average length of the alkyl substituents was 10 carbons long. Subsequent pyrolysis of the asphaltene resulted in the formation of alkanes (recovered in the maltene) with up to nC_{30}. At 450°C pyrolysis with tetralin caused double the amount of alkanes to be formed compared to the situation where no donor was used. It appeared that a large proportion of the alkyl content that was bound in the asphaltene structure could only be released under reducing conditions. If no H-donor was present the alkane yield in the maltene was much lower. What is surprising is that it was the yield and not the average chain length which was affected by the presence of the donor.

GC-MS analysis of recovered maltenes has demonstrated that the formation of alkene fragments was common where no donor was available but this was prevented in the presence of a H-donor. At 400-450°C the maltenes recovered were dominated by homologous series of n-alkanes. Once the temperature was increased to 500°C, the product distribution changed dramatically and was now dominated by substituted benzenes (even in the presence of excess H-donor), suggesting that a reforming reaction had occurred.

Increasing donor loading (450-500°C) was found to improve the conversion of the initial asphaltene to a maximum of around 77%. The high molecular weight material recovered under these optimal upgrading conditions was very resistant to further degradation. Increasing the duration of pyrolyses at 400°C also dramatically improved the amount of useful degradation which occurred to the asphaltene (compared to lower contact times). A high yield in alkanes from the recovered maltene and an optimal conversion of around 9-10% of the initial starting weight of asphaltene, were established under these conditions.

Addition of small amounts of transition metal carbonyl compounds or sulphur radical initiators (as dehydrogenation promoters) to an asphaltene / tetralin mixture, during pyrolysis, caused small increases in donor utilization, indicating that these species did promote dehydrogenation of the tetralin or increased radical activity in the asphaltene.

Reaction of the asphaltene with sulphur radical initiators was found to dramatically increase the yield of high molecular weight products recovered on pyrolysis. In the absence of a H-donor or sufficient internal H-donor functionality the increase in radical activity led to regressive combination of high molecular weight, asphaltene derived species, eventually forming coke.

In this preceeding work, NMR spectroscopy was found to be very useful in providing an idea of the processes important in coke formation and how they are retarded in the presence of H-donors, however, more precise mechanistic details were required. Therefore from a practical/industrial point of view, this work was very useful but from a strictly chemical point of view, the information gained was somewhat imprecise. This was also true when considering the initial objectives of this chapter. In an effort to provide more detailed mechanistic information, it was thought that use of a deuterium labelled donor (in the pyrolyses of asphaltene) would be an ideal method of studying the upgrading reaction. The presence of the label could be followed in the pyrolysis products.

Chapter 5

The Reaction of d-$_{12}$ Tetralin with Bitumen Asphaltene

5.1 Introduction

It has already been demonstrated that H-donors are very useful in upgrading bitumen asphaltene to lower molecular weight products (chapter 4). Their presence was found to prevent regressive combination reactions from occurring (coke formation) and to increase the amount of useful low molecular weight products. Tetralin was found to be particularly efficacious in this role. Also, importantly, it was easy to remove from reaction products (3 ring H-donors were difficult to separate from the products formed).

5.1.2 Use of Deuterium Labels in Upgrading

Schweighart et al. [61] pointed out that deuterium labels could be employed to probe the course of conversion reactions. Deuterated tetralin was used in this role. Significant work has been carried out involving a deuterium label to follow coal liquefaction reactions [117-119].

Reaction of an Illinois No. 6 coal with d_{12}-tetralin was reported by King et al. [62]. Examination of the recovered tetralin revealed that the exchange, to coal molecules, had occurred rapidly and quite selectively at the 1-position. During reaction of d_8-naphthalene with the coal, exchange occured at the 1-position more rapidly than at the 2-position. However at short reaction times, the difference in selectivity was small. At longer reaction times the selectivity for exchange at the 1-position increased. This suggests that the coal radicals formed in the initial stages of conversion reacted in a non-discriminatory fashion. As the reaction proceeded the discrimination of the radicals increased.

The exchange reaction of the coal molecules was found to be reversible. This was established by back reacting the coal liquids with h_{12}-tetralin.

Franz et al. [63] examined the conversion of Kaiparowitz coal into THF soluble material in the presence of d_2-tetralin at 427°C. Deuterium was found to have exchanged into α,β,γ-aliphatic, as well as aromatic positions.

Skowronski et al. [64] reacted a Pittsburgh coal with d_{12}-tetralin and /or D_2 gas. It was found that exchange occurred from both gas and donor solvent. When the coal was reacted with D_2 gas alone, the deuterium content was found to increase with increasing molecular weight of the fraction. When d_{12}-tetralin was also used, a more uniform spread of deuterium was found. In all products, exchange into the benzylic positions predominated but some exchange was found in all possible environments.

5.2 Objectives and Stategy

The objectives of the following work were to use the deuterated equivalent of tetralin, in pyrolysis of asphaltene, in order to follow the transfer of the isotopic label into upgraded material, during pyrolyses. It was hoped that this could be achieved by pyrolyses of bitumen asphaltene at the same temperatures as used in previously described work (chapter 4), with labelled tetralin. The products of pyrolysis would be separated as before, into maltene (along with residual donor, used or unused), asphaltene, preasphaltene and coke. The residual donor would then be analyzed using ^1H NMR to study the selectivity of exchange (if any). GC analysis would reveal how much donor was dedeuterated during pyrolysis. The maltene would then be separated from the donor residue by column chromatography and then analysed by capillary GC-MS to look at the individual components. Finally the recovered asphaltene would be examined using ^2H NMR to locate the environments in which the

transferred deuterons found themselves.

5.3 Experimental

Using exactly the same pyrolysis procedure as before with the h_{12}-tetralin, the d_{12}-labelled analogue (Supplied by Aldrich at 99% isotopic purity) was now used. d-Tetralin (1.0g) was pyrolysed with 500mg of asphaltene in a tube bomb for an hour at different temperatures. The amounts of d-tetralin and asphaltene used were scaled down because of the high cost of the deuterated solvent. The pyrolyses products were separated in the same manner as in the previous chapter into maltene, asphaltene, preasphaltene and coke. The fractions were then analyzed using capillary GC-MS and NMR.

5.4 Results and Discussion

5.4.1 Product Distributions for Asphaltene Pyrolyses

The observed product distributions are shown in Table 25 where they were compared to those for the equivalent unlabelled pyrolyses, from Chapter 4. The carbon aromaticity of the recovered asphaltene was also included to give the reader some idea of how degraded the recovered, benzene soluble fraction was, on pyrolyses.

It was evident that the use of d-tetralin as opposed to h-tetralin did not make very much difference in terms of product distribution or in the carbon aromaticity of the recovered asphaltene.

Table 25. Product distribution and carbon aromaticity (recovered asphaltene) for pyrolyses comparing h-$_{12}$ tetralin/d-$_{12}$ tetralin.

Temp. (°C)	Add	%PSBS	% PSBI	% Coke	% Conversion	Fac
350	T	58.8	4.7	30.2*	6.2	0.56
350	TD	45.6	0	44.2*	10.2	0.57
400	T	53.9	5.5	12.4	28.2	0.60
400	TD	60.1	7.5	8.2	24.3	0.62
450	T	15.6	21.2	9.0	44.2	0.74
450	TD	16.2	18.0	10.0	55.8	0.76

T=tetralin TD=d-tetralin PSBS=asphaltene PSBI=preasphaltene

* At this temperature complete separation of pyridine soluble from insoluble material was very difficult because of the stickiness of the recovered products and it is strongly suspected that values for coke formed are too high and that values for pyridine soluble material are too low.

5.4.2 Analysis of the Recovered Asphaltene with ^{2}H NMR

The asphaltene recovered from the pyrolyses was analyzed using ^{2}H NMR. At 350°C the deuterium incorporation was found to be extremely low. The spectra obtained from the asphaltenes recovered at 400 and 450°C revealed that exchange had occurred in all possible environments, i.e. aromatic, benzylic and aliphatic. As was noted in work on d-pyrene (chapter 3), a disproportionate amount of exchange occurred in the benzylic position and again a back

exchange reaction of the recovered asphaltene (under the same conditions) revealed that this incorporation (benzylic) was reversible.

5.4.3 Extent of Deuterium Transferred from the D-Donor Solvent

The next step was to analyze the recovered D-donor solvent using GC to find out how much of the tetralin was converted into naphthalene. Table 26 illustrates the results of this study again compared to those of the unlabelled pyrolyses.

Table 26. GC analysis of recovered D-donor.

Temp. (°C)	Additive	% Naphthalene	% Tetralin
350	Tetralin	<1%	100.0
350	d-Tetralin	<1%	100.0
400	Tetralin	5.4	94.6
400	d-Tetralin	2.4	97.6
450	Tetralin	33.0	67.0
450	d-Tetralin	23.1	76.9

The results from the GC analysis (Table 26) give an idea of how much donor was dehydrogenated/dedeuterated during pyrolyses with the asphaltene. One can see clearly how temperature dependent the observed donor utilization was. It is also evident that there were differences in donor utilization when comparing data for d-tetralin and h-tetralin, at the same temperature.
At both temperatures where any tetralin was dehydrogenated to naphthalene (400 and 450°C) it was obvious that donor utilization was higher in the H-donor,

as opposed to the D-donor. This suggested a kinetic isotope effect which would indicate that initial breaking of a C-H bond in tetralin was involved in the rate determining step of the pyrolysis reaction, contrary to the widely held belief that required the rate determining step to be the initial homolysis of a C-C bond in the coal structure [101]. Studies with d-tetralin and D_2 gas, however, in coal liquefaction experiments by Brower et al. [122] and Skowronski et al. [64] revealed large kinetic isotope effects.

5.4.4 ^{1}H NMR Analyses of the Recovered, Exchanged D-donor

The next step was to study the recovered donor solvent using ^{1}H NMR to find out if the exchange from the deuterated solvent was selective. Figure 40 illustrates the resultant spectra where one is looking at protons which exchanged into the initially, fully deuterated tetralin. For comparison, the spectra of h-tetralin and naphthalene were included. Examination of the spectrum of the recovered solvent (pyrolysis at 400°C) revealed that transfer of deuterium from the d-tetralin had been highly selective from the Dα position. This agreed with work carried out by King et al. [62] on coal liquefaction. When the temperature of pyrolysis was increased to 450°C, the selectivity was still high, but less than at 400°C. This result suggested that the mechanism for H/D transfer involved the pathway outlined in Figure 41. The evidence for this mechanism was further reinforced by comparison to work carried out by Franz et al. [123] who studied the pyrolysis of dihydronaphthalene in a tube bomb at 300°C and found among the products tetralin and naphthalene (expected disproportionation products) and also a small amount of dimers of the 1-tetralyl, 1-hydronaphthyl and 2-hydronaphthyl radicals (C_{20} products) which were obviously intermediates in this reaction.

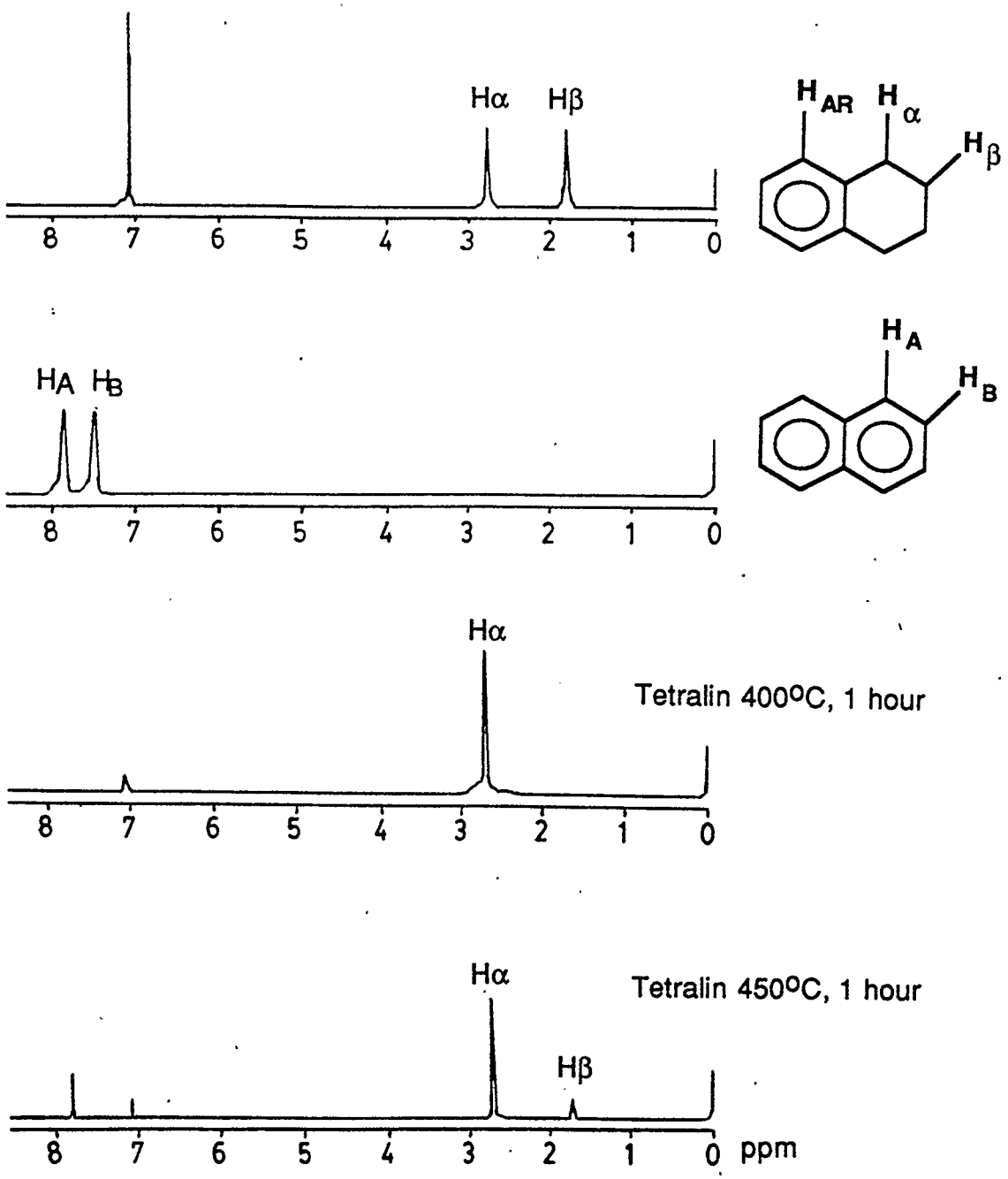


Figure 40. ^{1}H NMR of the recovered d-tetralin

Their pyrolysis was also carried out with deuterated dihydronaphthalene (at the 4 position), so that they can be more certain of the mechanistic interpretation of the product distribution. When the pyrolysis was carried out at higher temperatures the C_{20} products were insignificant and now there was H_2 formed in significant yields.

It was also interesting that in the recovered naphthalene (from pyrolysis at 450°C, this work) the selectivity was for exchange at the D_A position. Again this was observed by King et al. [62] in coal work. This exchange was expected based on what was said in chapter 3 about radical energies .

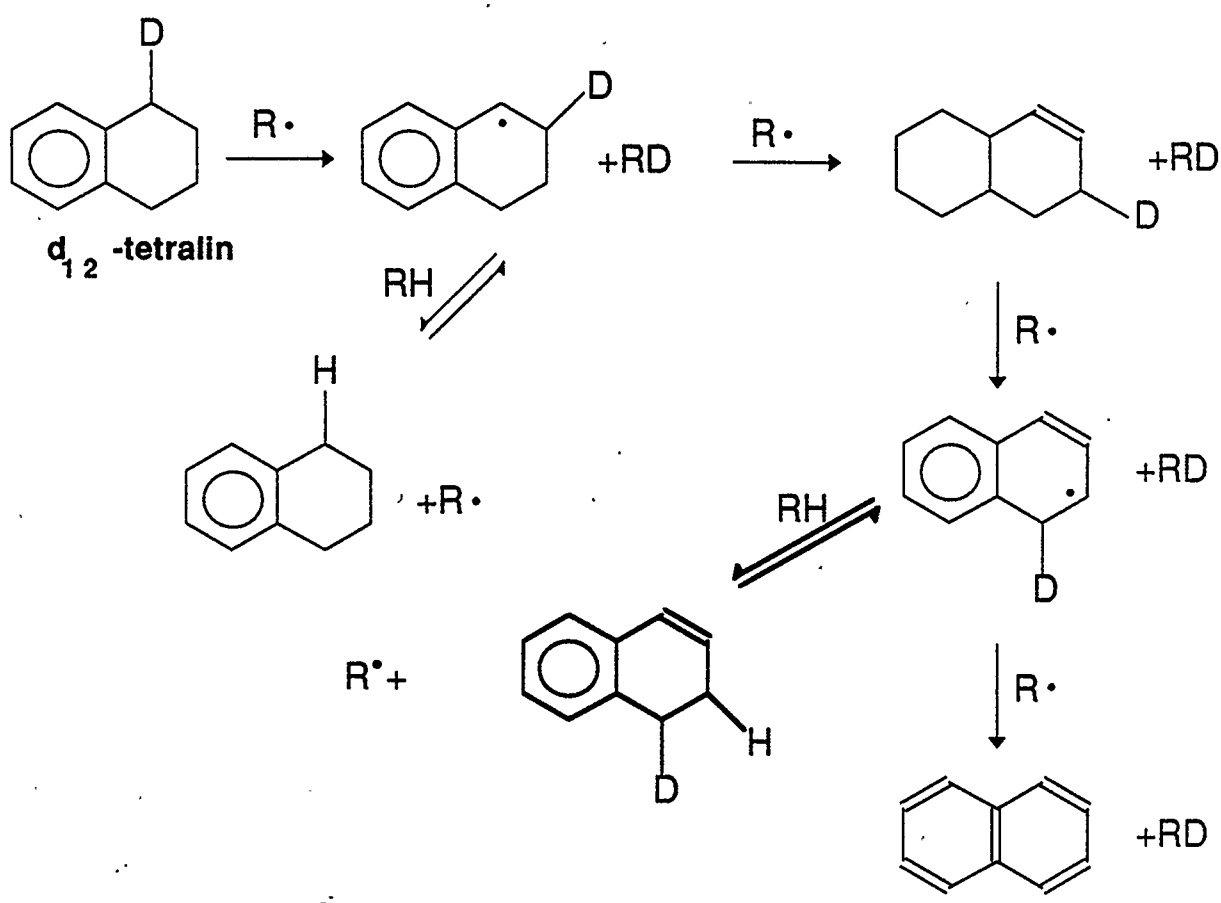


Figure 41. Mechanism for deuterium transfer from d-tetralin.

5.4.5 Analysis of Recovered Maltene using Capillary GC-MS

The isolated maltenes were analysed using capillary GC-MS. At the lower temperatures (350 and 400°C) little, if any, deuterium incorporation was detected. For example, at 400°C the series of n-alkanes (mentioned in chapter 4) was present at smaller concentrations compared to 450°C but found to be unexchanged (looking at the molecular ion peaks from the MS spectra of the individual alkanes). At 450°C the TIC of the maltene consisted of the expected homologous series of n-alkanes (Fig. 42) and exchange had now occured into the alkanes. The extent of exchange is displayed in Figure 43. The fragmentation patterns of the individual alkanes indicated that the exchanged deuterons were regularly spaced along the alkane chain.

d-Tetralin 450°C, 1 hour.

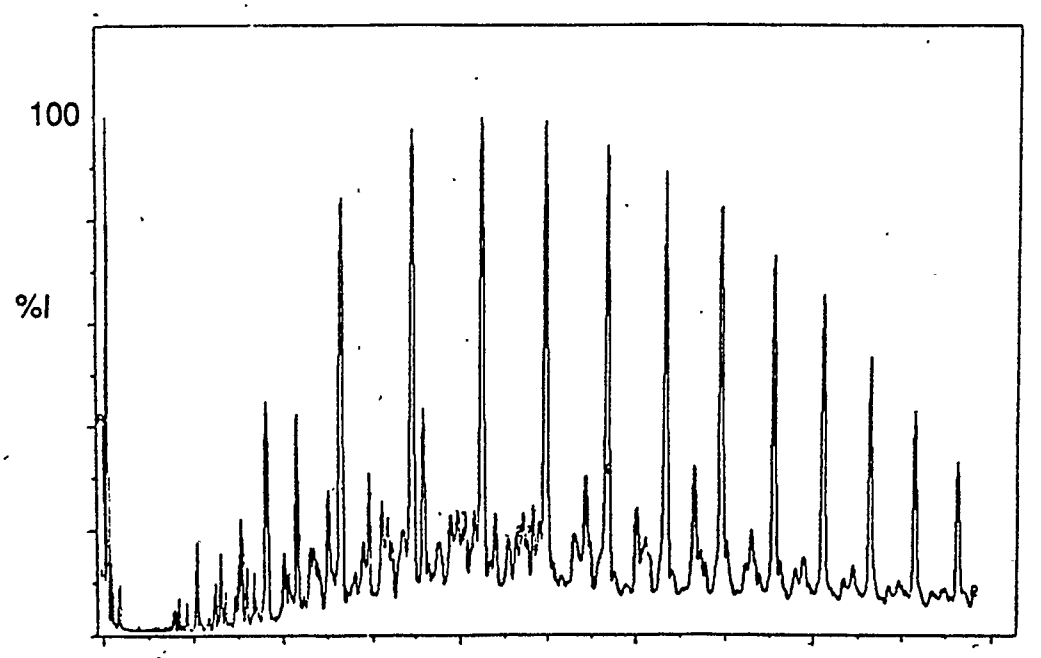


Figure 42. GC-MS TIC of the recovered maltenes.

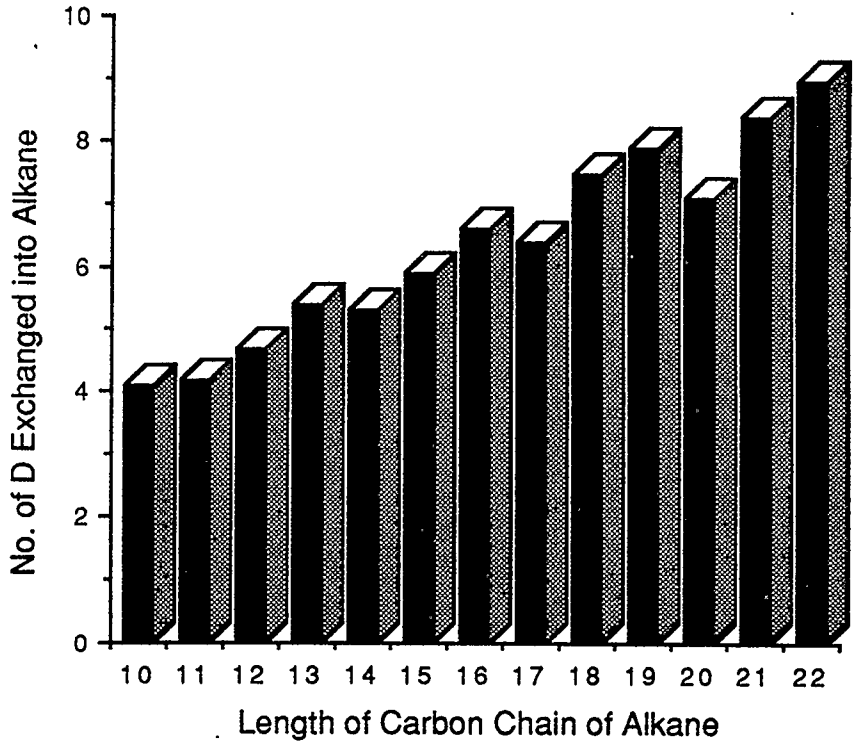


Figure 43. Deuteriums exchanged into carbon chains of alkanes from maltene from pyrolysis with d-tetralin at 450°C for 1 hour.

It was apparent (Fig. 43) that the incorporation of deuterium was high, i.e. 4 deuterons per n-C_{11} and 8 per n-C_{22}. This high level of incorporation was very surprising and raised questions as to the bonding of the alkanes within the asphaltene matrix, i.e. how can the high average level of substitution be explained, in terms of how the alkane resides in the asphaltene matrix before pyrolysis, assuming that deuterium found its way into the chain as a result of dealkylation.

5.4.6 Location of Alkanes in Asphaltene Structure

Early attempts to study the alkyl side chains in petroleum asphaltenes using NMR led to the conclusion that the average chain length was small and mainly methyl [124]. More recent studies by Takegami et al. using ^{13}C NMR suggested that the average chain length was actually larger [125]. Speight studied the pyrolysis products of Athabasca asphaltene and found straight chain alkanes up to C_{26}. In a similar study by Steedman et al. [126] straight chain alkanes were found up to C_{35} in coal asphaltene pyrolysis.

The nature of the alkanes in asphaltene is still not certain [127-128]. Bartle et al. [129] found that the yield of alkanes was much larger in a supercritical gas extraction (SCG) than in conventional solvent extraction procedures. It was suggested that the additional alkanes released in the SCG extraction were derived from those physically adsorbed in the coal matrix. Snape et al. [130] further suggested that these additional alkanes did not originate from the reduction of straight-chain fatty acids, but from those present in the pore structure or from the decomposition of alkyl chain structures bound within the coal matrix. In similar relevant work, Hayakawa et al. [131] liquefied 4 coals and studied the alkane content and cracking behaviour. It was found that the Wanodan coal contained 5.2 wt% (dry coal base) in the range C_{10} to C_{35} of n-alkanes.

5.5.6.2 Alkanes Recovered from Pyrolysis of Coal in the Presence of Tetralin

It is found by Baset et al. [132] that the yields of alkanes released during pyrolysis of coal with tetralin at 400°C, were 6-8 times greater than the yield obtained by Soxlet extraction with an azeotropic mixture of benzene and ethanol. This strongly suggested that at least some of the alkanes were not free

but required hydrogenation for maximum yields.

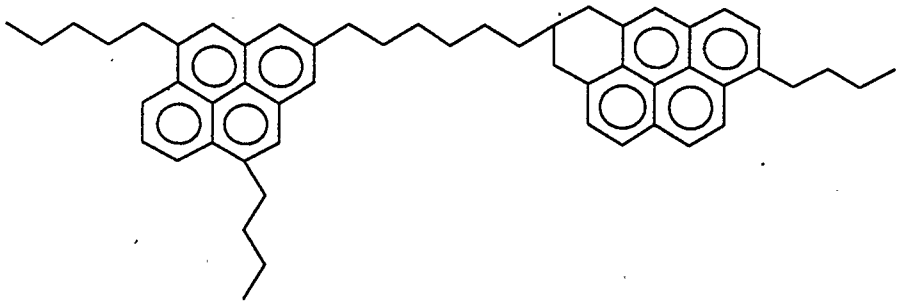
5.5.6.3 Ru (VIII) Catalyzed Oxidation of Athabasca Asphaltene

In order to learn more about the structural features of asphaltene, Strausz et al. [41] conducted studies involving very selective oxidation of Athabasca ashaltene with Ru (VIII). This method of selectively oxidizing is well known [133-134] and was used to convert alkyl side chains on aromatic nuclei to n-alkanoic acids. Polymethylene chains bridging two different aromatic nuclei were converted into α,ω-dicarboxylic acids. Once the asphaltene was oxidized it was reacted with excess diazomethane in order that the resultant mixture could subsequently be analyzed by GC-MS. On analysis it was found that the C_{15} sidechain was the most prevalent. Interestingly, the oxidation of the maltene fraction revealed a homologous series of esters from cleavage of the alkyl side chains, of which the C_{11} side chain was found to be the most common. In the asphaltene case, a series of diesters (formed from alkane chain originally connecting two aromatic nuclei) was also found, of which 1,12-dodecanedioate was the most common. In other work by Strausz et al. [135] a benzenetri- and tetracarboxylic acids were also found.

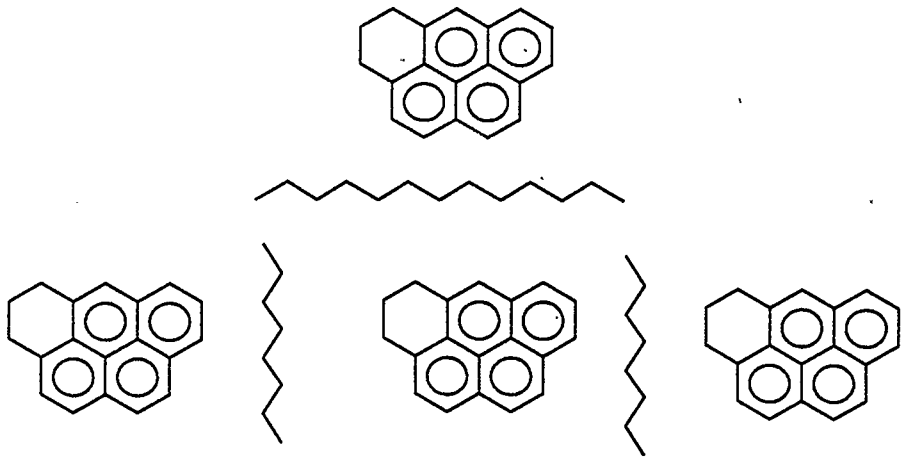
5.5.6.4 Models of Alkanes in Asphaltene

Figure 44 illustrates a much simplified picture of the suspected location of the alkane chains, in asphaltene. The first suggested possibility (1) involves the chains being bonded to smaller aromatic/hydroaromatic nuclei at one or both ends of the chains. There is evidence for this type of structure from the oxidation studies [41,136] using ruthenium tetroxide which was enlarged upon earlier. The

(1) Alkane bonded to aromatic nuclei.



(2) Occluded alkane.



(3) Multiple bonding to aromatic nuclei.

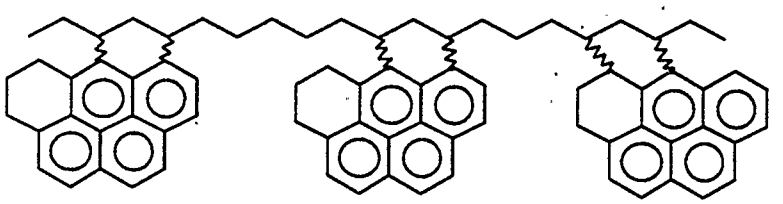


Figure 44. Simplified Ideas of alkane bonding within the asphaltene matrix.

second idea (2) suggests that the alkanes are occluded in the asphaltene/coal matrix without being chemically bonded [130]. This seems unlikely since multiple reprecipitation of the asphaltene does not diminish the presence of the alkanes on pyrolysis. Based on the present results a third structure (3) was considered. It appeared to be a possible way to explain the high level of incorporation.

5.6 Back Exchange of the Recovered Maltene

With this uncertainty surrounding the bonding of the alkanes, a further experiment was performed to try to clarify the situation. The recovered maltene (containing the exchanged alkanes) was back reacted with $h\text{-}_{12}$ tetralin under the same conditions as the initial exchange was conducted. If the incorporated deuterium could not be back exchanged out of the alkanes, then this would suggest that multiple bond breaking was involved in the evolution of the alkanes from the asphaltene. The back reacted maltene was analyzed using capillary GC-MS and the resulting deuterium incorporation is displayed in Figure 45. For comparison, the original incorporation (before back reaction) is also illustrated.

Looking at Figure 45 it was evident that back exchange of the deuterium from the alkane chains did not occur. The incorporation was, within experimental error, the same as observed before. The result of this experiment showed that under the initial pyrolysis conditions, irreversible incorporation of deuterium had occurred. This in turn suggested that the third structure (Fig. 44) involving multiple bonding to the aromatic nuclei was still a reasonable one.

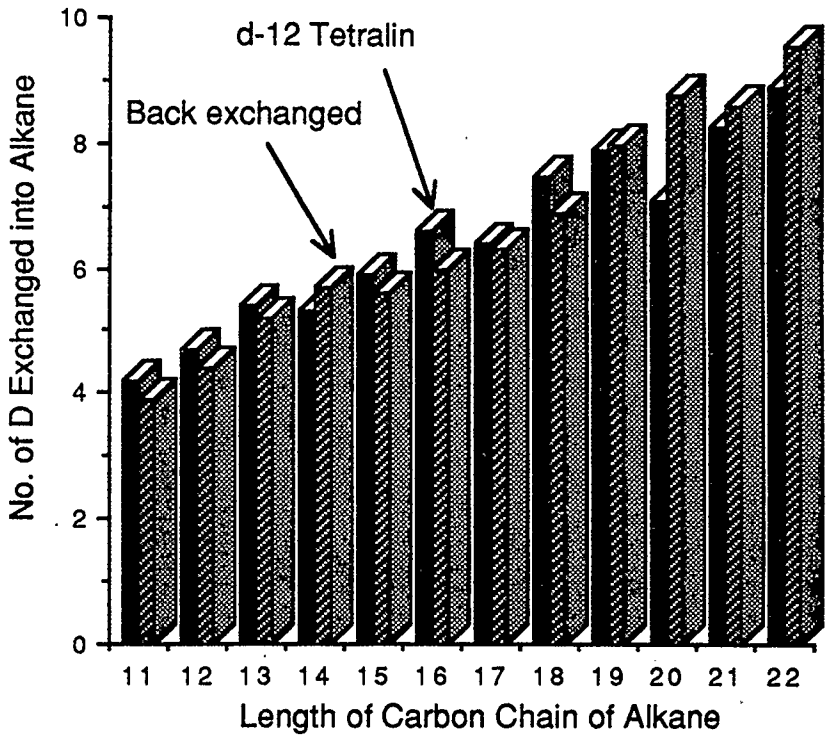


Figure 45. Extent of deuterium incorporation, (1) initially after reaction of d_{12}-Tetralin with asphaltene (450°C, 1hour) and then (2) after back exchange in the presence of h_{12}-Tetralin.

5.7 Spiking Reaction with n-C25/asphaltene/d-12 tetralin

A further experiment was conducted to clarify this problem. This involved pyrolysis of the asphaltene (277.8mg), d-$_{12}$ tetralin (582.2mg) and a spike of n-C_{25} (284.4mg). The pyrolysis was carried out at 450°C for 1 hour, again in the previously described tube-bomb. The idea was that if the multiple bonded structure (3) was valid then the spike of free n-C_{25} would not exchange with the available source of deuterium.

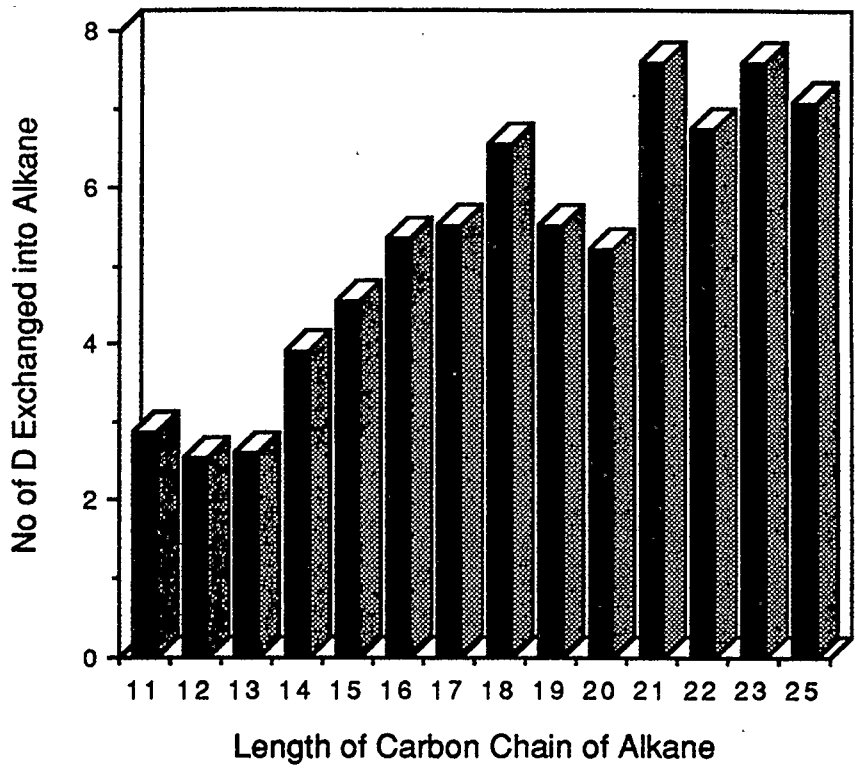


Figure 46. Deuterium exchange into nC_{25} spike (and maltene alkanes as well as alkane fragments from decomposition of nC_{25}) in the reaction of asphaltene/nC_{25}/d_{12}-tetralin at 450°C for 1 hour.

Figure 46 displays the results of the GC-MS analysis of the recovered alkane-rich maltene. As expected deuterium exchange had occurred into the n-alkanes initially thought to have evolved from the asphaltene. Again it was evident that the incorporation was high, ranging from 3 deuterons in n-C_{11} to 7 in n-C_{25}. Of more significance was the fact that the spike (nC_{25}) had exchanged an average of 7 deuterons per molecule. GC analysis of the recovered maltene revealed that only half of the original spike remained intact and that the other alkanes were present in much greater amounts than could possibly have been derived from the asphaltene, alone. The only explanation of these results was

that, under the reaction conditions, the n-C_{25} spike had partly cleaved into smaller alkanes. This result indicated that free alkanes were much more reactive under the conditions of pyrolysis, i.e. in the presence of asphaltene, than was previously thought.

5.7.2 Possible Direct Exchange between nC_{25} and d_{12}-tetralin

After the previous result, it was thought to be necessary to study the pyrolysis of a free alkane and d-tetralin (without the asphaltene being present), to find out if exchange occurred into the spike. The exchange reaction between nC_{-25} (100mg) and d_{-12} tetralin (200mg) was carried out at three different temperatures 400-450°C for 1 hour in the same tube bomb. The recovered nC_{-25} was then analyzed using GC-MS and it was found that even at 450°C only very limited exchange had occurred (approximately 1% of the possible sites in nC_{-25} had exchanged) and no cracking of the nC_{-25} had occurred. One must therefore conclude from this that the presence of asphaltene was required to catalyze the casual exchange that had been encountered previously. Concerning the structure of alkanes in the asphaltene; it now appears that the originally observed deuterium incorporation need not be explained by the "multiple bonding to aromatic nuclei", model (Figure 44). On the positive side, it was evident that on pyrolyses of asphaltene, "hot" radicals were formed which could randomly abstract protons from free alkanes. As shown in Figure 47 this would in turn lead to deuterium substitution of the nC_{25} or β-cleavage to a smaller alkane and alkene which might further react with the d-donor to form small alkanes with deuterium exchanged into them.

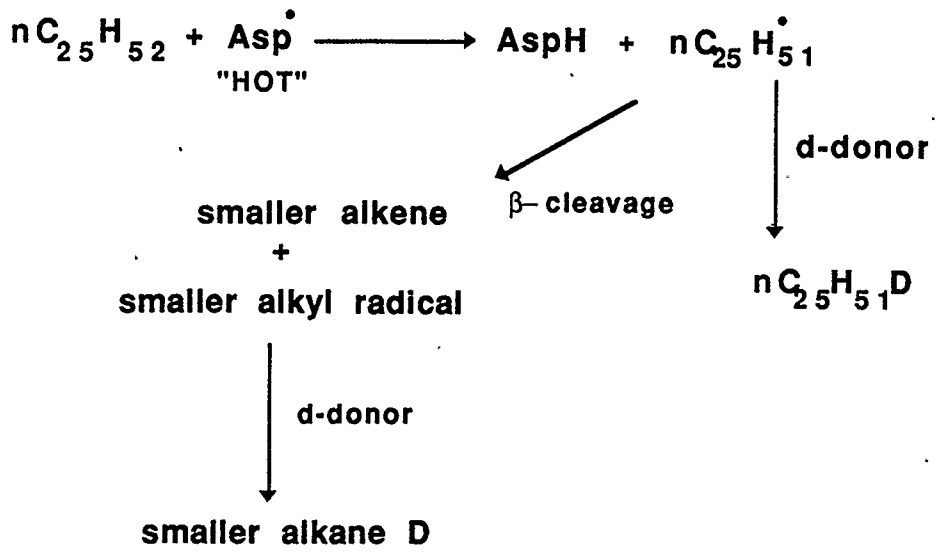


Figure 47. Mechanism for incorporation of deuterium and cleavage of free alkane.

5.8 Concluding Discussions

Mechanistically, the tetralin was found to behave in the expected manner when involved in pyrolyses with asphaltene, i.e. selectivity for exchange at the α-position was noted. Recovered naphthalene was also found to have exchanged in the α-position, agreeing with what was stated in chapter 3 concerning radical energies formed on hydrogen atom addition to an aromatic species.

A kinetic isotope effect was observed. This indicated that the breaking of the C-D bond in tetralin was at least sometimes rate-determining. However the C-D abstraction by a "hot" asphaltene derived radical was probably not of this type (see Figure 48).

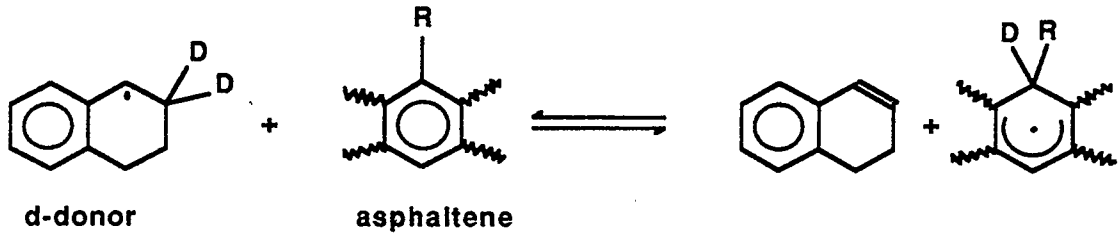


Figure 48. Rate-determining reaction involving d-tetralin.

The ^2H NMR analyses of the recovered asphaltene from pyrolysis of virgin asphaltene with d-tetralin revealed deuterium exchange into all possible environments but disproportionately more in benzylic positions. Back reaction managed to exchange out the incorporated benzylic deuteriums but none of the others.

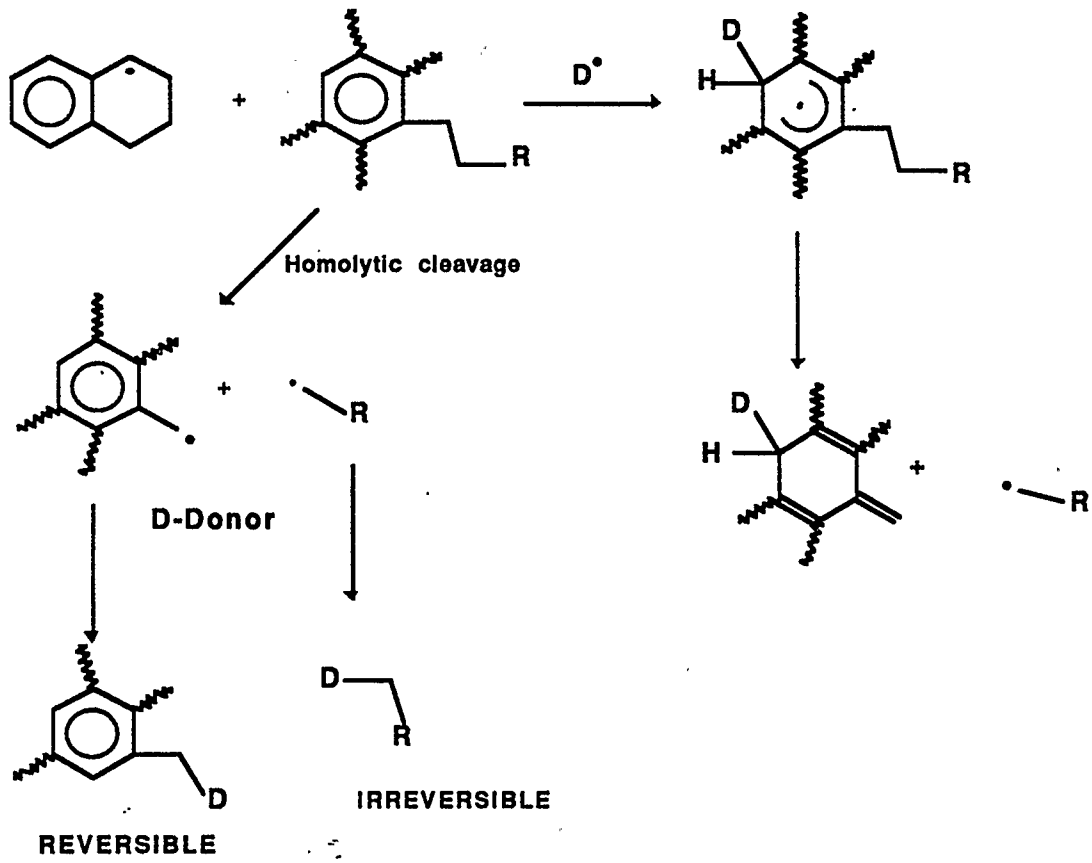


Figure 49. Cleavage within the asphaltene in the presence of a D-donor.

From work reported in chapter 4 it was known that dealkylation was an important process, under these conditions. Figure 49 illustrates the different available cleavage pathways which leads to the production of reactive alkyl radicals.

The maltenes recovered from pyrolyses of d-tetralin with asphaltene were found to contain a homologous series of n-alkanes with large scale deuterium incorporation. With asphaltene present, even free alkanes could exchange with d-tetralin and cleave into smaller alkanes. Neither exchange nor cleavage were seen in the absence of the asphaltene. Obviously, the asphaltene had to have been the source of the "hot" radicals which caused the observed exchange.

The presence of the "hot" radicals detected in this work was very relevant to the previous discussion in chapter 3, concerning coke formation. Phenyl type radicals were predicted as necessary for the formation of oligomers of aromatic hydrocarbons (chapter 3). From this it was evident that in the absence of stabilizing mechanisms, e.g. from H-donors, pyrolysis of asphaltene would lead to the formation of higher molecular weight material and eventually coke (Figure 50).

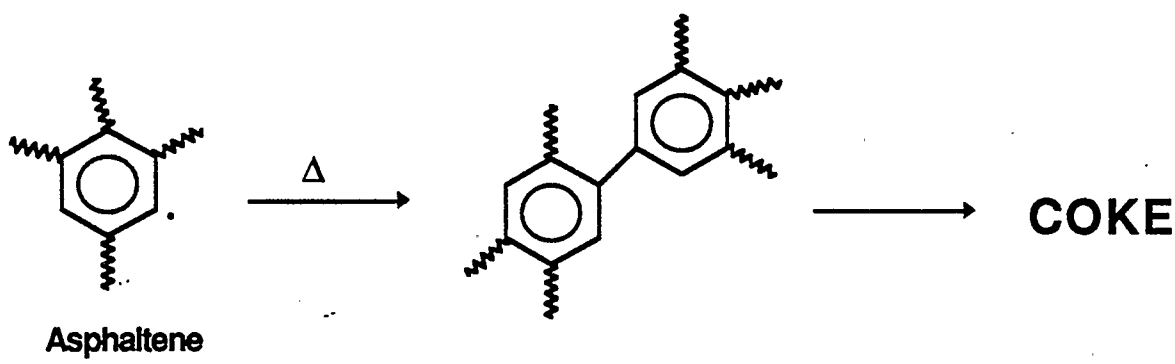


Figure 50. Mechanism for formation of coke.

Chapter 6

Model Compound Cracking Reactions

6.1 Introduction

From the ^1H NMR study of the recovered asphaltenes, produced from pyrolysis of asphaltene with hydrogen donors (reported in chapter 4), it was evident that dealkylation had occurred. It was also observed that a series of n-alkanes was evolved, presumably from the aforementioned dealkylation reaction.

It was also evident from earlier work (reported in chapter 3) that radical coupling of aromatic species was a process which occurred under the conditions of this study and it is known to be a good tar and eventually, coke forming reaction. This chapter looks further at these dealkylation reactions using selected compounds to model the asphaltene structure.

6.2 Strategy and Objectives

One has great difficulty in extracting mechanistic details from the pyrolyses reactions of asphaltene and this leads one to consider the use of selected model compounds in the place of the asphaltene. It was decided that a high molecular weight alkyl aromatic compound would be one suitable model of the asphaltene and 9-nonylanthracene appeared an appropriate choice. The alkyl side chain had to be long enough so that it would show up in the GC-MS analysis of the cracked products. Cracking the model compound, in the presence of a deuterium donor would hopefully provide even more mechanistic information than the product analysis alone.

6.3. Pyrolyses of Model Compounds

Vernon [137] carried out relevant model cracking reactions of dibenzyl at 450°C in the presence of tetralin or gaseous hydrogen/tetralin. Toluene was produced by a thermal cracking reaction in which the rate determining-step was thermal cleavage of the β-bond in dibenzyl (235 kJ/mol). Benzene and ethylbenzene were produced by a hydrocracking reaction as illustrated in Figure 51. In the presence of tetralin only, the predominant reaction was β-cleavage. When gaseous hydrogen was present the stronger α-bond in dibenzyl (406kJ/mol) was broken and significant amounts (dependent on H_2 pressure) of benzene and ethylbenzene were found in the cracked products.

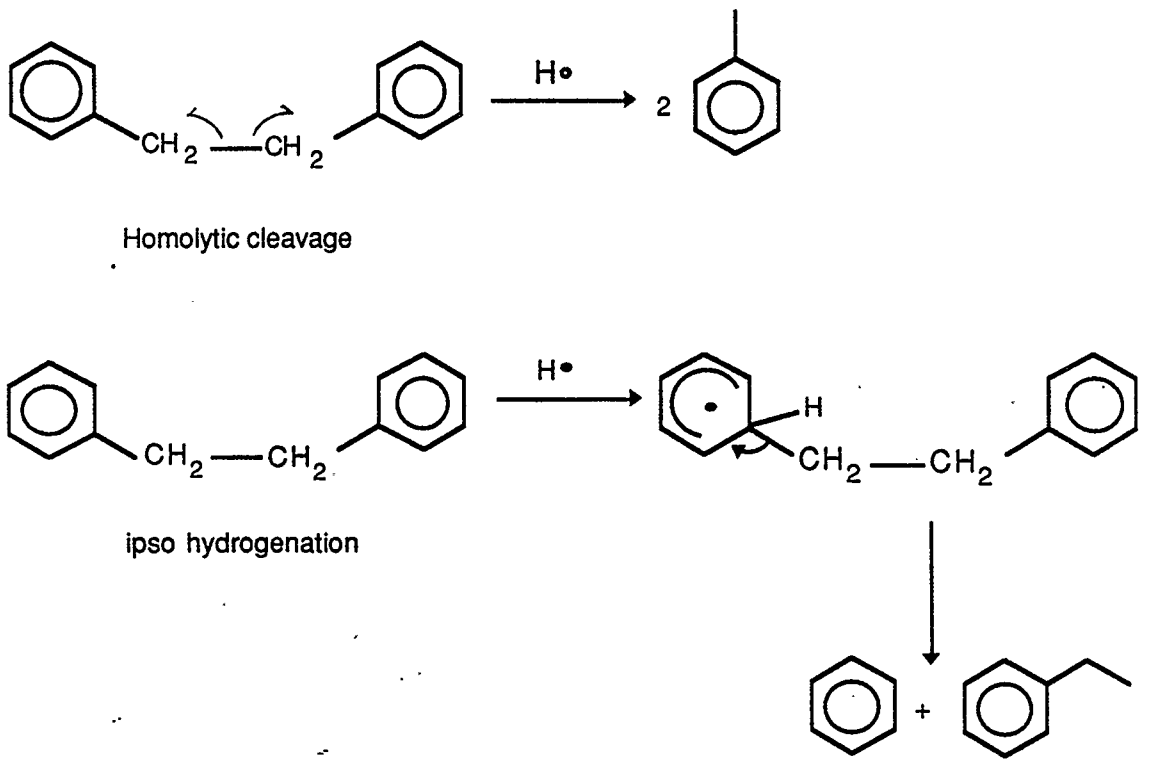


Figure 51. Possible decomposition mechanisms of dibenzyl.

Savage et al.[138] studied pyrolysis of pentadecylbenzene (PDB) at 375, 400, 425 and 450 °C. At 400°C, the major products were found to be toluene, 1-tetradecene, n-tridecane, styrene and ethylbenzene. At longer reaction times, in lower yields, a series of n-alkanes and 1-olefins containing 6-14 carbon atoms as well as 1-phenylalkanes and phenylolefins with alkane chains containing 2-12 carbon atoms, were found. The final conversion of PDB at 400°C for 3 hours was 73%. Some coke was formed under these conditions. At 425°C, toluene was again the major product. At shorter reaction times, at this temperature, 1-tetradecene followed toluene in abundance. The other major products were n-tridecane, styrene and ethylbenzene. At longer reaction times the tetradecene and styrene yields decreased rapidly.

Two possible mechanisms were discussed to explain the observed product distribution. These included an intramolecular retro-ene mechanism and a free radical chain reaction (Figure 52).

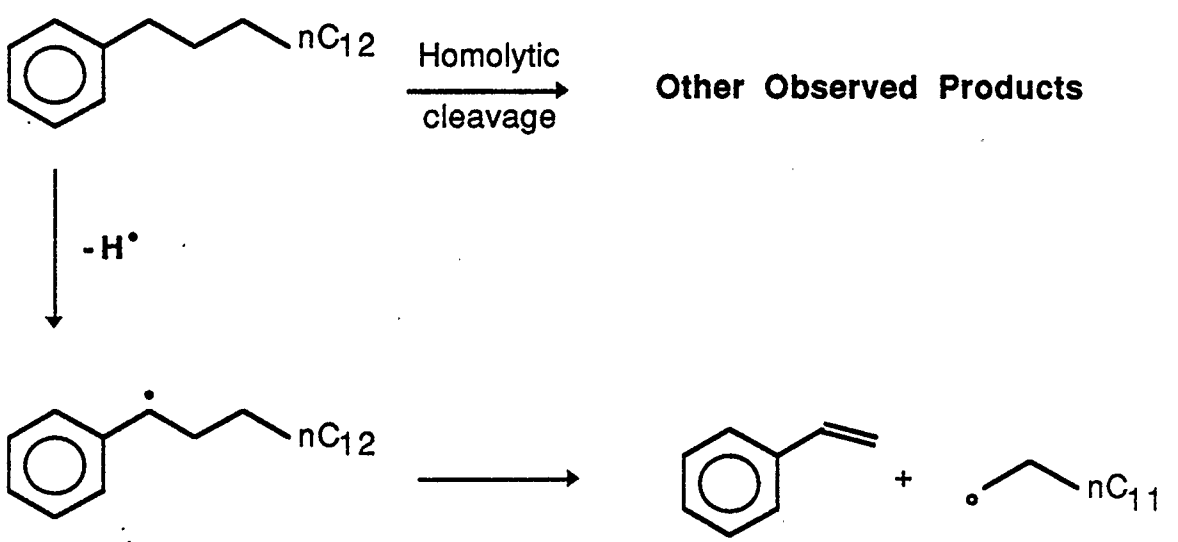


Figure 52. Free radical degradation of pentadecylbenzene.

The concerted mechanism, considered on its own, failed to account for the formation of all of the products observed. It was therefore concluded that the most likely explanation of the observed products involved the free radical chain reaction dominated by a β-scission process.

Alkyl aromatics tend to produce coke more readily than alkanes because of the stability of benzyl radicals and the ease with which they can combine to produce higher and higher molecular weight species [139-140].

6.3.2 Other Model Compounds

Various other relevant model pyrolyses have been carried out [141]. Thermal cracking of n-hexadecane evolved mainly C_{1-3} products. Dealkylation of alkyl aromatics was found to occur at a rate lower than that of alkanes. Pyrolyses of n-olefins proceeded at a rate similar to alkane cracking with little isomerization occurring. Cracking of naphthenes proceeded at a lower rate than was found for alkanes.

6.4 Experimental

6.4.1 Synthesis of 9-nonylanthracene

n-Nonyl bromide (20.0g, 96.7 mmoles, supplied by Aldrich and distilled and dried before use) was slowly added to a refluxing mixture of magnesium (4.00g, 167 mmoles, supplied by Fisher and used without purification) and very dry ether (40 ml), for a period of a few hours until most of the Mg was reacted. To this mixture was added 6.2g (32 mmoles) of 9-anthrone (supplied by Aldrich and used without further purification) dissolved in 20 ml of ether, over a period of 15 minutes, at room temperature. The reaction mixture was then added to a mixture of 30g of ammonium sulphate and 40g of ice. The combined mixture

was placed in a separating funnel and the ether layer separated, dried and then evapourated on the Roto-vap. This product was then placed on a silica gel chromatographic column and eluted with n-pentane. These fractions were analysed using GC and those found to contain the desired product were combined to give nonylanthracene in 97% purity (yield was 0.85g). The product was finally characterized by MS (major peaks at 304, 205, 192, 179).

6.4.2 Cracking of 9-Nonylanthracene

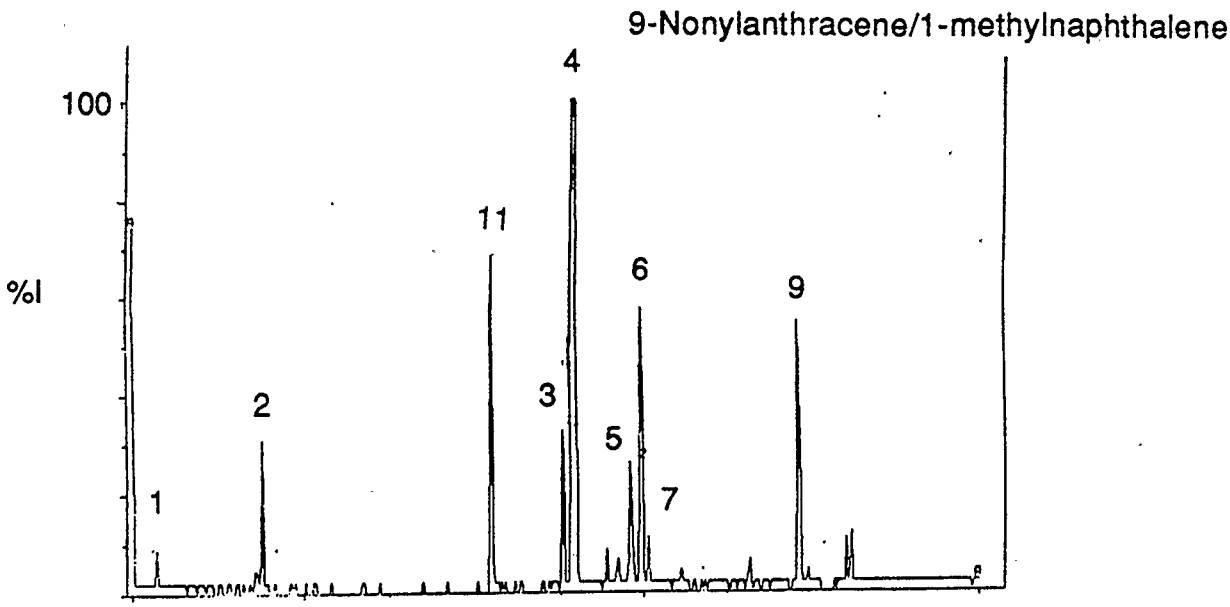
In tube bomb pyrolyses, 9-nonylanthracene (100mg) was pyrolyzed, separately, with d_{12}-tetralin (335mg) and methylnaphthalene (1.2g) under the same conditions as used in previously described work (chapter 4) ie. 450°C for 1 hour. In this way both H-donor and non-donor vehicle pyrolyses were modelled. The reaction products were then extracted with heptane and subjected to capillary GC-MS analysis.

6.5 Results and Discussion

6.5.1 Analyses of the Pyrolyses Products

The TIC's resulting from capillary GC-MS analyses of the pyrolyses products are shown in Fig 53. The most interesting feature was the observation of an nC_9 alkane from cleavage of the sidechain. In the case of the methylnaphthalene and to a lesser extent, d-tetralin pyrolysis, one can see that some octane (from β-cleavage) was also formed (about 15% of the recovered alkane sidechain in the methylnaphthalene case). Some of the major products are identified in Table 27 . Not surprisingly, in the d-donor situation, various deuterated anthracene species were found. In the methylnaphthalene case,

2-methylnaphthalene and the dimethylnaphthalenes were impurities in the original solvent.



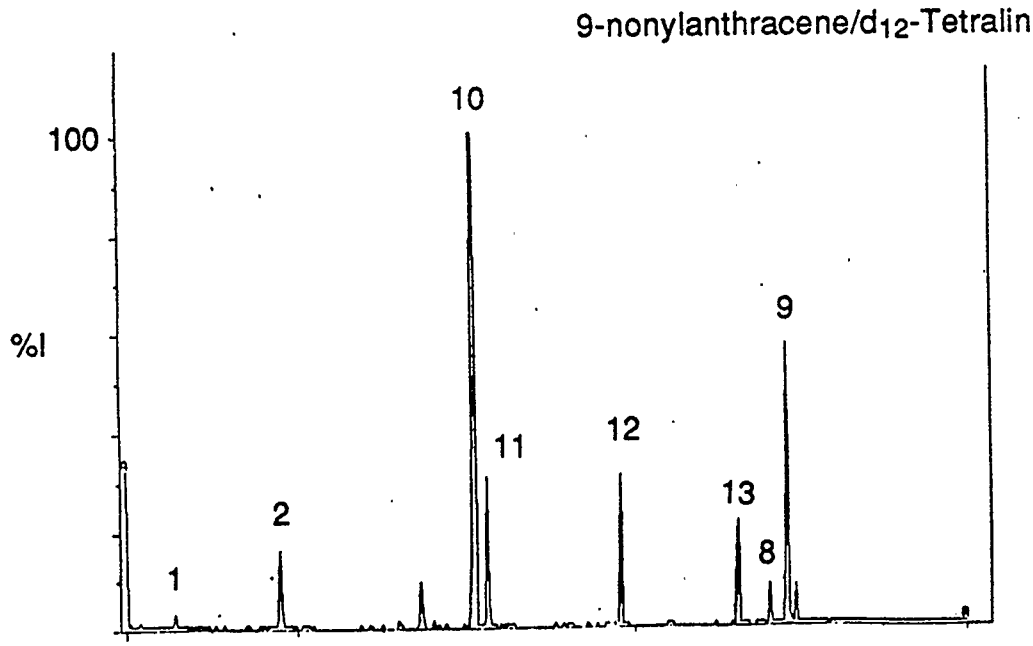


Figure 53. GC-MS TIC's of products of model cracking pyrolyses.

Table 27. Analysis of products of model compound cracking of 9-nonylanthracene.

No.	Identity of Compound
	Nonylanthracene/1-Methylnaphthalene.
1	Octane
2	Nonane
3	2-Methylnaphthalene
4	1-Methylnaphthalene
5	Dimethylnaphthalene
6	Dimethylnaphthalene
7	Dimethylnaphthalene
9	Anthracene
	d_{12}-Tetralin/Nonylanthracene
1	Octane
2	Nonane (d1)
10	Tetralin
11	Naphthalene
12	nC_{14} (spike)
13	Tetrahydroanthracene (d7)
8	Dihydroanthracene (d5)
9	Anthracene (d4)
14	Unreacted Nonylanthracene

GC analysis of the reaction products revealed that in the case of the D-donor run about 50% of the initial nonylanthracene was recovered, unreacted. This did not show up on GC-MS analysis because the retention time was too long on the particular column used. If formation of a radical species (of nonylanthracene) was required for cleavage to occur, then the presence of a donor solvent would have been expected to inhibit this reaction. Complete cleavage in the other cracking experiment was found. This was confirmed by ^{2}H NMR analysis of the recovered, cracked products.

GC-MS analyses of the reaction product mixtures revealed the extent of deuterium substitution (for the d-tetralin run), on cracking. The approximate values determined are shown in Table 27. Examination of the fragmentation patterns from the MS spectrum of the recovered nonane (d-donor) revealed that the deuterium incorporated was fairly selectively to be found in a methylic position as expected.

Clearly, in the d-donor situation, a mechanism explaining the almost exclusive α-cleavage is required. It is unlikely that this cleavage was the result of a homolytic fission but might be explained by the mechanism outlined in Figure 54 and involved ipso addition of a hydrogen atom, forming a stabilized radical (although interrupting the aromatic system of anthracene) which dealkylates to restore the aromatic system.

For the α-cleavage to occur a source of hydrogen atoms was obviously required and therefore this mode of dealkylation would not be expected in the methylnaphthalene (which is not a H-donor) case. Clearly, from the GC-MS analysis of the methylnaphthalene situation, β-cleavage was more important, compared to the donor situation, but still the minor route to dealkylation. A likely pathway for β-cleavage is illustrated in Figure 55.

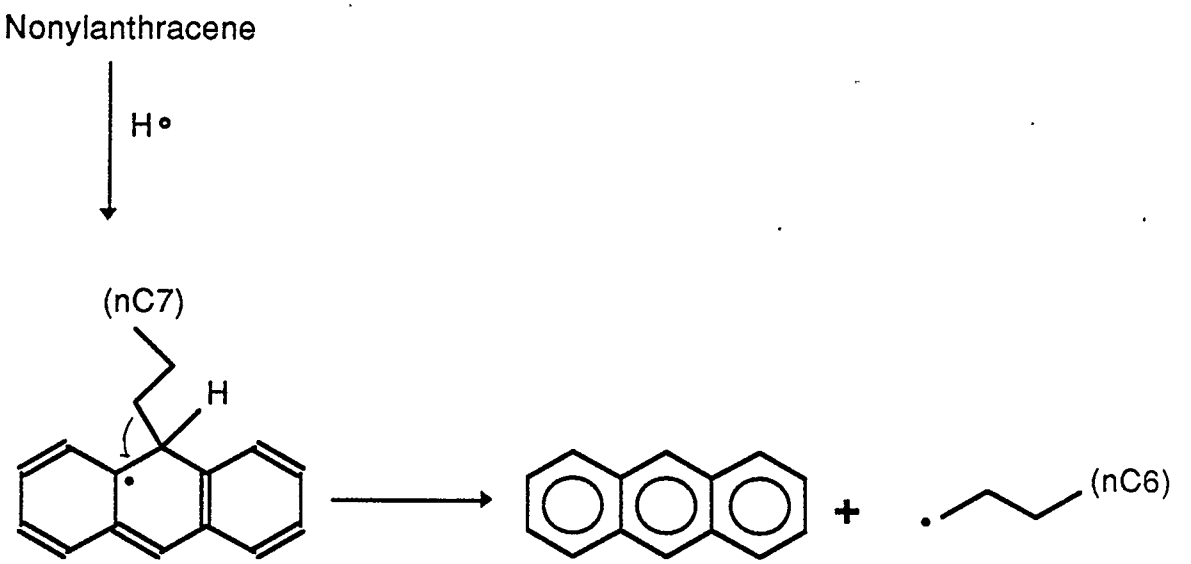


Figure 54. Possible mechanism of α-cleavage of nonylanthracene.

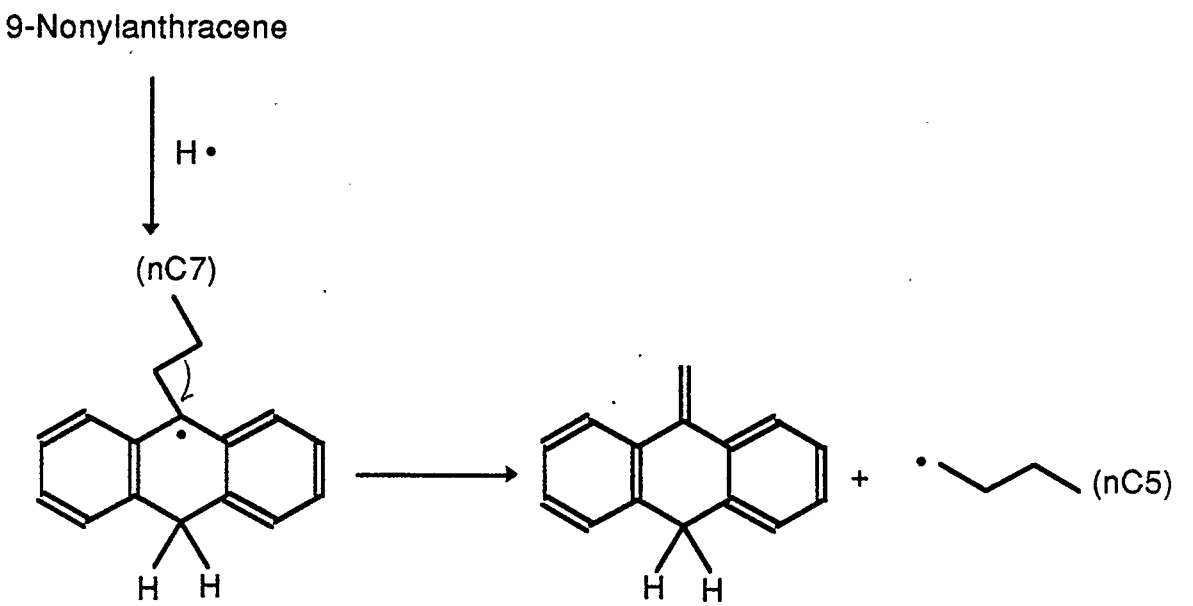


Figure 55. Possible β-cleavage pathway for Nonylanthracene.

This mechanism involved initial transfer of hydrogen atom forming another resonance stabilized radical which decomposed (β-bond) to form an exocyclic double bond.

Without a hydrogen source (methylnaphthalene) one might predict that β-homolysis would now predominate since such processes do not require H-transfer. Experimentally, this was not the case and α-cleavage predominates. It is therefore very difficult to explain the observed cleavage and the associated stoichiometry. One unlikely explanation involves initial homolysis of the sidechain which then acts as a hydrogen atom source, itself being transformed into a polyene. This was not consistent when the anthracene/alkane ratios (from GC-MS) were compared for the d-donor and methylnaphthalene pyrolyses, i.e. one would expect disappearance of octane or nonane in the methylnaphthalene situation.

Both of the proposed pathways involved interruption of the aromatic system of the anthracene. The total resonance energy for anthracene is 352 kJ/mol and for benzene 151 kJ/mol [142]. Attack at the 9,10 position of anthracene eg. hydrogenation leading to dealkylation involved loss of only 50 kJ/mol since two benzene rings remained intact. For the same process of dealkylation to happen in a similar fashion to a substituted benzene would involve the loss of 151 kJ/mol of resonance energy. It is possible therefore, that if the alkyl chain were attached to a benzene, the energy loss would be much higher and a different cleavage mechanism might be involved. To test this idea, further experimentation involving a substituted benzene compound was required. This is relevant because both types of aromatic species are found in the virgin asphaltene

6.6 Further Experimentation

From NMR evidence (reported in chapter 4) for cleavage of alkyl aromatics in the asphaltene and from the fact that the resonance energy of the aromatic species had to be overcome for dealkylation to occur (proposed

mechanisms), it was decided that an experiment should be carried out where (under the same conditions) another model compound (alkyl benzene) was cracked in the presence of tetralin and 1-methylnaphthalene. By studying the product distribution it would be possible to determine if α-cleavage was still the dominant dealkylation process involved or if the resonance energy loss, of benzene, was too high and some other mechanism was involved.

6.6.2 Results

In exactly the same fashion as with the nonylanthracene, n-butylbenzene (240.4mg, supplied by Aldrich at 99+% purity and was used without further purification) was cracked (in the same tube bomb) in the presence of tetralin (1.2102g) at 450°C for one hour. This was repeated with 1-methylnaphthalene (1.2109g) and n-butylbenzene (258.2mg). The pyrolyses products were removed from the bomb with pentane and subsequently analyzed using GC. The identity of the products was established by comparing retention times with those of pure samples of the suspected cracked compounds

Table 28 illustrates the proportion of products recovered from the pyrolysis of n-butylbenzene with tetralin or 1-methylnaphthalene.

Table 28. GC analysis of cracked products in pyrolysis of n-butylbenzene with 1-methylnaphthalene or tetralin at 450°C for one hour.

Pyrolysis Product	% Recovered	Pyrolysis solvent
benzene	0	tetralin
toluene	5.3	
Ethylbenzene	4.4	
unreacted n-butylbenzene	90.3	
benzene	0	1-methylnaphthalene
toluene	12.9	
Ethylbenzene	16.5	
unreacted n-butylbenzene	70.6	

6.6.3 Discussion

Obviously, from the product distributions shown in Table 28 α-cleavage of the model compound (n-butylbenzene) was not occurring, i.e. no benzene was formed. One can see that toluene and ethylbenzene were formed and therefore β and γ-cleavage were both occurring to approximately the same extent. With the H-donor present there was a slight preference for the β-cleavage pathway. When 1-methylnaphthalene was used (Table 28), a slight preference for γ-cleavage was detected . It was interesting that the product distributions were so similar for the different cracking media. It was evident that the presence of the H-donor restricted the dealkylation reaction to some extent. This would be expected if the first step involves formation of a radical which might be quenched by the H-donor. Possible cleavage mechanisms are

illustrated in Figure 56.

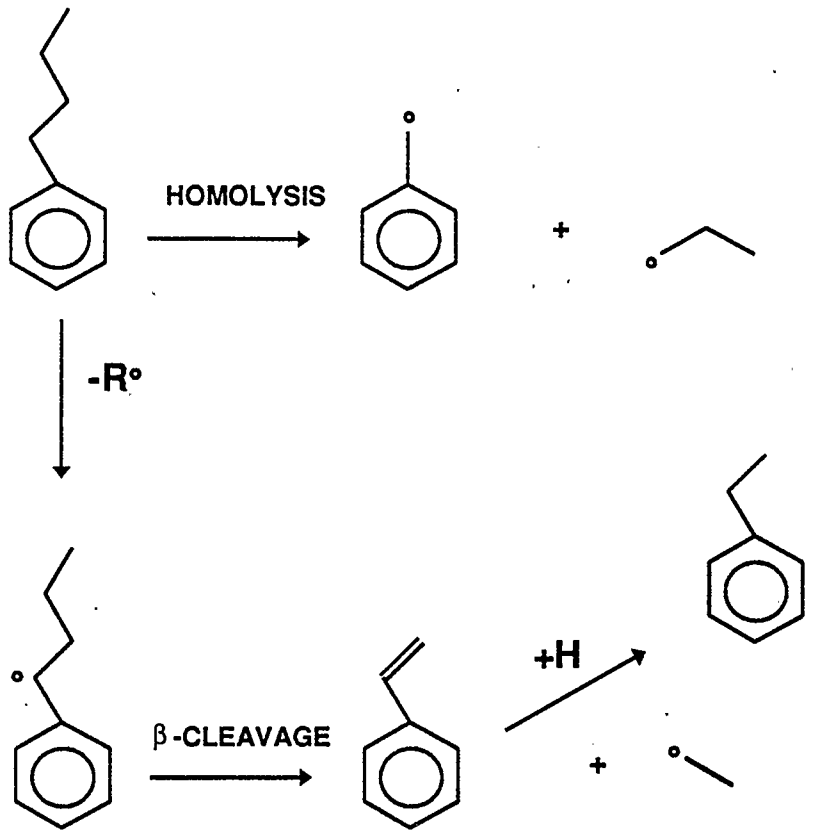


Figure 56. Possible cleavage mechanisms for n-butylbenzene accounting for the observed product distribution.

6.7 Conclusions

It has clearly been demonstrated that dealkylation of the model alkyl aromatic compound (9-nonylanthracene) proceeded predominantly by an α-cleavage route. Comparing both sets of model cracking results, the mode of dealkylation depended on the nature of the aromatic nucleus to which the alkyl chain was attached and this can be correlated with how much resonance energy loss was involved in interrupting the aromatic system in question. If the loss in resonance was small (as for anthracene) then H-transfer to the aromatic

species was possible. If the energy cost was too high then cracking presumably occurred in a homolysis of the alkyl chain, the specific site of cracking depending on the relative bond dissociation energies. It seems reasonable that in the asphaltene the same rules for dealkylation will apply.

Deciding which mode of dealkylation is predominant in the asphaltene obviously depends on the types of aromatic ring systems present. Previous work (reported in chapter 4) on the pyrolyses of the asphaltene (GC-MS analyses of the recovered maltene) suggested that benzene substituted species were more abundant than naphthalene, anthracene or pyrene (although these were detected). Care has to be used in making conclusions from pyrolyses studies of this type, in that the larger aromatic species are more likely to form higher molecular weight material and not appear as maltene. Snape et al. [89] also found that in-situ analyses of the asphaltene using spin-echo NMR techniques showed very little evidence of quaternary carbon atoms associated with large ring systems, again indicating that substituted benzene species predominated.

Chapter 7

Hydrous Pyrolysis Reactions of Bitumen Asphaltene

7.1 Introduction

In recent times there has been research carried out in the study of the reaction of bitumen/coal/kerogen with subcritical H_2O. The reason for this interest is that modern "in situ" recovery techniques used for extraction of bitumen, where surface mining is impractical, often use steam drive. This involves injection of superheated steam into a tar sand formation, where the high temperature reduces the viscosity of the bitumen sufficiently to allow it to flow, which then makes recovery possible. These temperatures are sufficiently high that chemical reactions are expected to occur, modifying the recovered bitumen. Some effort has been made to to discover the reaction types which occur under these conditions [143].

In the industrial process for converting ethane (or propane, butane, naphtha and gas oil) to ethylene, a mixture of the hydrocarbon stream and steam are passed through a high temperature reactor zone for a very short duration [144]. The steam is present to prevent unwanted radical combination reactions from occurring. The steam acts as a diluent, in this situation, to physically separate ethyl radicals from each other so that they do not combine to form higher hydrocarbons.

Another interest in hydrous pyrolysis arises because it can be used to artificially mimic the natural process of catagenesis. If a kerogen is subject to hydrous pyrolysis it is degraded in such a way as to resemble the products which would arise due to extensive aging over a geological timescale [145]. It turns out that the products arising from dry pyrolysis do not produce the hydrocarbons formed in natural catagenesis [146].

Also, interestingly, Hoering [145] found that extensive deuterium substitution occurred in Messel shale heated at 330°C for 3 days in the presence of D_2O.

Batts et al. [147] found that hydrous pyrolysis of mature coals led to higher liquefaction yields than for immature coals, rich in carboxylic acids. The mature coals gave higher liquefaction yields using hydrous pyrolyses than with hydrogenation.

7.2 Objectives

In this work it was hoped that hydrous pyrolysis of bitumen asphaltene would lead to enhanced yields of upgraded material, compared to dry pyrolysis. This might happen because of the diluent effect already mentioned. More importantly, study of the reactions during hydrous pyrolysis of asphaltene would hopefully lead to a more complete understanding of coke formation. Hydrous pyrolyses with D_2O would be a useful means of introducing an isotopic label whose incorporation might be followed using ^2H NMR and GC-MS. An added advantage of this would be the ease with which the residual deuterium source could be removed from product maltene, so that the maltene itself could be analyzed using ^2H NMR.

7.3 Experimental

The reaction of H_2O with asphaltene at different temperatures was carried out in tube bombs in exactly the same manner as in the previous pyrolyses with the H-donors. The loading of H_2O was 1.2g and the asphaltene was 600mg. The products were separated into maltene, asphaltene, preasphaltene and coke in the same manner as previously described. One interesting result was that when the bombs were opened subsequent to the

hydrous pyrolysis, a crust of gold coloured crystals was observed. These were presumably FeS_2. This was significant in that the iron content of the asphaltene or the steel from the bomb itself was involved in the reaction. Once pyrolysis was complete the maltene was analyzed using capillary GC-MS and ^2H NMR and the recovered asphaltene (if any) was also subjected to ^2H NMR analysis.

7.4 Results and Discussion

7.4.1. Product Distribution

Table 29 illustrates the product distribution found on pyrolysis under different conditions (temperatures and time of pyrolysis). For comparison, data is shown from pyrolyses involving other situations (donor and no additive upgrading data from chapter 4).

Comparing the hydrous pyrolysis runs to those from dry pyrolyses (previously discussed in chapter 4) it was evident that the product distributions were very similar. Looking at the H_2O/D_2O runs one can see that at all temperatures the coke formation was lower for the D_2O runs, whereas the recovery of pyridine soluble material as well as the overall conversion was higher, when compared to the equivalent H_2O runs. This strongly suggested a kinetic isotope effect where breaking of a O-H or O-D bond was involved in the rate determining step of the reaction. These differences (as well as the deuterium incorporation in the recovered maltene and asphaltene) also confirmed that the H_2O/D_2O was chemically involved in the asphaltene degradation and not simply acting as a physical diluent as might have been expected.

Table 29. Product distribution found on hydrous pyrolysis (H_2O/D_2O) of asphaltene at different temperatures and various durations compared to those where no additive was employed.

Run no	Additive	Temp.(°C)	Time (h)	%Pyr. Sol.	%Coke	% Conversion
164	H_2O	350	24	42.3	41.4	16.3
159	D_2O	350	24	52.2	30.4	17.5
171	None	400	1	68.9	13.6	17.5
204	H_2O	400	1	49.1	25.0	25.9
203	D_2O	400	1	58.7	24.9	16.4
33	None	450	1	6.3	60.0	33.7
141	H_2O	450	1	1.6	62.0	36.7
131	D_2O	450	1	5.9	48.1	46.0
163	H_2O	450	24	0	64.9	35.1
139	D_2O	450	24	3.1	53.6	43.3
41	None	500	1	0	61.3	38.7
123	H_2O	500	1	0	67.3	32.7
162	D_2O	500	1	3.6	50.9	45.8

7.4.2 Analyses of the Recovered Maltene

7.4.2.2 GC-MS Analysis of Recovered Maltenes

GC-MS analyses demonstrated that under mild conditions of hydrous pyrolysis (eg. 350°C for 1 hour or 450°C for 1 hour) the maltenes recovered were very similar to those obtained, from dry pyrolyses. They consisted predominantly of a homologous series of alkanes from nC_9 extending to nC_{30}. The TIC's are shown in Figure 57. As well as the n-alkanes there were lower concentrations of substituted alkanes and substituted benzenes. When the severity of hydrous pyrolysis was increased (eg. 450°C for 24 hours and 500°C for 1 hour) the product distribution in the maltene changed drastically, but in a similar way to that seen before in dry pyrolyses and in the presence of H-donors (Chapter 4). The reformed components consisted mainly of aromatic species, e.g. substituted benzenes, indenes, benzothiophenes, naphthalenes, fluorenes, biphenyls, dibenzothiophenes, anthracenes, phenanthrenes and pyrene. These high temperature pyrolyses were repeated in the presence of D_2O and high levels of deuterium incorporation were found in the maltene components.

It has already been reported in chapter 5 that pyrolyses of bitumen asphaltene in the presence of d_{12}-tetralin resulted in a large amount of deuterium becoming exchanged into the n-alkanes which were produced. It was found that reaction of the asphaltene with D_2O under the same conditions gave the exchange illustrated in Figure 58.

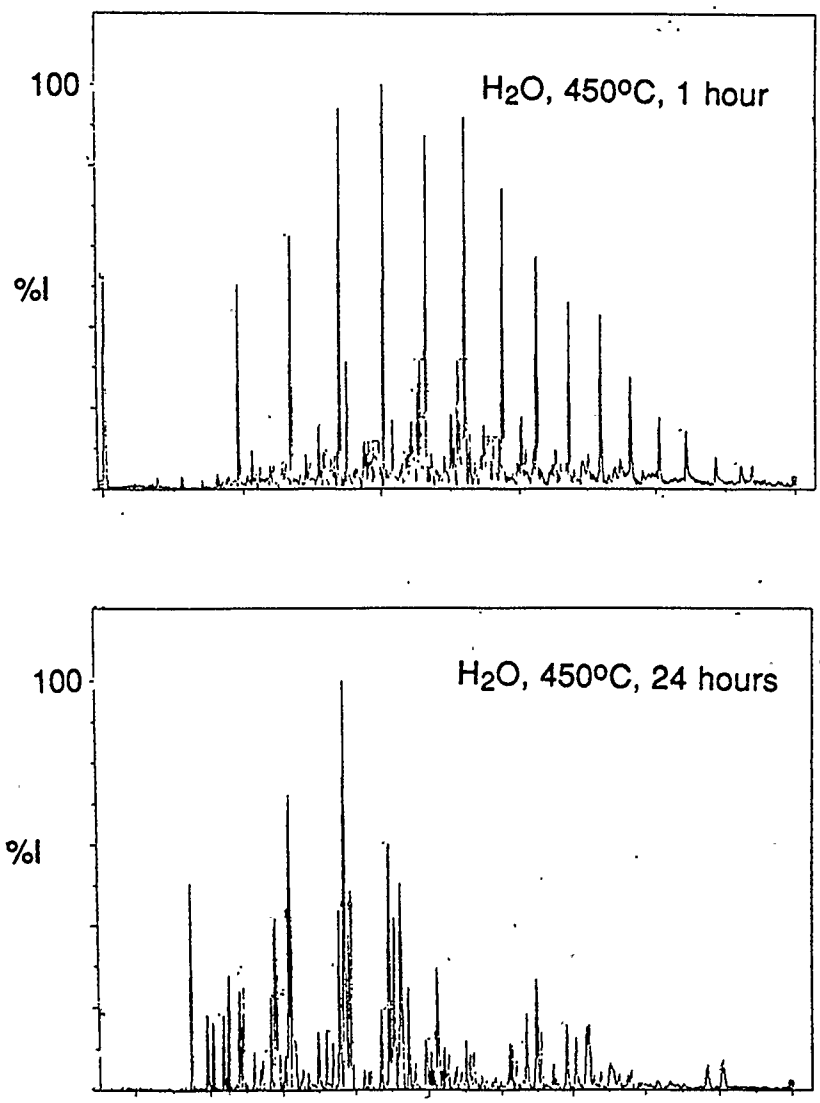


Figure 57. GC-MS TIC's of recovered maltenes from hydrous pyrolyses.

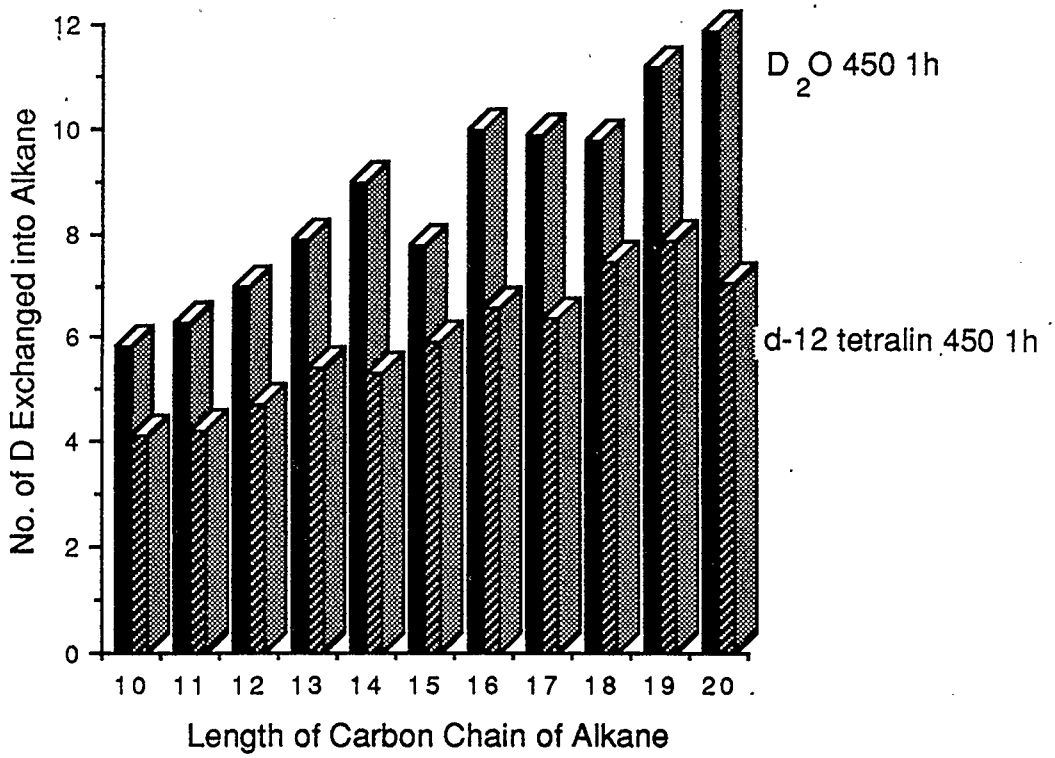


Figure 58. Incorporation of deterium label in alkanes derived from pyrolysis of asphaltene with D_2O and d_{12}-tetralin.

The deuterium exchange was compared with that reported in the previous chapter where d-tetralin was used under the same conditions. It was evident that the trends in incorporation were similar in both cases. There was higher overall exchange in the D_2O pyrolysis, but one has to remember that there was more deuterium available in the D_2O pyrolysis (on a molar basis). Also, when the actual yields of the alkane fractions were compared, the yield found in the H-donor situation was roughly double that found for the D_2O situation, again showing that the molar ratio of deuterium to alkane was higher (D_2O). For both the runs described in Figure 58 the deuterium incorporation

increased regularly with increasing chain length of the alkane. This suggested the possibility of a statistical incorporation, which would not be very useful as far as learning about mechanism of degradation was concerned.

The next step was to repeat the experiment under milder conditions to try and reduce the overall exchange and improve the selectivity. Figure 59 illustrates the results of exchange into the maltene alkanes from pyrolysis of asphaltene with D_2O at 350°C for 24 hours.

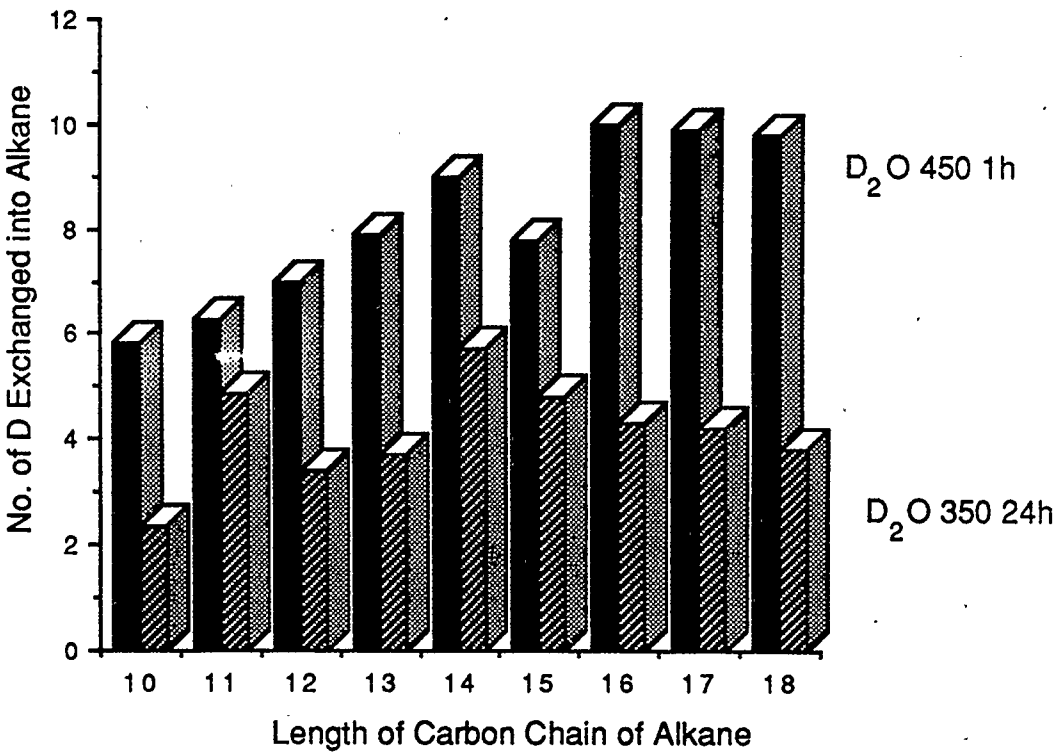


Figure 59. Deuterium exchanged into alkane fraction produced in pyrolyses of asphaltene and D_2O under different conditions.

From Figure 59, it is evident that significant incorporation of deuterium still occurred at 350°C. Hoering [145] carried out sub-critical hydrous pyrolysis of a Messel shale in the presence of D_2O for 3 days at 330°C and found

widespread deuterium exchange. Incorporation was found to range from 0-14 deuterium atoms per alkane chain. In model compound pyrolyses (hydrous) with n-docosane (nC_{22}) and the shale using D_2O (under the same conditions) it was found that exchange (in the n-docosane) was very low, ruling out simple exchange as a major pathway in the original shale hydrous pyrolysis. Another model hydrous pyrolysis (D_2O) was carried out with the shale and 1-octadecene again under the same conditions. Analysis of the products revealed that 60% of the original alkene was converted to the corresponding alkane. Also reported was the presence of H_2 in the resulting products.

From the data on exchange under different conditions (shown in Figure 59) one can see that the upward trend for increasing incorporation as the chain length increases (450°C for 1 hour) had ceased at 350°C (24h). It was hoped that the milder conditions would lead to higher selectivity and this seemed to have been justified. The previous trends in exchange suggested the possibility of statistical incorporation, i.e. that the incorporation observed was not a reflection of degradative bond cleavage but that the alkanes were exchanging subsequent to dealkylation (in the presence of the asphaltene) under the prevailing conditions of pyrolysis. This was found in the experiment involving the d-tetralin, asphaltene and a spike of free nC_{25}, where a large degree of exchange into the free alkane spike, as well as widespread fission of the nC_{-25} molecules, was observed (reported in chapter 5). Another way of looking at this data was to normalize the exchange into the alkanes in terms of the number of possible sites of exchange. Figure 60 illustrates the results of this analysis.

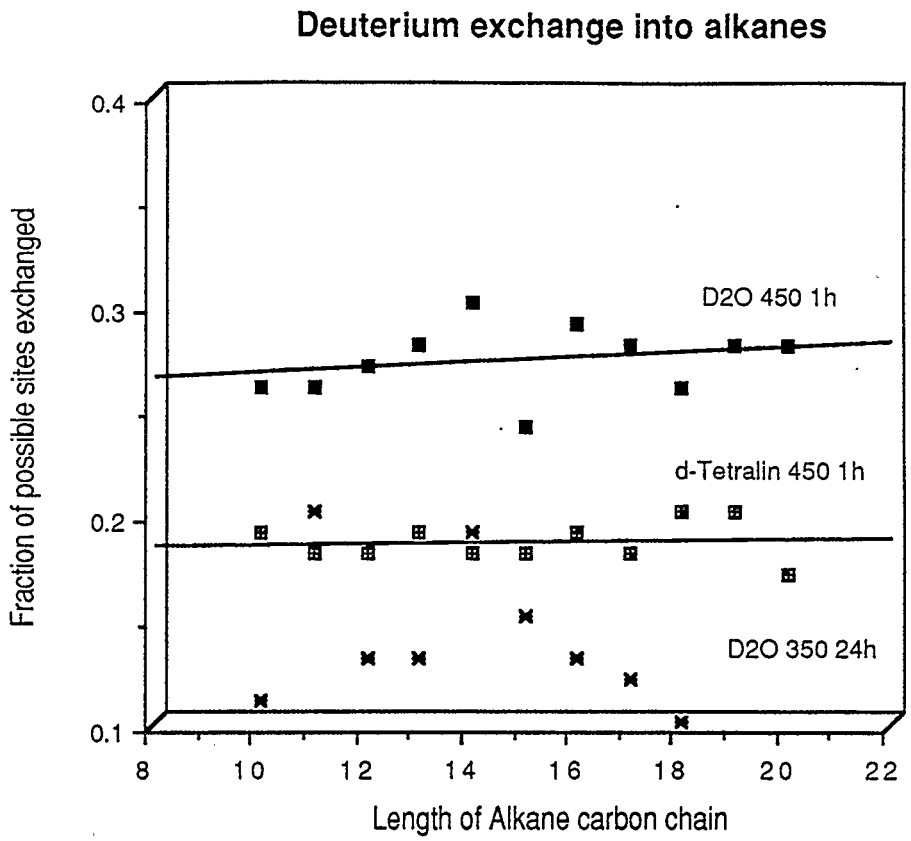


Figure 60. Normalized deuterium incorporation into alkane fractions generated under different conditions during the pyrolysis of bitumen asphaltene.

Judging from the data displayed in Figure 60 it looked as if the exchange in both runs at 450°C (D_2O and d-tetralin) may indeed have been statistical but the same was not true for the run at 350°C for 24h. At this stage it was hoped that the ^2H NMR analysis of the recovered maltenes and asphaltenes would reflect the additional selectivity of exchange at low temperature.

7.4.2.3 ^1H NMR of the Recovered D_2O

The recovered D_2O from hydrous pyrolyses was analyzed using ^1H NMR. The amount of hydrogen exchanged into the D_2O was quantified by adding a known amount of H_2O and measuring the difference in peak area. The

recovered D_2O (450°C, 1h) was found to contain approximately 5% hydrogen. The D_2O from the pyrolyses at higher temperature (500°C, 1h) resulted in almost the same level of exchange. This information gave an idea of the level of exchange to expect in the recovered fractions, subsequent to hydrous pyrolyses.

7.4.2.4 ^2H NMR Analyses of the Recovered Maltenes

The ^2H NMR spectra of the product maltenes recovered under different conditions of temperature and duration of pyrolysis (loading of D_2O and asphaltene were constant) are shown in Figure 61. It is evident that at high temperature the deuterium exchanged into maltenes were largely aromatic. The obvious high level of exchange found in all environments limited the usefulness of these particular analyses. Under milder conditions one can see that the aromatic and benzylic incorporation were much lessened. Remembering that under these conditions the maltene was found to be composed largely of the homologous series of n-alkanes, the ^2H NMR spectra showed that there was a proportionately higher exchange into methylic rather than methylene chain environments. This suggested that the release of the alkanes from the asphaltene involved more bond cleavage at the end of the chains. This agreed with the previously described oxidation studies of Strausz et al. [41,135]. Pyrolyses under milder conditions than illustrated in Figure 61, caused the yield of alkanes to decrease. The selectivity of exchange did not increase and the proportion of aromatic, benzylic and aliphatic incorporation remained the same.

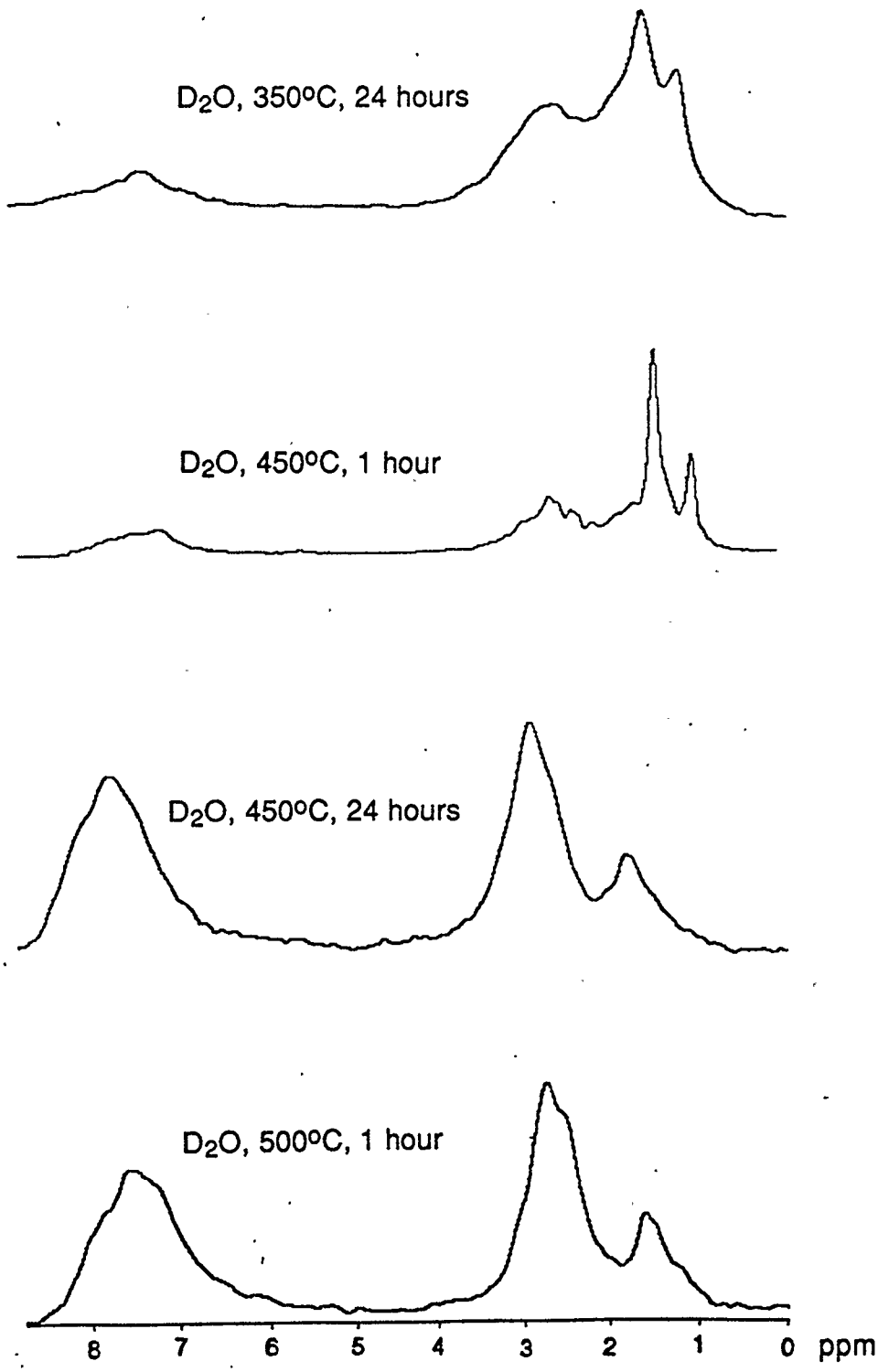


Figure 61. ^{2}H NMR of the recovered maltenes from hydrous pyrolysis runs.

7.4.3 Analyses of Recovered Asphaltene

7.4.3.2 ^{1}H NMR Analysis of the Recovered Asphaltenes

Previously, it was demonstrated that the product distributions derived on hydrous pyrolysis of asphaltene, were fairly similar to those achieved from dry pyrolysis. It was believed that comparison of the ^{1}H NMR analyses of the recovered asphaltenes would further our understanding of the degradation involved in hydrous pyrolyses. Comparison of the recovered asphaltene to the unreacted material would also be useful in achieving this goal.

Table 30. Comparison of ^{1}H NMR analyses of recovered asphaltenes from hydrous and dry pyrolyses at different temperatures.

Run	Add	Temp(°C)	Har	Hα	Hβ	Hγ
Virgin asphaltene			0.135	0.258	0.468	0.139
39	None	400	0.095	0.183	0.531	0.185
204	H_2O	400	0.158	0.255	0.428	0.159
33	None	450	0.255	0.264	0.389	0.074
178	H_2O	450	0.184	0.209	0.434	0.174

It was evident in comparing the recovered asphaltenes from hydrous and dry pyrolyses (Table 30) that there were substantial differences in the structures of the recovered asphaltenes and hence in the degradation involved. At low temperature (400°C) very little had happened to the initial asphaltene (on hydrous pyrolysis). With dry pyrolysis at 400°C, one can see that the aromatic

and the benzylic hydrogen content were found to be lower, whilst the Hβ and Hγ were higher. This indicated that compared with dry pyrolysis, at this temperature, less dealkylation (or ring opening reactions) had occurred with hydrous pyrolysis. The presence of H_2O has obviously modified internal hydrogen distribution reactions. When the temperature of the hydrous pyrolysis was increased to 450°C the Hγ and Hβ hydrogen content were somewhat increased (compared to hydrous pyrolysis at 400°C and to the virgin asphaltene) in contrast to dry pyrolyses where decreased Hγ and Hβ were observed on increasing temperature. Compared to the recovered asphaltene obtained at the same temperature, under conditions of dry pyrolysis, the aromaticity was now lower as was the benzylic hydrogen. The Hβ and Hγ were both substantially higher and closer to the virgin asphaltene values (for hydrous pyrolysis. This strongly suggested that the presence of H_2O has supressed reactions leading to dealkylation and aromatization seen in the dry pyrolysis situation.

7.4.3.3 ^{2}H NMR Analyses of Recovered Asphaltenes

The asphaltenes recovered from hydrous pyrolyses with D_2O were also analyzed by ^{2}H NMR. The resultant spectra are shown in Figure 62. The asphaltenes from more severe pyrolyses were recovered in very small yields, if at all, and were not analyzed. The overall deuterium incorporation into the asphaltene was small. The peak at 7.3 ppm was due to natural abundance deuterium in residual benzene (the asphaltene fraction is defined as the benzene soluble portion of the pyrolysis product and it was impossible to remove the last traces of benzene used in the extraction). It was evident that the

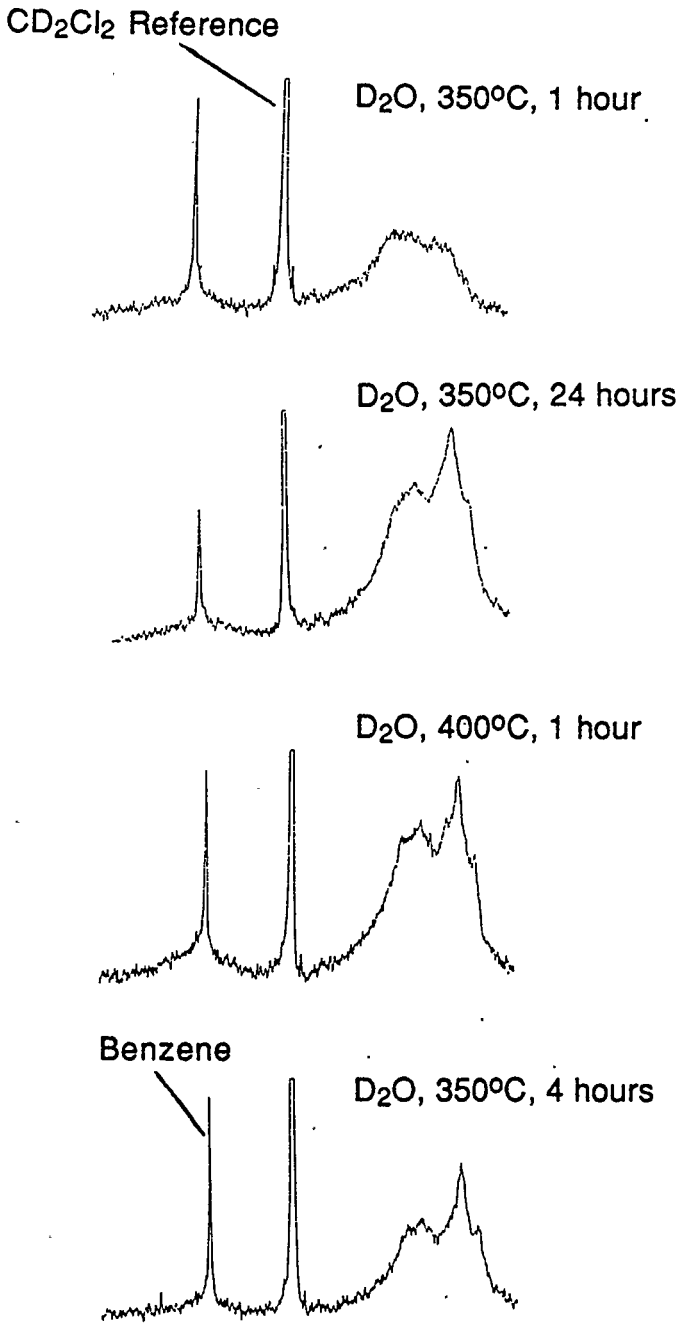


Figure 62. ^{2}H NMR of recovered asphaltenes from hydrous pyrolysis runs.

exchange into aromatic environments was small and about the same under the range of different pyrolyses conditions studied. Most exchange had occurred into Hα (benzylic) and Hβ environments. As the severity of the pyrolysis was increased there was an increase in the Hβ incorporation, relative to Hα. Not surprisingly, exchange into Hγ environments was not much in evidence which was desirable as far as selectivity was concerned, i.e. exchange into Hγ environments might only be expected if random exchange was in evidence. One has to remember that under these mild pyrolyses conditions (350°C for 1, 4 hours and 400°C for 1 hour) the alkane and maltene yields were low and the recovered asphaltene was very similar to the virgin asphaltene in structure. This meant that the exchange reactions occurring were low energy and possibly reversible. Radical processes were suspected because of the analyses of the product maltene (mainly n-alkanes) would not have been expected from electrophilic types of reactions involving transfer of H^+.

Further Experimentation

7.5 Reaction of D_2O with Asphaltene and a Radical Initiator

It was reported in chapter 4 that the presence of a sulphur radical initiator drastically increased coke formation due to the increased radical activity. In studying hydrous pyrolysis one knew that the H_2O/D_2O was chemically involved because of the differences in product distribution, comparing equivalent H_2O/D_2O pyrolyses and also because of the H/D exchange found in subsequent fractions arising from reactions of asphaltene and D_2O. To confirm the suspected radical nature of the hydrous pyrolysis an experiment was conducted where asphaltene (600mg) was pyrolyzed in the presence of D_2O (1.2g) as well as a small amount of PhSSPh (100mg), which had already

shown itself to be a radical initiator under these reaction conditions. One would suspect that the presence of the radical initiator would cause increased exchange into the alkanes (as well as other product fractions), recovered in the maltene, if indeed the free radical route was important. The conditions were the same as previously used (24 hour pyrolysis at 350°C in a tube bomb). The recovered alkane fraction was analyzed using GC-MS and the resultant exchange is illustrated in Figure 63.

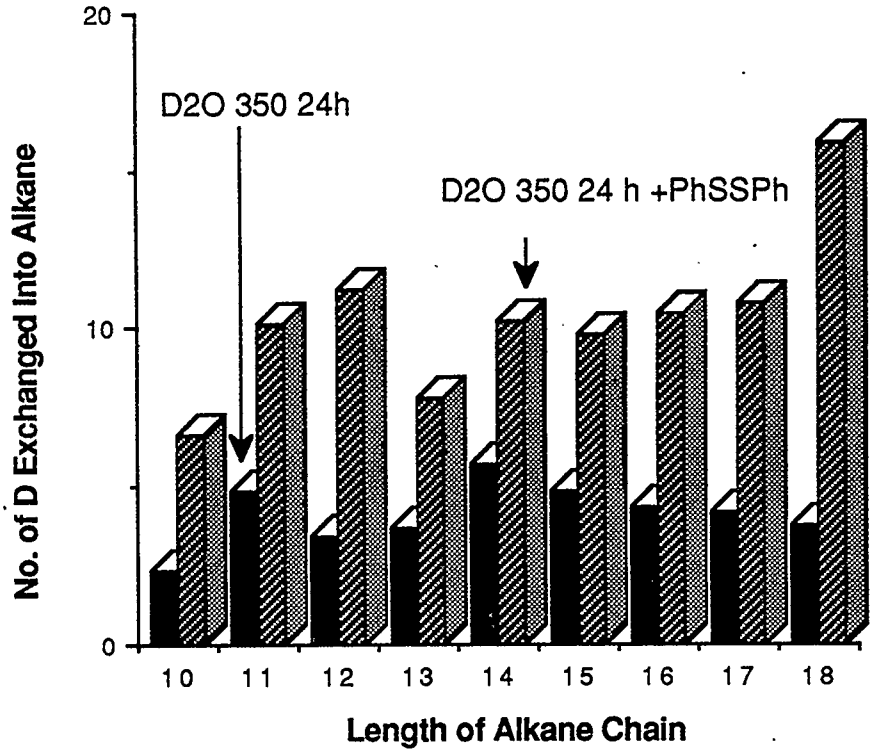


Figure 63. GC-MS analysis of recovered alkanes derived from pyrolysis of asphaltene in the presence of D_2O and PhSSPh.

Obviously the presence of the radical initiator did indeed accelerate radical processes leading to increased exchange into the maltene alkanes. It would therefore appear that a radical mechanism was involved in the exchange of deuterium into the n-alkanes released during hydrous pyrolysis.

7.6 Hydrous Pyrolyses of Model Compounds

Earlier, (reported in chapter 6) model compounds were pyrolyzed with d-tetralin and 1-methylnaphthalene in order to investigate the mode of dealkylation, under these conditions. The same compounds were cracked under conditions of hydrous pyrolysis in order to find out if the mechanisms of dealkylation were the same.

7.6.2 Procedure

In exactly the same manner (as reported in chapter 6) 9-nonylanthracene (100mg) was pyrolyzed in the presence of D_2O (375mg) at 450°C for an hour in a tube bomb. n-Butylbenzene (217mg) was cracked in the presence of H_2O (1.22g) under the same conditions. The products from both pyrolyses were analyzed using GC and GC-MS.

7.6.3 Results

GC-MS analyses of the products of the 9-nonylanthracene reaction revealed that none of the starting material had survived. The major product was anthracene. The side chain survived mainly as nonane with approximately 15% as much octane. Clearly this was a situation similar to the 1-methylnaphthalene one (reported in chapter 6) where dealkylation occurred primarily α to the aromatic system. Again, without a source of available deuterium it is difficult to explain the stoichiometry involved in the dealkylation.

Analysis of the products of the n-butylbenzene pyrolyses revealed that toluene and ethylbenzene were found to be the major cracked products. The GC analysis is shown in Table 31. Again, the product distribution (and extent of cracking) was found to be very similar to the 1-methylnaphthalene situation. No benzene was found and therefore one suspects that the dealkylation mechanism involved homolysis or β-cleavage.

Table 31. GC analysis of cracked products in pyrolysis of n-butylbenzene with H_2O at 450°C for one hour.

Pyrolysis Product	% Recovered
benzene	0
toluene	11.6
ethylbenzene	13.7
unreacted n-butylbenzene	74.8

7.7 Sequential Reaction of Asphaltene with H_2O and then d-Tetralin

Earlier, when the alkane fraction formed on pyrolysis of asphaltene in the presence of H_2O was compared to that using tetralin (same conditions, 450°C for 1 hour), the yield in the H-donor situation was approximately twice that found in the hydrous pyrolysis experiment. Previously, it was demonstrated that the average chain length of alkyl substituents (from ^1H NMR analysis) was around 10 in the virgin asphaltene and the presence of the much larger chains seen on pyrolysis cannot easily be explained. This raised interesting questions concerning the structure of the alkane precursor in the asphaltene. It suggested

that there were alkanes formed through simple cleavage of pendant alkyl groups and also from another source which required hydrogenation before liberation. In order to probe this finding, it was decided to react the asphaltene with H_2O (to cleave the pendant alkyl groups) and then recover a pyridine soluble fraction from the pyrolysis products. This fraction was then reacted with d_{12}-tetralin to see if a further yield of alkanes could be recovered or if they were now irreversibly bound or already reformed in the pyridine soluble fraction. d-Tetralin was used in the hope that if any further alkanes were liberated, more might be learnt about where they came from by studying the deuterium which had become incorporated into their structure. Obviously, success in liberating further alkanes from the pre-pyrolzed pyridine soluble material would be very useful in explaining the high deuterium exchange found in both hydrous pyrolysis experiments and those involving d-tetralin.

The result of this experiment was somewhat disappointing in that no further alkane content was released in the second pyrolysis. This suggested that the precursor structure to the extra alkane content released on hydrogenation was reformed, irreversibly, in the initial absence of a hydrogen donor, e.g. hydroaromatic structures were aromatized.

7.8 Concluding Discussion

In terms of product distributions, hydrous pyrolyses led to very similar yields as were encountered in dry pyrolyses experiments, however, ^1H NMR analysis of the recovered asphaltenes from both conditions revealed that there were substantial differences in the structures and mechanistic pathways of degradation. It appeared that the presence of H_2O, had supressed dealkylation and internal H-transfer reactions, which were more in evidence in the dry pyrolysis experiment. The recovered asphaltenes from hydrous pyrolyses were

found to be closer, structurally, to the initial virgin material, when compared to dry pyrolyses.

The hydrous pyrolyses revealed very similar maltene composition to that reported for the H-donor pyrolyses. It was, however, found that the yield of alkanes produced from hydrous pyrolyses experiments were much lower than those found in equivalent H-donor experiments.

The high level of deuterium incorporation found in the recovered alkanes from supercritical hydrous pyrolyses was not fully understood and was similar to that found in d-donor work discussed to some extent in chapter 5. One possible explanation for this was put forward by Hoering [145] who suggested that the alkane chains in the kerogen might contained oxygen functionalization, e.g. keto or ester groups. Adjacent hydrogen atoms would presumably then be acidic enough for exchange to occur (Figure 64).

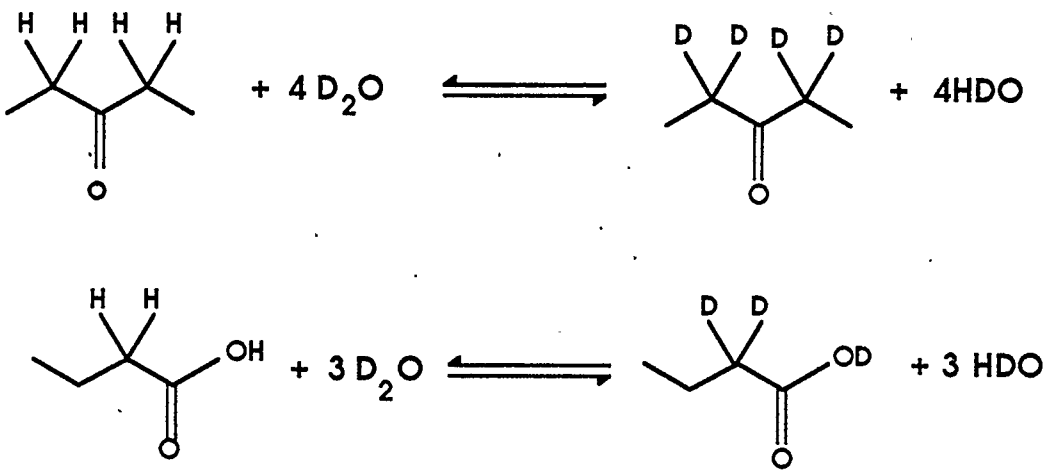


Figure 64. Possible mechanisms for H/D exchange during hydrous pyrolyses.

One might then wonder why the exchanged (oxygen containing) chains would appear as n-alkanes in the product maltenes. According to Batts [147], esters, alcohols, ethers, acids and ketones/aldehydes were converted to alkanes under conditions of hydrous pyrolysis. This explanation, although plausible, was thought unlikely to represent the real situation.

Another explanation of the high level of exchange does not require the presence of the oxygen functionalization but involves disproportionation of "hot' radical species formed (initially) in the homolytic dealkylation of the asphaltene (Figure 65).

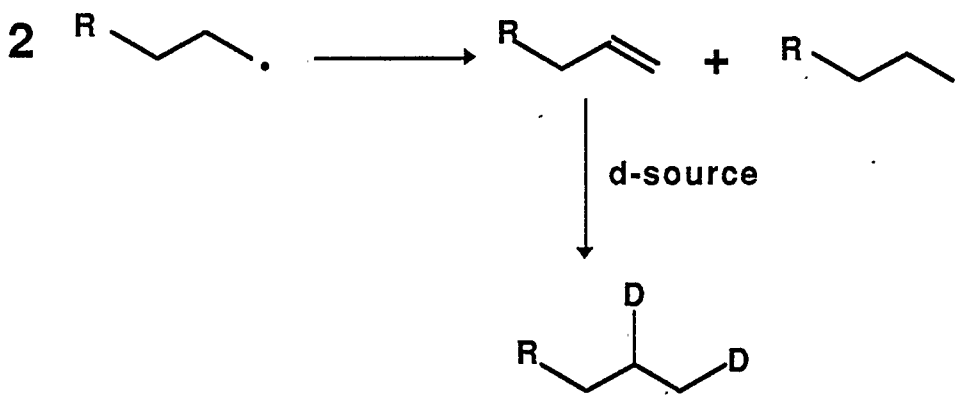


Figure 65. Disproportionation mechanism for "hot" radicals.

Subsequent abstraction of a proton from other positions in the alkyl chains would be required to explain the high level of exchange observed. It is difficult to imagine H_2O/D_2O as a source of hydrogen/deuterium radicals because of the large associated O-H, O-D bond strengths and so the exact mechanism of initial transfer is, as yet, undetermined.

One worry about the observed exchange was that it might have been catalyzed by the walls of the tube bomb (as evidenced by the presence of

FeS_2) but hydrous pyrolyses conducted by other researchers, in gold lined vessels showed no difference in product distribution compared to those carried out in stainless steel vessels [145].

Comparing product distributions from H_2O as opposed to D_2O, a kinetic isotope effect was found and the level of degradation occurring was higher for H_2O. The involvement of H_2O in the degradation reaction may occur by a radical mechanism, in that increased exchange with D_2O was found when a radical initiator was added to the asphaltene/D_2O mixture before pyrolyses. The complexity of the asphaltene does not, however, preclude other mechanisms, e.g. an electrophilic substitution mechanism, being involved [148].

On the basis of ^2H NMR analyses of the products of hydrous pyrolysis in the presence of D_2O, it was possible to probe low temperature processes which led to deuterium incorporation. Under mild hydrous pyrolyses, it was demonstrated that incorporation into the asphaltene occurred preferentially in methylic positions. This indicated bond cleavage of termini of pendant/connecting alkyl chains, agreeing with observations of Strausz et al.[41,135].

Cracking of the model alkyl aromatic compounds (using hydrous pyrolysis) was found to occur in a similar manner to that (reported in chapter 6) involving the non-donor (1-methylnaphthalene) , i.e. the mechanism of cracking depended on the resonance energy of the aromatic system, involved.

Chapter 8

8.1 Final Conclusions

The study of the coking reaction (Chapter 1) revealed that attempts to modify the product distribution (coke formation and aromaticity of the diesel fraction) by adding small amounts of selected compounds (prior to coking) were unsuccessful. The mechanisms important in the coking of bitumen appeared to be largely thermal ones. The addition of large quantities of Lewis acids did result in significant product modification. Large undesirable increases in coke formation were one result. It appeared that a carbonium ion pathway was now the favoured mechanism. Evidence for this included a large amount of rearrangement of the product alkanes (from GC-MS analyses). It was decided that use of a mechanistic probe, added to the bitumen prior to coking, would lead to a clearer understanding of the processes involved in the coking reaction.

In Chapter 2 d_{10}-pyrene (mechanistic probe) was added to the bitumen prior to coking. The exchange of the label occurring during the coking process was then followed by studying the product CGO fractions using ^2H NMR. The result of this study was that very extensive H/D exchange occurred in all possible chemical environments. There was however proportionately more exchange found in the aromatic and benzylic enviroments. The benzylic exchange was found to be reversible whilst the deuterium in aliphatic (non-benzylic) and aromatic locations was irreversibly bound.

The next series of experiments focussed on the pyrolysis of the asphaltene fraction (known to be very good at forming coke on pyrolysis). Without the bitumen maltene present it was hoped to be able to examine the processes important in coke formation. Also, by replacing the maltene fraction (richer in hydrogen than the asphaltene fraction) with a pure hydrogen donor, it

was hoped that the stabilization mechanisms involved in the prevention of coke formation could be studied. It was found that in the absence of the maltene pyrolysis of the asphaltene led to extensive coke formation which could be largely prevented by the presence of a number of hydrogen donors. Surprisingly, it was also found that the presence of a non-donor such as 1-methylnaphthalene would also substantially reduce coke and other high molecular weight material from being formed.

Examination of recovered asphaltene (using NMR) revealed that the pyrolyses of asphaltene with or without a donor being present were characterized by dealkylation, aromatization, condensation, and at low temperature, ring opening reactions.

The presence of a donor during pyrolyses did reduce coke formation and was also found to substantially increase the amount of useful, lower molecular weight material formed. Optimized conditions were found where overall useful conversion was approximately 77% of the starting weight of the initial asphaltene.

In further experiments it was found that it was possible to promote (to a small extent) the dehydrogenation of the hydrogen donor using certain sulphur and metal carbonyl compounds.

The use of a deuterium probe (this time in the asphaltene pyrolysis) could lead to more precise mechanistic information. This was reported in chapter 5. The deuterated equivalent of tetralin was pyrolyzed with the asphaltene. Interestingly an effective kinetic isotope effect was found (when comparing the amount of H/D expressed from the H or D-donor) indicating that breaking of the benzylic C-D bond in the tetralin was involved in the rate determining step of the upgrading reaction. Analyses of the pyrolyses products revealed widespread exchange. Again exchange into benzylic environments

predominated and was found to be reversible. Of particular interest was the recovered maltenes which contained a homologous series of n-alkanes with widespread H/D exchange along their chains. This was further investigated using model compounds. Pyrolysis of the D-donor with free $nC_{25}H_{52}$ and subsequent GC-MS analyses of the products, revealed that casual (non-degradative) exchange was not occurring into the alkane spike. When this experiment was repeated but now with some asphaltene present it was found that widespread exchange into the alkane chains had now occurred and also 50% of the original spike had cracked into smaller alkanes. This indicated that the formation of "hot" radicals (on pyrolyses of the asphaltene) was necessary to explain the level of exchange and the cracking. The types of mechanisms which could possibly explain the observed exchange were discussed.

Studying the bitumen or even the asphaltene is very difficult because of the complexity of these systems. At this stage it was thought that model compounds should be used to try and simulate the bitumen or asphaltene systems in cracking/upgrading reactions. This was reported in chapter 6. In chapter 4 it was found that the reactions of asphaltene with tetralin at different temperatures left the concentration of benzylic hydrogens in the recovered asphaltene relatively unchanged, on pyrolysis, indicating that dealkylative cleavage was occurring β to the aromatic ring system. This was not too surprising because of the stability of the resulting benzylic radicals formed by this type of dealkylation. In order to probe the mechanism of dealkylation and compare pathways in different cracking media, two model alkyl aromatic compounds were pyrolyzed in donor/non-donor media. GC-MS analyses of the products revealed that if the aromatic system was larger than benzene, cleavage occurred predominantly α to the aromatic ring in both donor and non-donor media. Surprisingly, the presence of the hydrogen source retarded the

rate of dealkylation when compared to the non-donor situation. When the alkylbenzene was cracked, cleavage occurred β and γ to the ring. Mechanisms explaining the different cleavage pathways were proposed. The trends of cleavage, depending on the size of the attached aromatic ring, were thought to relate to the loss in resonance energy needed to be overcome in order to interrupt the aromaticity of the system, in an initial H-transfer (to the ring) required for α cleavage to occur. Understanding the mode of dealkylation in the real bitumen or asphaltene system was important since the dealkylated aromatic species forms the template for coke formation.

Finally, in Chapter 7 another, somewhat unrelated, study of hydrous pyrolysis of the bitumen asphaltene was reported. Various reasons for studying this topic were presented in the introduction to Chapter 7. Comparison of pyrolyses of asphaltene in the presence of H_2O compared to donor/non-donor solvents revealed that the presence of the H_2O supressed dealkylation and internal H-transfer reactions, i.e. the recovered asphaltenes (from hydrous pyrolyses) were closer, structurally, to the initial virgin material. The amount of useful, lower molecular weight material recovered (on hydrous pyrolysis) was much lower than for the equivalent H-donor experiment.

When the hydrous pyrolysis experiments were repeated with D_2O, GC-MS analyses of the recovered maltenes revealed, as in the D-donor situation, that widespread H/D exchange had occurred into the series of n-alkanes. Again the presence of the asphaltene was necessary for these "hot" radical reactions to occur. Comparison of the levels of degradation occuring in H_2O/D_2O experiments revealed an effective kinetic isotope effect which meant that breaking of a D-O/H-O bond was involved in a rate determining step. The mechanism of exchange from the D_2O was difficult to imagine because of the high dissociation energy of this bond to form OD and D radicals and yet a

further experiment involving pyrolysis of asphaltene/D_2O and a small amount of a sulphur radical initiator revealed that the H/D exchange (into the recovered alkanes) was greatly increased when compared to the control situation (no sulphur radical initiator).

When the model compounds (used in Chapter 6) were cracked using H_2O it was found that the same cleavage mechanisms were observed as in the H-donor/non-donor situations. The extent of cleavage of the model compounds under conditions of hydrous pyrolysis were similar to those experienced in the presence of the non-donor (Chapter 6) and much more than the equivalent H-donor cracking reactions.

8.2 Further Work

8.2.1 H-Donors

In the work already carried out, it was realised that the n-heptane insoluble, benzene soluble (asphaltene) portion of the whole bitumen (amounting to approximately 10 wt%) had a particular propensity for forming coke, on pyrolysis. In an effort to concentrate on coke formation this fraction was isolated (from Syncrude bitumen) and pyrolyzed in the presence of model hydrogen donors, e.g. tetralin which are known to prevent regressive combination of reactive fragments which would otherwise form higher molecular weight material and eventually, coke. It was found that various H-donors were very successful at preventing this, e.g. under optimized conditions the higher molecular weight material formed was reduced to 25% of the starting weight of asphaltene. In industry there are several processes which have run on a pilot plant scale, involving H-donors. One of these is the Gulf DRB process. Another has been developed by Exxon and is known as the Exxon donor solvent (EDS) Process Development Project, which is a coal liquefaction project. In an

industrial situation the H-donor solvent is generated downstream and is usually a mixture of compounds from a distillation cut. The Gulf process utilizes a middle distillate cut, which on depletion is recycled after rehydrogenation under hydrogen pressure. During the start-up of these processes, the H-donor comes from an external source. Some easily available H-donor solvents are creosote and anthracene oils (from coal). These industrial H-donors are complex mixtures of hydroaromatic compounds which have the ability to transfer hydrogen from their saturated structure to form unsaturated products and at the same time, enrich the hydrogen content of the species being upgraded. The ability of the aromatic compounds being formed (once hydrogen has been donated) to be partially rehydrogenated (decalin and tetrahydroanthracene are examples of over hydrogenated materials which are very poor hydrogen donors) is not clear and it is proposed that the recycle ability of some H-donors (particularly the hydroaromatic compounds found in industrial H-donor mixtures) should be studied.

In this work there were indications that it might be possible to promote the dehydrogenation of the H-donor using certain additives. In an industrial situation this would lead to a very desireable lowering of the required contact time of the H-donor with the material to be upgraded, since the first step in the dehydrogenation (of the donor) was found to be the rate determining step in the upgrading process. It is proposed that a study be made of possible promoters in the H-donor reaction with the ultimate goal of discovering a promoter which could cause rapid transfer of hydrogen from the donor and rehydrogenation (of the donor) from a hydrogen cover gas.

Once reduction of coke formation is optimized (using asphaltene) it is proposed that the whole bitumen be upgraded in the presence of the suitable H-donor mixture possibly with promoter. Obviously, in an industrial situation this

is what would happen. Initial studies with the asphaltene allows one to concentrate on the particular fraction of the whole bitumen, largely responsible for coke formation.

8.2.2 Study of Recovered Asphaltene and Preasphaltene

In this work on pyrolyses of bitumen asphaltene, in the presence of H-donors, the products were separated as maltene (n-heptane solubles), asphaltene (recovered), preasphaltene (pyridine soluble, benzene insolubles) and coke (pyridine insolubles). The recovered asphaltene was studied using ^{1}H and ^{13}C NMR which gave valuable information on the structure of the recovered, degraded material. It was remarkable just how different the recovered asphaltene was from virgin material. By characterizing this recovered material and comparing it to the virgin sample it is possible to determine the reaction types which were important in its degradation and subsequent coke formation. It is proposed that this NMR information coupled with molecular weight and elemental analyses be used to generate average structures of the recovered material as it is obviously on the way to becoming coke. Also, the preasphaltene is intermediate (in molecular weight) between asphaltene and coke and a structural examination of this would lead to a clearer understanding of coke formation. Very little is known about the structure of this coke precursor. It would also be possible to incorporate an isotopic label (by pyrolyzing the asphaltene in the presence of a deuterium donor and analyzing the subsequent exchange into the preasphaltene using ^{2}H NMR in order to follow the deuterium in the course of pyrolysis.

8.2.3 Model Cracking Reactions

In this work it has been shown that pyrolyses of bitumen asphaltene in the presence of d_{12}-tetralin (reacted in a tube bomb at 450°C for 1 hour) resulted in widespread H/D exchange. It was unexpected that the homologous series of n-alkanes (recovered in the maltene, on pyrolyses) were so heavily substituted with deuterium (4 in nC_{10} up to 9 in nC_{22}). One had expected exchange to indicate points of attachment of the alkane chains to the aromatic nuclei of the asphaltene. A model pyrolyses was then carried out to find if it was possible to exchange deuterium into a free alkane chain. The free alkane (nC_{25}) was pyrolyzed in the presence of d-tetralin and asphaltene and widespread exchange was found along with substantial cracking of the alkane. As a control, the same experiment was conducted without the asphaltene being present and almost no H/D exchange or cracking of the free alkane was found. Obviously, a "hot" radical is being generated (by the asphaltene) which is capable of abstracting a proton from the free alkane. One would like to know the source (functionality) in the asphaltene, of these "hot" radicals since they are thought to be crucial in coke formation. It is proposed that model compound studies be carried out to ascertain how they are formed. Two possible candidates are primary alkyl and phenyl radicals. These radicals could be generated at relatively low energy cost by pyrolyses of $PhS\text{-}CH_3$ to generate the alkyl and PhS-Ph to generate the phenyl radicals. Cracking reactions would be carried out with these compounds in the presence of a free n-alkane, e.g. nC_{25} and of course, the d-donor. The results of these studies (in terms of deuterium exchanged) would then be compared to the situation where the asphaltene was used.

Also, from this work concerning NMR analyses of asphaltene pyrolyses, it was found that dealkylation was an important process accompanying coke formation. In model dealkylation it was found that 9-nonylanthracene cracked primarily α to the aromatic ring. In the same study it was noted that the dealkylation was inhibited by the presence of a H-donor. Interestingly, the dealkylation proceeded to completion in the presence of 1-methylnaphthalene and D_2O (which have no net H-donor ability). In a further study (other work) it was shown that under the conditions studied, 1-methylnaphthalene would significantly demethylate/methylate, giving naphthalene and dimethylnaphthalene as pyrolysis products. It is proposed that the the mechanism involved in this side chain mobility be studied (using model compounds) since condensation of aromatic species is required for coke formation to occur.

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