7 WAXY OIL MODIFICATION

7.1 Introduction

The modification procedures employed to increase the anisotropy of the coke serve to retard the onset of carbonisation, allowing for maximum fluidity of the system during mesophase formation. This is achieved by stabilising thermally reactive organic moieties prior to carbonisation. Due to the complexity of comparing analyses of the modified Waxy Oil, the analyses have been colour coded as shown in Table 7-1.

Table 7-1 Experimental conditions and colour coding for modified Waxy Oils[19]

Sample	Waxy Oil modification	Colour coding
A	No modification	Orange
B	Sample A filtered through 0.5 µm sieve	Blue
C1	Sample B distilled (480 °C at -0.9 kPa)	Red
C2	Sample B distilled (440 °C at -0.9 kPa)	Grey (80%)
D1	Sample B thermally treated (400 °C, 5 bar, 2 h)	Dark yellow
D3	Sample B thermally treated (410 °C, 5 bar, 2 h)	Bright green
D4	Sample B thermally treated (420 °C, 5 bar, 2 h)	Dark red
E2	Sample B thermally treated (410 °C, 1 h at 5 bar and 1 h at 1 bar)	Pink
E1a	Sample B thermally treated (410 °C, 1 h at 5 bar and 1 h at 1 bar)	Black
E1b	Sample E1a distilled (325 °C under nitrogen)	Sky blue

7.2 Modification of Waxy Oil

7.2.1 No modification of Waxy Oil (Sample A)

This sample is used as a reference against which filtered Waxy Oil (Sample B) is compared. The description of the catalyst's effect on the quality of Waxy Oil coke (discussed in Chapter 6, Section 6.5.1) was based on commercial samples. Sample A was carbonised in a test tube and the coke will be compared with those produced by the other modifications discussed in Chapter 8. Thus, Sample A excludes any potential variability between commercial and laboratory process conditions.

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[19] Apart from Sample A, all the samples in Table 7-1were filtered prior to any further modification.

7.2.2 Waxy Oil Filtration (Sample B)

A sample (40 ℓ) of Waxy Oil was obtained from the commercial delayed coker at Secunda, South Africa. As it was not possible to determine the Particle Size Distribution (PSD) of the solids in the Waxy Oil sample, this analysis was conducted on the Synthol Decant Oil (SDO).[20] The solids include any minerals and carbonaceous solids. The PSD is shown in Figure 7-1.

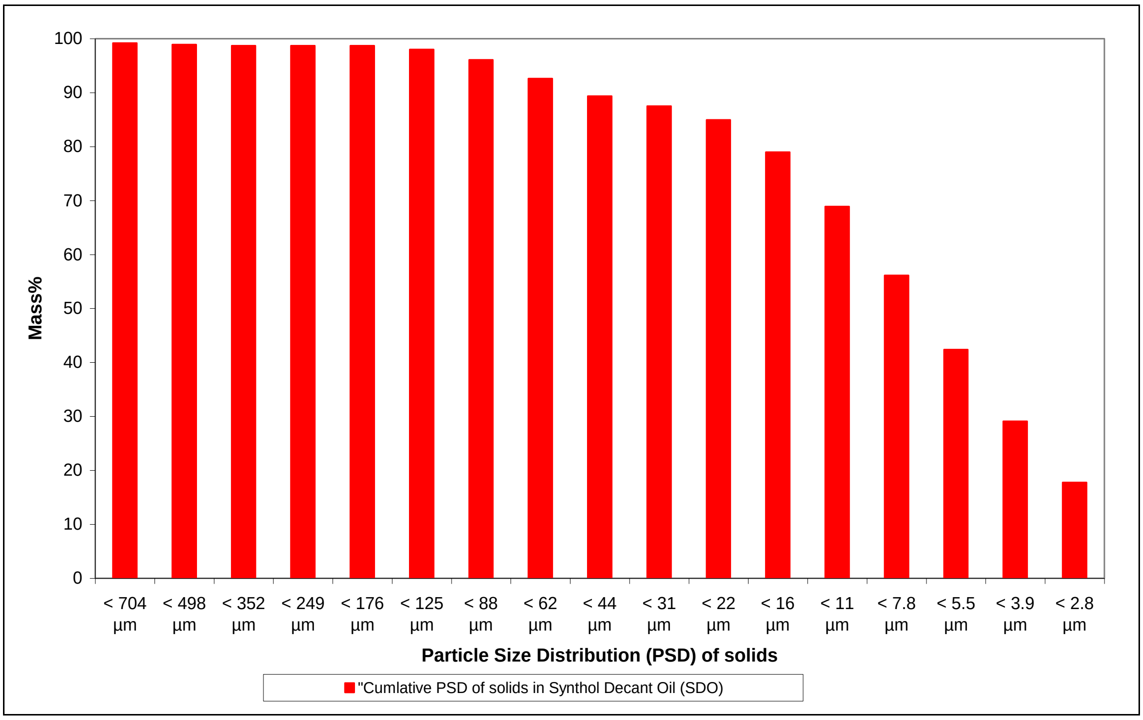

Figure 7-1 Particle Size Distribution (PSD) of solids in Synthol Decant Oil (SDO)

The PSDs of Waxy Oil catalyst particles and carbonaceous solids are less than 100 µm. It is possible to remove the catalyst partially by centrifugation, but not with the efficiency required for needle coke specifications. The effect of filtration on the levels of catalyst (as determined by the ash content) in Waxy Oil filtrates is discussed below.

Waxy Oil was heated to 90 °C and filtered through various sintered metal plates (2.0–0.5 µm). The ash and carbonaceous Mass Insoluble in Quinoline (MIQ) were determined on three samples of the virgin Waxy Oil feed and a series of filtrates. A detailed experimental procedure and description of the filtration apparatus is given in Chapter 5, Section 5.4.1. The results are shown in Table 7-2.

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[20] The Synthol Decant Oil (SDO) is the heavy residue product of the Synthol reaction; it is distilled to form the Waxy Oil, which is the residue of the distillation (as shown in Figure 3-1).

Table 7-2 Ash and carbonaceous MIQ[21] content of Waxy Oil blanks and filtrates [obtained through a series of sintered metal plates (2.0–0.5 µm)]

Sample	Units	Filter description	Ash content 1	Ash content 2	Carbonaceous MIQ
Waxy Oil blank 1	**Mass %**	**None**	1.649	1.694	1.065
Waxy Oil blank 2	**Mass %**	**None**	1.699	1.673	0.916
Waxy Oil blank 3	**Mass %**	**None**	1.609	1.593	0.802
Test 1	**Mass %**	**2 µm filter**	0.132	0.139	0.336
Test 2	**Mass %**	**1.0 µm filter**	0.076	0.085	0.153
Test 3	**Mass %**	**0.5 µm filter**	0.006	0.006	not determined
Test 4[22]	**Mass %**	**0.5 µm filter**	0.004	0.003	not determined

Three different samples of Waxy Oil were independently obtained from the 40 ℓ sample. This was done to establish a level of confidence in the determination of the ash content of Waxy Oil, which is dependent on obtaining representative samples. All the Waxy Oil blank samples (named Test 1, 2 and 3) yield ash contents between 1.6 and 1.7%, with carbonaceous MIQ contents between 0.8 and 1.1%.

The use of a 2.0 µm sintered metal plate (Test 1) reduced the ash content to 0.134% (or a 92% reduction) based on the average of the two duplicate results. The 1 µm sintered metal plate (Test 2) reduced the ash content further to 0.081% (or a 95.1% reduction), and the 0.5 µm sintered metal plate (Tests 3 and 4) reduced the ash content further to between 0.004 and 0.006% respectively (or a 99.6% reduction).

It was decided to produce the feed for distillation and thermal treatment (3 ℓ) using the 0.5 µm sintered metal plate to achieve the maximum ash reduction. Furthermore, based on the requirement of needle coke specifications (ash content 0.2% maximum), only the filtrate from Tests 3 and 4 would yield a calcined coke with an acceptable ash content (based on an estimated 10% yield from the fresh Waxy Oil feed).

7.2.2.1 Analysis of unfiltered and filtered Waxy Oil[23]

TGA[24] and DTG were conducted on Samples A and B. The results are shown in Figures 7-2 and 7-3 respectively. A detailed discussion of the experimental procedure is given in Chapter 5, Section 5.4.3.

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[21] The determination of the ash content to three decimal places for Waxy Oils with high catalyst concentrations is not as accurate as indicated. This procedure is, however, followed to show the comparative ash contents of the filtered Waxy Oil.

[22] Test 4 is a duplicate of Test 3 conducted to establish a level of confidence.

[23] The research for Chapter 7 (Sections 7.2.2.1–7.5) was conducted by the author at the Instituto Nacional del Carbón (INCAR) in Oviedo, Spain under the tutorship of Dr Ricardo Santamaria.

[24] TGA of Waxy Oil is not to be read as a distillation reaction. Although the mass loss in the initial temperature range is a result of distillation, at 400–430 °C (depending on the stability of the molecules) thermal cracking occurs, releasing lighter hydrocarbon distillates and gas. Between 450 and 500 °C carbonisation occurs. Both these reactions involve a chemical change in the molecular composition of the feed.

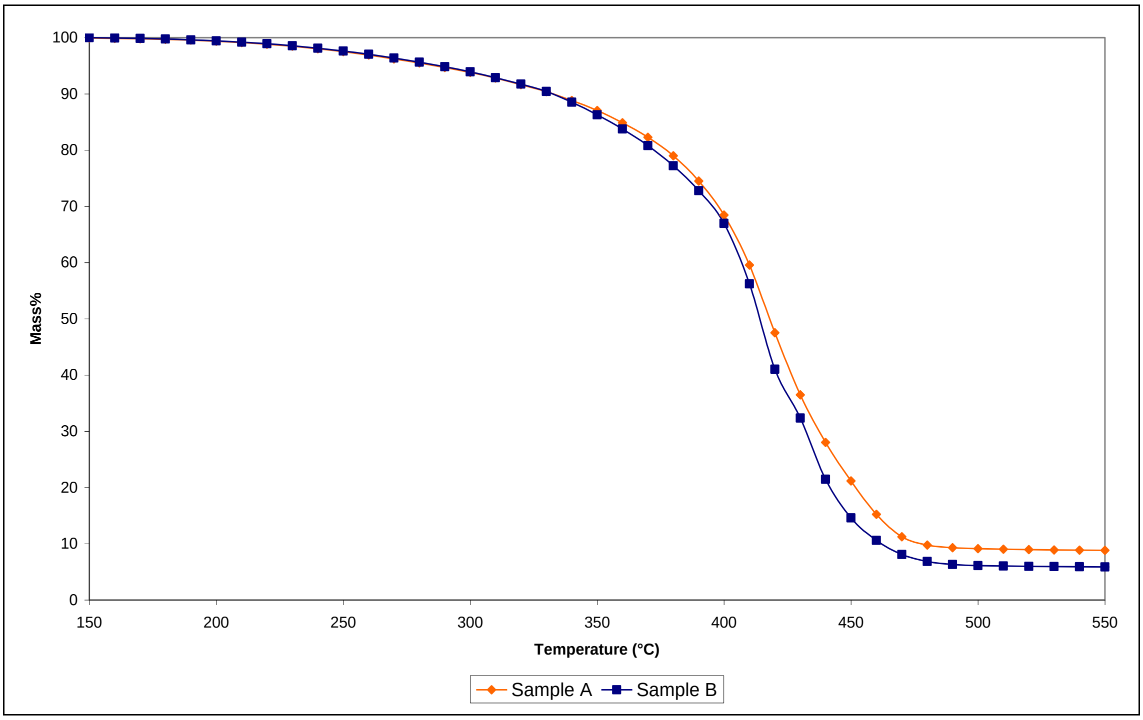

Figure 7-2 Thermogravimetric Analysis (TGA) of Samples A and B

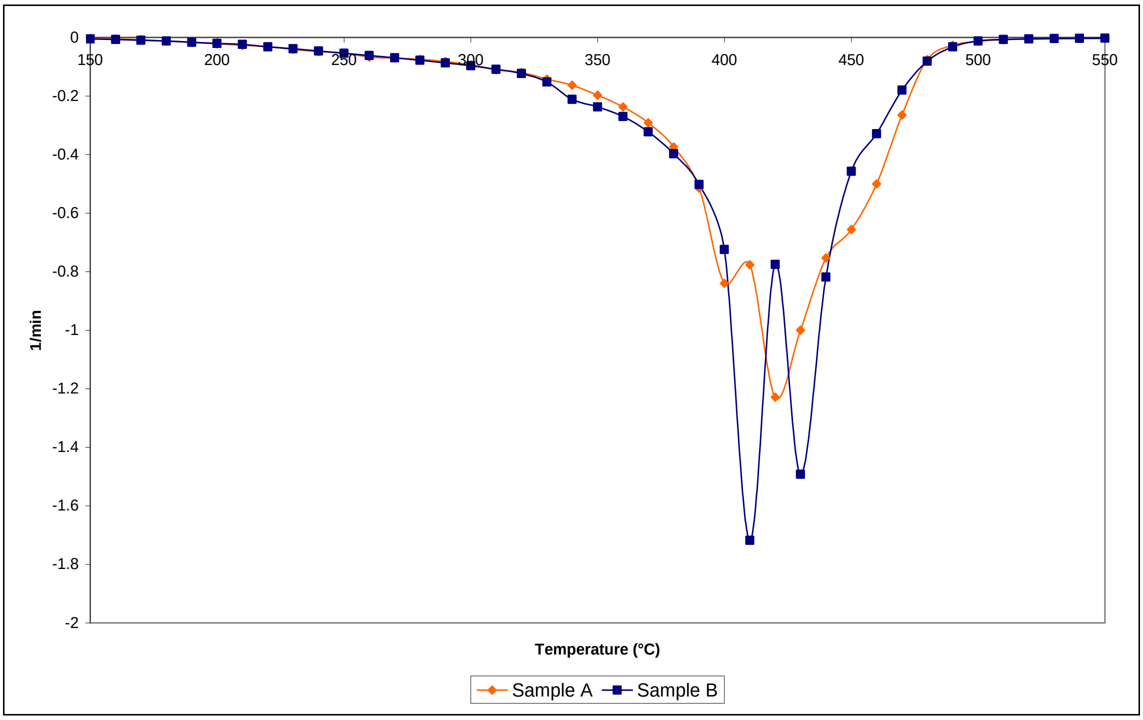

Figure 7-3 Differential Thermogravimetry (DTG) of Samples A and B

The TGA curves of Samples A and B (Figure 7-2) are similar between 200 and 340 °C (which is not unexpected as the only variant is the catalyst content). However, as Waxy Oil is the product of a flash distillation, there is a small percentage of lighter boiling components as witnessed by a 5% mass reduction to 290 °C. The residuum of Sample A (9.34%) is higher than that of Sample B (6.30%), both being determined at 500 °C. The difference between the residua of Sample A and B is ascribed partly to the mass contribution of the catalyst (1.67%).

With regard to the remaining 1.37% differential, this is ascribed to the effect of iron catalysis in promoting oxidative polymerisation and thus increasing the carbon yield, as described by Wang *et al.* (2001).

The DTG (Figure 7-3) of Sample B indicates two peaks at 410 and 430 °C. Given their proximity, they may constitute only one peak. While Waxy Oil and petroleum pitches differ vastly in respect of their composition, a similar DTG behaviour (including one peak which is the product of both endothermic distillation and exothermic cracking reactions) has been previously reported by Perez *et al.* (2002) using petroleum residues. The peak for Sample A at 420 °C is shallower than that for Sample B. The probable reason is that due to the higher ash content of Sample A, there is a smaller percentage of organic residue and thus the intensity of cracking based on the relative mass percentage is lower.

As it was not possible to conduct a GCMS on Sample A (due to the ash content), Sample B was refluxed in toluene (which was used as a solvent for the GCMS). The whole of Sample B was soluble in toluene. The GCMS of filtered Waxy Oil (Sample B) is shown in Figure 7-4 and the procedure explained in greater detail in Chapter 5, Section 5.4.5.

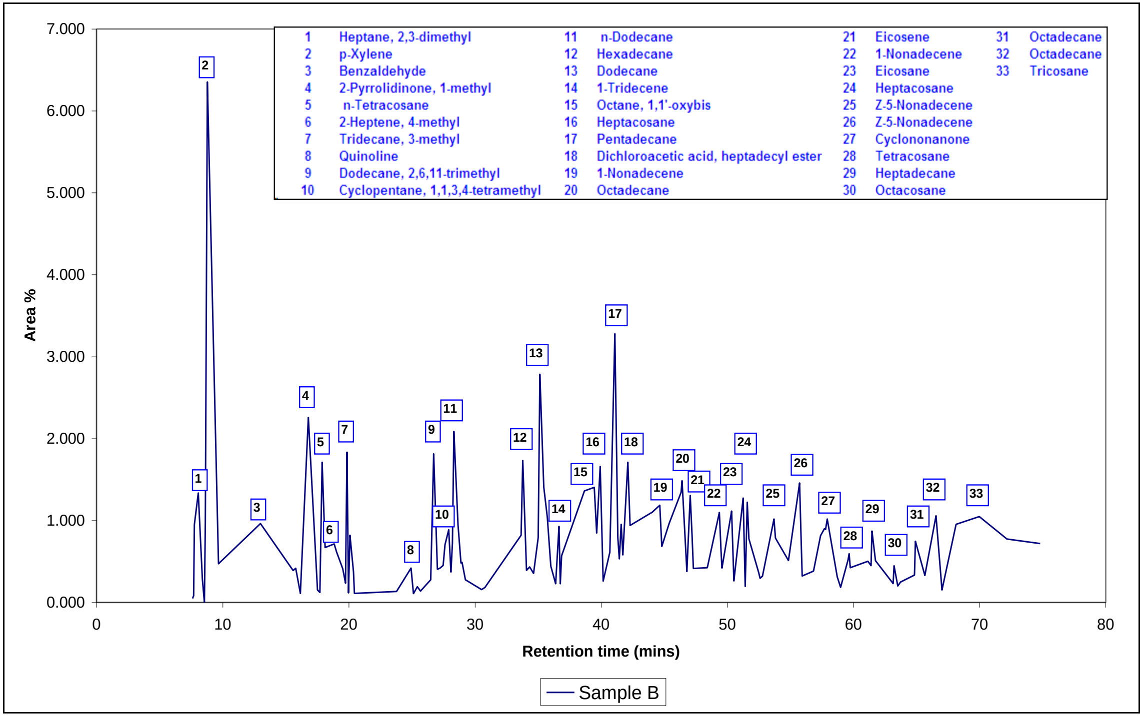

Figure 7-4 Gas Chromatography–Mass Spectroscopy (GCMS) of Sample B

The GCMS trace (Figure 7-4) shows the elution of many hundreds of organic molecules within a retention time of up to 70 min. Molecules identified in the index of the GCMS trace (shown in Figure 7-4) have area percentages of half a per cent or greater. Of particular importance is the variance in the molecular weight of oxygenates. Within the first 20 min only 24% of oxygenates elute and similarly between 20 and 40 min (16%), between 40 and 60 min (52%) and finally above 60 min (8%). The major oxygenate groups in Sample B (total 13.12%) include esters (3.94%), ketones (3.28%), alcohols or phenolics (2.07%) and epoxides (1.32%). Peaks 1 to 10 are composed largely of alkylated aromatics and alkanes. In the latter portion of the trace (Peaks 11 to 33) there is a predominance of normal alkanes ranging from C_{10} to C_{30}.

The composition of molecules eluting within the first 30 min include cyclo-aliphatics and iso-alkanes typically lower than tridecane (C_{13}). While not specifically indicated in the figure, there is a host of alkylated aromatics which present in smaller concentrations eluting within this time period. The higher molecular weight molecules eluting after 30 min comprise mainly normal alkanes and alkenes (C_{10}–C_{30}). The area percentage of normal alkanes (especially in the C_{20}–C_{30} range) is of particular importance to this study. However, in Sample B, although their presence is identifiable, they do not emerge as dominating peaks in the GCMS trace.

The GCMS trace of a single sample of filtered Waxy Oil heavy residue has limited value. However, as discussed later, by overlaying the traces of two samples it is possible to determine general **qualitative** differences in their molecular composition.

In the study of how the composition of heavy residues affects the microstructure of the green coke produced, the concentration of single components is of lesser importance than that of “families” of components into which they may be grouped, specifically in relation to their thermal reactivity (during the onset of carbonisation) and thus their propensity to produce cokes with either mosaic or domain flow microstructures.

The individual components have been classified[25] into “families” or groups of similar composition for Sample B and are shown in Table 7-3.

Table 7-3 Molecular compound groups in Sample B filtrate

Molecules	Unit	Sample B
Alkylated aromatics	**Area %**	9.13
Pure aromatics	**Area %**	0.84
Iso-alkanes	**Area %**	14.10
Normal alkanes	**Area %**	38.18
Oxygenates	**Area %**	13.12
Cyclo-alkanes	**Area %**	2.02

The organic composition of Sample B is dominated by both normal alkanes and alkylated homologues thereof. While there is a comparatively small concentration of pure aromatics, the concentration of alkylated aromatics is comparatively large. However, of particular interest is the concentration of oxygenates, which is not unexpected as oxygen functionalities may be introduced from carbon monoxide during the Fischer-Tropsch reaction with hydrogen.

The change in the concentration of alkylated aromatics, alkylated alkanes and especially oxygenates as a result of Waxy Oil modification is key to controlling the reaction rate during carbonisation as all of the abovementioned groups are known to increase the reaction rate during carbonisation, as previously described by Obara *et al.* (1981) and Sima *et al.* (2003). This promotes the formation of mosaic microstructures which, in the current study, is deemed detrimental. While the removal of reactive molecular components is important, the increase in the concentration of thermally “stable” molecules is of equal interest. The totals of all pure

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[25] The classification of molecules into similar groups was conducted in line with the requirements of this study and does not represent all possible classifications. The area percentage contribution of each molecular component was manually calculated from the GCMS data table.

normal alkanes (C_{10}–C_{30}) were manually calculated from the GCMS data table and are shown in Table 7-4.

Table 7-4 Normal alkanes (C_{10}–C_{30}) in Sample B residue

Molecule description	Carbon number	Unit	Sample B
Decane	**C10**	**Area %**	0.00
Undecane	**C11**	**Area %**	0.00
Dodecane	**C12**	**Area %**	7.69
Tridecane	**C13**	**Area %**	2.78
Tetradecane	**C14**	**Area %**	0.76
Pentadecane	**C15**	**Area %**	3.54
Hexadecane	**C16**	**Area %**	2.83
Heptadecane	**C17**	**Area %**	4.14
Octadecane	**C18**	**Area %**	4.64
Nonadecane	**C19**	**Area %**	1.05
Eicosane	**C20**	**Area %**	2.86
Heneicosane	**C21**	**Area %**	1.58
Docosane	**C22**	**Area %**	0.00
Tricosane	**C23**	**Area %**	1.82
Tetracosane	**C24**	**Area %**	0.00
Pentacosane	**C25**	**Area %**	0.38
Hexacosane	**C26**	**Area %**	0.72
Heptacosane	**C27**	**Area %**	2.94
Octacosane	**C28**	**Area %**	0.45
Nonacosane	**C29**	**Area %**	0.00
Contane	**C30**	**Area %**	0.00
TOTAL		**Area %**	**38.18**

As Waxy Oil is the commercial residue product of flash distillation to remove lighter petrol and diesel intermediates, it is not unexpected that Sample B would contain small amounts of typical normal alkanes in the diesel range. However, at a combined concentration of approximately 12%, these alkanes are unexpectedly high. The normal alkanes constitute only a total of 38.18%, being dominated by lighter fractions (26.39%; C_{12}–C_{18}).

With regard to the iso-alkanes and oxygenates identified, it is necessary to determine methods of stabilisation to decrease their potential reactivity during carbonisation. At the same time it is necessary to identify and maximise molecules with a higher thermal stability that promote the formation of the anisotropic flow patterns previously discussed in Chapter 6. The concentration of heavier normal alkanes (typically from eicosane [C_{20}] to contane [C_{30}]) may present the best option for aromatisation and the subsequent formation of flow domains during carbonisation.

The influence of highly aliphatic residues, e.g. petroleum vacuum residues, on the quality of coke (and thus the necessity for stabilisation) was argued previously by Marsh *et al.* (1999) who linked the reactivity of these residues to a premature increase in the matrix viscosity, smaller optical textures and the resultant increase in the CTE. However, reactivity is not linked solely to the aliphatic nature of feeds, as shown by Calemma & Rausa (1997) who studied highly aromatic asphaltene feeds.

7.2.3 Waxy Oil filtration and distillation

Filtration of Waxy Oil is a necessity in connection with the ash content requirement of needle coke. Sample B is thus considered the base product against which all other modifications of the organic composition of Waxy Oil are compared. In terms of potential pre-carbonisation costs (not including filtration), distillation to produce a heavier Waxy Oil would be the most viable and least capital-intensive method of modification on a commercial scale as the distillation temperature of the existing column could merely be increased. The efficacy of distillation would rely on the molecules that serve to increase the reactivity of the Waxy Oil being concentrated within the lower molecular weight fractions and thus reporting to the distillate.

The distillation of Waxy Oil was conducted in the laboratory using approximately 250 g of filtered Waxy Oil (Sample B) at the maximum vacuum pressure achievable of -0.9 kPa. Waxy Oil was distilled to residue temperatures of 340 °C (Sample C2) and 380 °C (Sample C1) respectively. A detailed description of the distillation procedure is provided in Chapter 5, Section 5.2.2.

The residue and distillate yields of the vacuum distillations are shown in Table 7-5.

Table 7-5 Waxy Oil residue and distillate yields from vacuum distillation of Sample B

Experiment No.	Sample	Residue temperature (°C)	Vacuum (kPa)	Residue (%)	Distillate (%)
C1	**Filtered Waxy Oil**	**380**	**-0.9**	87.0	13.0
C2	**Filtered Waxy Oil**	**340**	**-0.9**	94.3	5.7

The distillation of Waxy Oil proved problematic as the maximum vacuum achievable (-0.9 kPa) provided only a small amount of distillate before the residue started cracking at approximately 350 °C. Sample C1 is thus not a “true distillation” but rather a mild thermal treatment reaction. Mild thermal cracking serves to increase the distillate[26] yield (compared with Sample C2 distillate) due to the production of lighter cracked molecules. However, the Waxy Oil residue produced from the distillation reaction of Waxy Oil at 380 °C is not insignificant, with specific reference to the amount of oxygenates left in the residue, shown in Table 7-6 and discussed later in this section. Much of the wax distillate of Sample C2 solidified in the condenser, causing blockages as shown in Figure 7-5.

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[26] The distillate yield is calculated as 100% minus the residue yield. The distillate is the product of both lighter liquid hydrocarbons and hydrocarbon gases. The GCMS analysis on the distillate pertains only to the liquid distillate. The same holds true for all distillates produced by Waxy Oil modifications discussed in this chapter.

Figure 7-5 Photo of solidified wax distillate in the condenser

TGA and DTG were conducted on Samples C1 and C2 and compared with Sample B as shown in Figures 7-6 and 7-7 respectively.

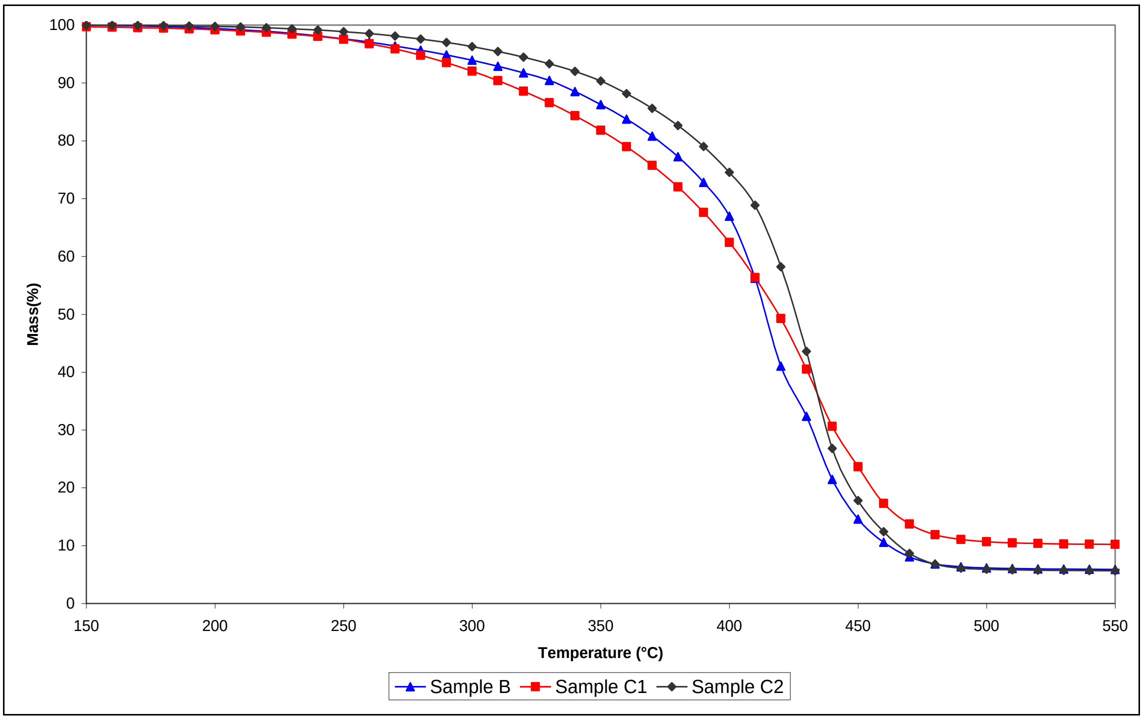

Figure 7-6 Thermogravimetric Analysis (TGA) of Samples B, C1 and C2 residues

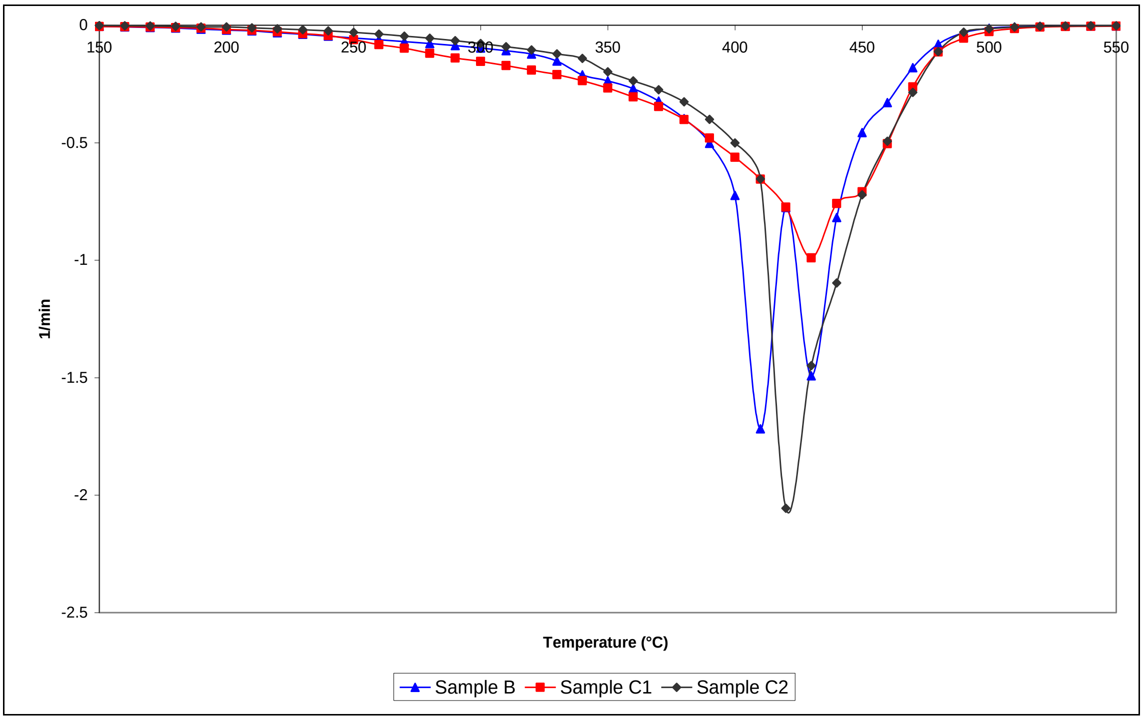

Figure 7-7 Differential Thermogravimetry (DTG) of Samples B, C1 and C2 residues

Both Samples C1 and C2 show an initial mass loss at approximately 200 °C (Figure 7-6). However, compared with Sample B, Sample C2 distillation removes lower molecular weight molecules above 250 °C, as indicated by the slightly steeper mass loss curve of Sample B within this temperature range. However, the opposite is true for Sample C1: the initial mass loss curve is steeper than that of Sample B, indicating that the planned "distillation" turned into a mild thermal treatment producing a small increase in the concentration of lower molecular weight hydrocarbons. Thus, even though the mass loss curve of Sample C1 is steeper than that of the other samples within the lower temperature range, the residuum of Sample C1 (10.68%) is greater than that of Sample C2 (5.90%).

In the corresponding DTG (Figure 7-7), Sample C2 exhibits a single peak of maximum mass loss rate at 420 °C (similar to Sample B). The first peak for Sample C1 is associated with mass loss of lighter cracked hydrocarbons below 350 °C; given the even distribution, a definable peak is not visible. The second is a more intense peak at 430 °C. The second peak (for Sample C1) is less intense than the singlet peak corresponding to Sample C2 due to the higher dilution factor of Sample C1. It also occurs at a slightly higher temperature (430 °C) compared with the second peak of Sample C2 at 420 °C.

Distillation to pre-cracking temperatures (below 350 °C) is a physical reaction, removing molecules without chemical reaction. However, the mild thermal treatment producing Sample C1 involves a small degree of molecular breakdown. The second mass rate peak (for Sample C1) is of great interest and is described throughout the course of this chapter for all the modifications. In general, the intensity of the carbonisation peak is inversely comparable to the amount of lighter cracked hydrocarbons remaining in the residue (i.e. the first peak). The temperature of the second peak in the cracking region (approximately 420–460°C) is dependent on the concentration of higher molecular weight, thermally stable normal alkanes.

Comparing the GCMS traces of Sample B with those of Samples C1 and C2 is useful for determining the effect of distillation on the general molecular composition. However, as the GCMS traces are complex, comparing more than two samples in the same figure may prove confusing. Thus the GCMS of Sample B and Sample C2 residues are initially compared as shown in Figure 7-8.

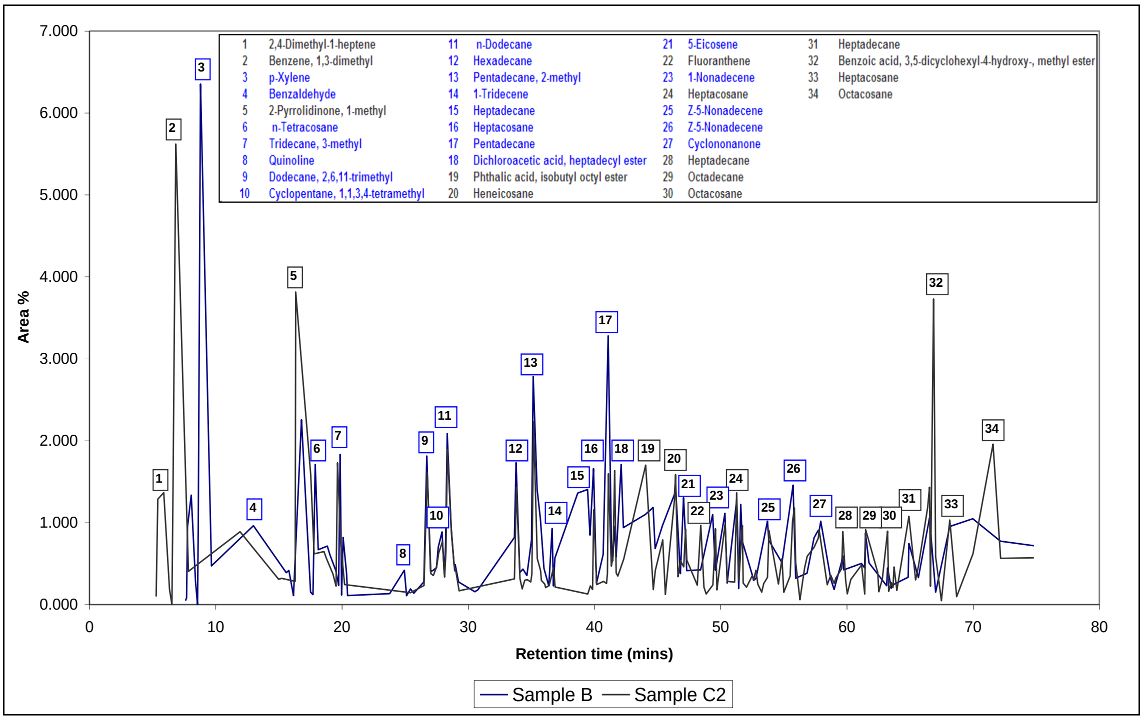

Figure 7-8 Gas Chromatography–Mass Spectroscopy (GCMS) of Samples B and C2 residues[27]

As the residue yield of Sample C2 is 94.3%, it stands to reason that a qualitative GCMS comparison of the trace (with Sample B) would be similar. As shown in Figure 7-8, the distillate component of Sample C2 indicates the removal of a small concentration (approximately 1%) of alkanes from C_{10} to C_{28}. It should be noted that the distillation (below cracking temperatures) to produce Sample C2 involves no chemical modification of Waxy Oil molecules.

The GCMS of Sample B and Sample C1 residues are compared in Figure 7-9.

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[27] The GCMS traces of the two samples have been overlaid for comparative purposes and each sample is represented by a different colour as previously mentioned. The numbers identifying the peaks are related to the individual molecules in the index. Both the peak numbers and their corresponding descriptions in the index are colour coded in terms of the sample they represent. When the peaks of the two samples overlap, the peak is colour coded according to the sample with the largest comparative area percentage for that specific molecule.

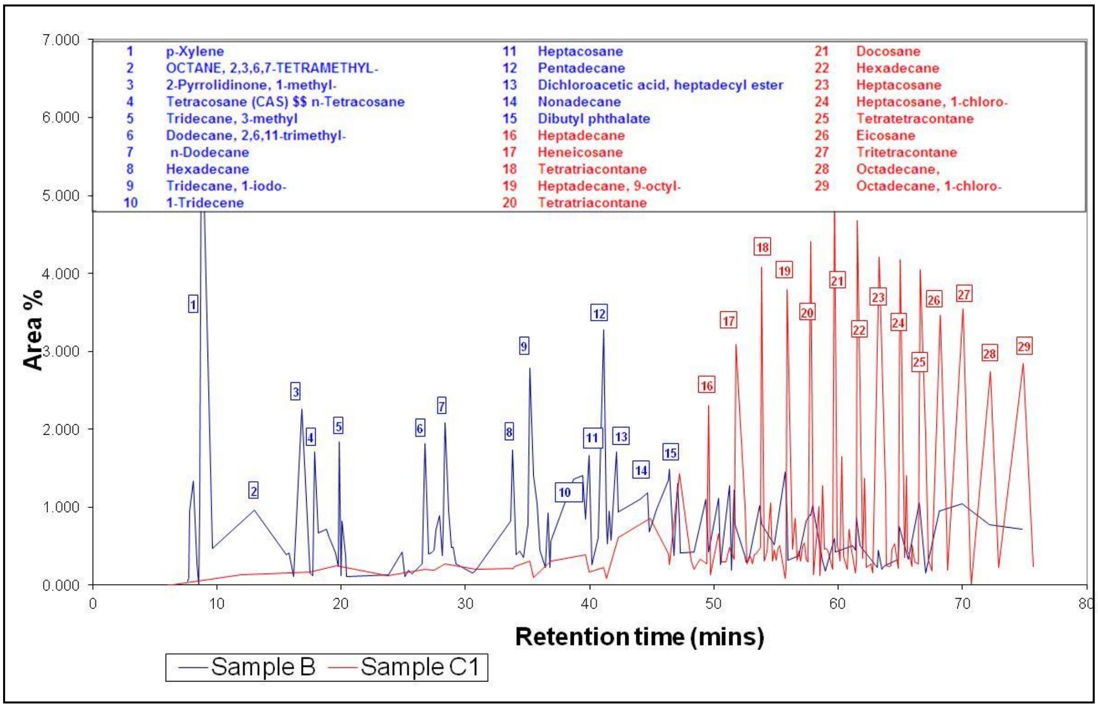

Figure 7-9 Gas Chromatography–Mass Spectroscopy (GCMS) of Samples B and C1 residues

There is a substantial difference in the GCMS traces of Samples B and C1. Compared with Sample B, the trace of Sample C1 shows substantial depletion of lighter hydrocarbons below a retention time of 40 min (peaks 1–15). The lower concentration of molecules within this area of the trace indicates the propensity of thermally unstable molecules to pyrolyse, forming lower molecular weight organics which distil below a temperature of 380 °C. This may include the distillation of a small amount of pure aliphatics. However, in comparison with Sample B, there is evidence of an increase in the area percentage of heavier molecular weight normal alkanes after a retention time of 50 min (peaks 16–29) in the C_{17} to C_{28} range. This range of pure normal alkanes increases from less than 1% (Sample B) to between 2 and 5% in Sample C1. The increase is due mainly to a reduction of the dilution factor (i.e. the removal of lighter hydrocarbons at lower retention times) and bears further witness to the relative stability of this group of heavier normal alkanes.

As Sample B does not have a distillate fraction, it is only possible to compare the GCMS traces of the distillates from Samples C1 and C2 shown in Figure 7-10.

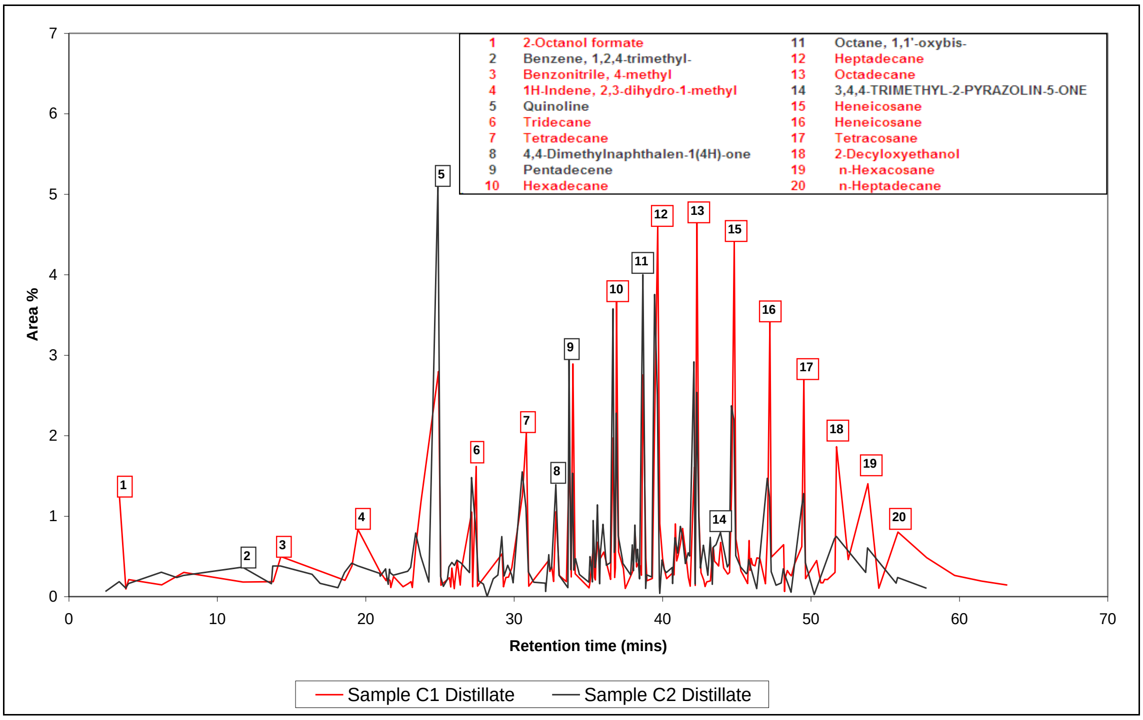

Figure 7-10 Gas Chromatography–Mass Spectroscopy (GCMS) of Samples C1 and C2 distillates

Within the first 20 min the distillate of Sample C1 appears to contain a similar, if not slightly higher, concentration of lighter components than the distillate of Sample C2. This may be due to the distillation of lighter cracked hydrocarbons. However, the major peaks identified do not indicate a complete dealkylation reaction. Given the higher reaction temperature, it is not unexpected that the Sample C1 distillate would contain a greater proportion of heavier aliphatics (peaks 12–20).

The Sample C1 reaction produces a heavier Waxy Oil residue, thus increasing the concentration of higher molecular weight components (especially normal alkanes from C_{17} and higher) under mild thermal cracking conditions. However, what a comparison of the GCMS trace is incapable of determining is the quantitative variation in groups of similar molecules. For this reason the individual components have been classified into "families" or groups of similar composition for Samples C1 and C2 and are shown in Table 7-6.

Table 7-6 Molecular compound groups in Samples C1 and C2 residues

Molecules	Unit	Sample C1	Sample C2
Alkylated aromatics	Area %	1.00	7.18
Pure aromatics	Area %	0.00	6.31
Iso-alkanes	Area %	5.33	14.10
Normal alkanes	Area %	46.39	30.12
Oxygenates	Area %	10.34	11.05
Cyclo-alkanes	Area %	0.00	0.30

Sample C2 shows a greater area percentage of both pure and alkylated aromatics in comparison with Sample C1. A greater amount of alkylated aromatics may have been dealkylated and the aromatics produced removed in the distillate of Sample C1. The same holds true to a lesser degree when comparing the relative concentrations of alkylated alkanes. This results in a reciprocal increase in the concentration of normal alkanes in Sample C1.

Although Sample C1 was initially considered a “mistake” in terms of the original planned distillation, it is included in the discussion as it holds a wealth of information. Mild cracking (at 380 °C) has a substantial effect on the aliphatic to aromatic ratio, but there is only a slight decrease in the concentration of oxygenates. Very much the same holds true for Sample C2. Thus in terms of stabilising the Waxy Oil, both distillations were unsuccessful in reducing the oxygenate concentration substantially.

The major oxygenate groups present in Sample C2 (total 11.05%) include alcohols/phenolics (5.31%), carboxylic acids (3.52%) and ethers (0.49%). The major oxygenate groups present in Sample C1 (10.34%) include carboxylic acids (5.37%), alcohols/phenolics (1.33%) and phthalates (0.49%).

In order to study the nature of the oxygenate molecules in Sample C1 in greater detail they have been listed (along with their retention times and area percentages) in Table 7-7.

Table 7-7 Oxygenate molecules in Sample C1 residue

Molecules	Retention time (min)	Area (%)
Benzaldehyde	11.93	0.129
2-Butyn-1-OL, 4-Methoxy-	17.45	0.168
2-Butyn-1-OL, 4-Methoxy	19.60	0.244
3,3-Bis(methoxymethyl)oxacyclobutane	27.45	0.188
Phthalic acid, monoamide, N-ethyl-N-(3-methylphenyl),-undecyl ester	46.35	0.406
Hexyl octyl ether	48.41	0.196
2-Pentadecanol	49.39	0.274
Hexyl octyl ether	50.66	0.296
1-Octanol, 2-butyl	52.95	0.365
7-Hydroxy-3-(1,1-dimethylprop-2-enyl)coumarin	53.41	0.398
1-Eicosanol	54.24	0.419
1-Hentetracontanol	56.29	0.460
Ethanol, 2-(dodecyloxy)	57.10	0.495
(meso)-3,4-dihydroxymethyl-3,4-dimethylhexane	57.41	0.329
Ethanol, 2-(dodecyloxy)	58.47	1.005
Ethanol, 2-(dodecyloxy)	58.57	0.342
Ethanol, 2-(dodecyloxy)	59.00	0.468
9,10-Secochola-5,7,10(19)-triene-3,24-diol	59.54	0.204
Nonahexacontanoic acid	60.44	0.370
Nonahexacontanoic acid	60.75	0.198
Nonahexacontanoic acid	60.83	0.721
7-Hydroxy-3-(1,1-dimethylprop-2-enyl)coumarin	61.36	0.157
1a,9b-dihydro-4-methyl-1H-phenanthro[9,10-b]azirine	66.42	0.268
Nonahexacontanoic acid	67.06	1.920
Nonahexacontanoic acid	67.56	0.316

The bulk of oxygenates (93%) elute after 46 min. Thus even though mild cracking (380 °C) and distillation may increase the coking residue (as established in Figure 7-6), these experimental conditions do not serve to stabilise the residue in terms of substantially reducing the oxygenate content. As previously mentioned, oxygenates are distributed throughout the molecular weight range of Waxy Oil. Thus even if the vacuum pressure were to be increased (to reduce cracking), the residue would still contain substantial amounts of oxygenates, which is contrary to the aim of this set of experiments. This is seemingly in contradiction to the findings of Perez *et al.* (2002) who determined that the bulk of oxygenates identified within petroleum residues were concentrated in the lower molecular weight molecules. However, given the difference in the origins of the two feeds, it is not entirely unexpected. Another factor to consider is that temperatures greater than 380 °C would need to be employed to destroy the concentration of oxygenates. This presents a challenge as not only are oxygenate molecules eluted at higher retention times, but also they do not appear to have been reduced to any substantial degree by mild cracking and distillation at 380 °C. Quite apart from the quality of the residues, the quality of the distillates is core to the production of petrol and diesel intermediates for the refinery. If distillation were able to increase the concentration of higher molecular weight molecules in the distillate, this may induce challenges in keeping the diesel intermediate fractionation cut within specification.

The concentrations of normal alkanes in Samples C1 and C2 are shown in Table 7-8.

Table 7-8 Normal alkanes (C_{10}-C_{30}) in Sample C1 and C2 residues

Molecule description	Carbon number	Unit	Sample C2	Sample C1
Decane	**C10**	**Area %**	0.00	1.73
Undecane	**C11**	**Area %**	0.00	0.00
Dodecane	**C12**	**Area %**	0.00	2.94
Tridecane	**C13**	**Area %**	0.00	0.00
Tetradecane	**C14**	**Area %**	0.21	3.21
Pentadecane	**C15**	**Area %**	0.27	2.77
Hexadecane	**C16**	**Area %**	6.32	1.42
Heptadecane	**C17**	**Area %**	4.84	3.46
Octadecane	**C18**	**Area %**	0.00	4.01
Nonadecane	**C19**	**Area %**	0.22	0.77
Eicosane	**C20**	**Area %**	4.15	6.43
Heneicosane	**C21**	**Area %**	4.64	6.37
Docosane	**C22**	**Area %**	5.26	3.36
Tricosane	**C23**	**Area %**	0.00	0.13
Tetracosane	**C24**	**Area %**	0.00	0.30
Pentacosane	**C25**	**Area %**	0.00	1.86
Hexacosane	**C26**	**Area %**	0.00	0.51
Heptacosane	**C27**	**Area %**	4.21	2.93
Octacosane	**C28**	**Area %**	0.00	3.93
Nonacosane	**C29**	**Area %**	0.00	0.00
Contane	**C30**	**Area %**	0.00	0.26
TOTAL		**Area %**	**30.12**	**46.39**

Apart from the obvious increase in the area percentage of normal alkanes in Sample C1 compared with Sample C2, for reasons discussed earlier (with the exception of heptacosane), the bulk of Sample C2 normal alkanes appear to be concentrated in the C_{16} to C_{22} range. In contrast, Sample C1 normal alkanes appear over a greater carbon number distribution, if not slightly higher as well.

7.2.4 Waxy Oil filtration and thermal treatment

Filtered Waxy Oil was thermally treated in a Pyrex glass test tube inside a reactor connected to a smaller vessel to collect distillates. A complete description of the experimental procedure is given in Chapter 5, Section 5.2.3. The aim of thermally treating Waxy Oil is:

- Cracking Waxy Oil to produce both stable heavier alkanes and lighter hydrocarbon distillates
- Destruction of reactive hydrocarbons, especially iso-alkanes organics and oxygenates at pre-carbonisation temperatures (400–430 °C), thus reducing the propensity of the residue to produce mosaic microstructural domains during the onset of carbonisation
- Increasing the green coke yield
- Decreasing the temperature range over which carbonisation occurs, which means increasing the temperature of initial poly-condensation reactions

7.2.4.1 Waxy Oil thermal treatment at 5 bar pressure

Waxy Oil (approximately 50 g) was thermally treated for 2 h in a Pyrex glass test tube at temperatures of 400, 410, 420 and 430 °C.

The yields of the thermal treatment experiments at 5 bar pressure are shown in Table 7-9.

Table 7-9 Waxy Oil residue and distillate yields from thermal treatment reactions at 5 bar pressure

Experiment number	Temperature (°C)	Time [1] (h)	Pressure (bar)	Residue (%)	Distillate (%)	Distillation coefficient (%)
D1	**400**	**2**	**5**	73.1	26.9	87.0
D3	**410**	**2**	**5**	58.7	41.3	62.2
D4	**420**	**2**	**5**	45.2	54.8	57.1

[1] Duration of thermal treatment at maximum heat treatment temperature

A notable exclusion from the experimental data in Table 7-9 is the reaction conducted at 430 °C (Sample D2). At this temperature small amounts of mosaic semi-coke (secondary QI) were observed in the modified Waxy Oil residue. The sample was discarded and no analyses were conducted. The philosophy of this chapter is the production of modified residues with no QI. From an experimental viewpoint the production of mosaic QI from highly reactive species followed by filtration is possible, as described by Calemma and Rausa (1997) who studied residues with high concentrations of asphaltenes. However, it is the author’s opinion that such a process would have very limited potential for commercial application.

A temperature increase from 400 to 420 °C during thermal treatment serves to decrease the residue yield. Due to the production of a greater concentration of lighter hydrocarbons, the distillate yield is similarly increased. The “distillation coefficient” (referred to in Table 7-9) is defined as the percentage of lighter hydrocarbons produced by cracking reactions yet remaining in the residue below a temperature of 320 °C and corresponding to the maximum mass loss rate in Sample D4 (prepared under the most severe thermal conditions). The efficiency with which lighter cracked hydrocarbons are removed from the residue is reduced as the soaking temperature increases from 400 °C (87%) in Sample D1 to 420 °C (57.1%) in Sample D4.

With regard to the thermal treatment experiments at 5 bar pressure, two variables need to be discussed. The first variable is the residue yield and the second variable is the concentration of lighter hydrocarbons that remain in the residue. To demonstrate this, the TGA and DTG of Samples D1, D3 and D4 are shown in Figures 7-11 and 7-12 respectively. Sample B is included as a comparison.

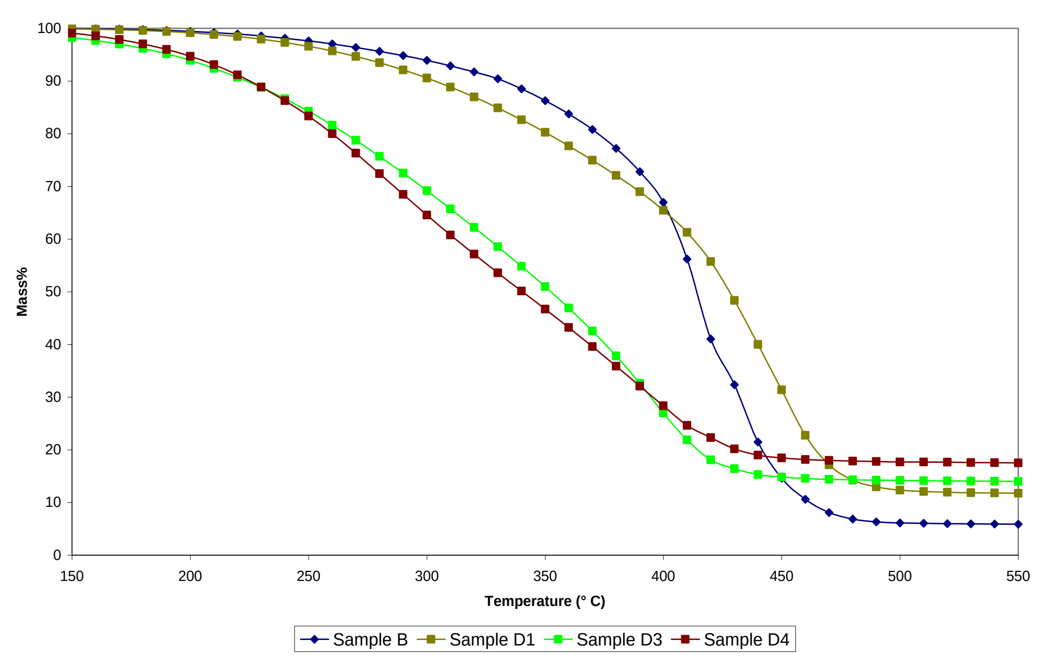

Figure 7-11 Thermogravimetric Analysis (TGA) of Samples B, D1, D3 and D4 residues

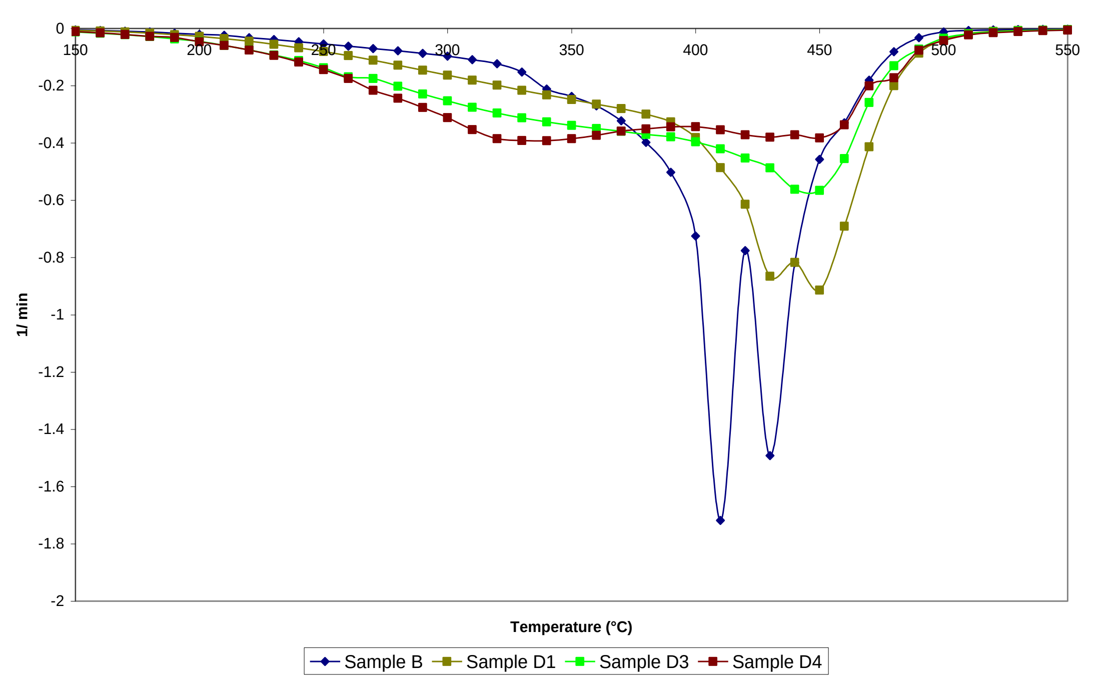

Figure 7-12 Differential Thermogravimetry (DTG) of Samples B, D1, D3 and D4 residues

Increasing the thermal severity of cracking reactions increases the percentage of lighter hydrocarbons produced, thus indicating a steeper distillation gradient of the traces in the lower temperature range of the TGA (Figure 7-11) from Samples D1 to D4. Samples D4 and D3 exhibit initial mass loss at 110 and 130 °C respectively, while Sample D1 exhibits initial mass loss at approximately 200 °C. The increase in mass loss between 200 and 400 °C with thermal severity has quite the opposite effect on the residuum percentages of Sample D1 (12.35%), Sample D3 (14.18%) and Sample D4 (17.70%).

Thermal treatment under pressure increases the percentage of both the lighter hydrocarbons, which cannot escape, and the heavier thermally stable hydrocarbons. The DTG (Figure 7-12) of the three samples is therefore characterised by increased rates of mass loss below 320 °C and two more intense peaks, corresponding to carbonisation reactions, between 440 and 450 °C. As the thermal severity of cracking increases, so the intensity of the first peak increases and that of the second peak diminishes. This is in general agreement with the findings of Perez *et al.* (2002) who observed a similar relationship between the first and second reaction peaks when studying thermal cracking of petroleum pitches. As the mass of lighter hydrocarbons increases (from Samples D1 to D4), Sample D4 produces a shallow broad peak at 320 °C. Given the increased thermal stability of the heavier molecules, it is not surprising that the second peaks are at a higher temperature corresponding to greater thermal severity (Sample B – 420 °C; Sample D1 – 430 °C; Sample D3 – 440 °C; Sample D4 – 450 °C). An increase in thermal treatment severity (Samples D1 to D4) also decreases the intensity of the second series of peaks. This loss of intensity of the second peak is due to higher dilution effects caused by the first peak, especially in Sample D4 in which the intensity of the first and second peaks is similar.

The GCMS of Sample D1 residue is initially compared with Sample B residue in Figure 7-13 and Sample D3 residue with that of Sample D4 in Figure 7-14.

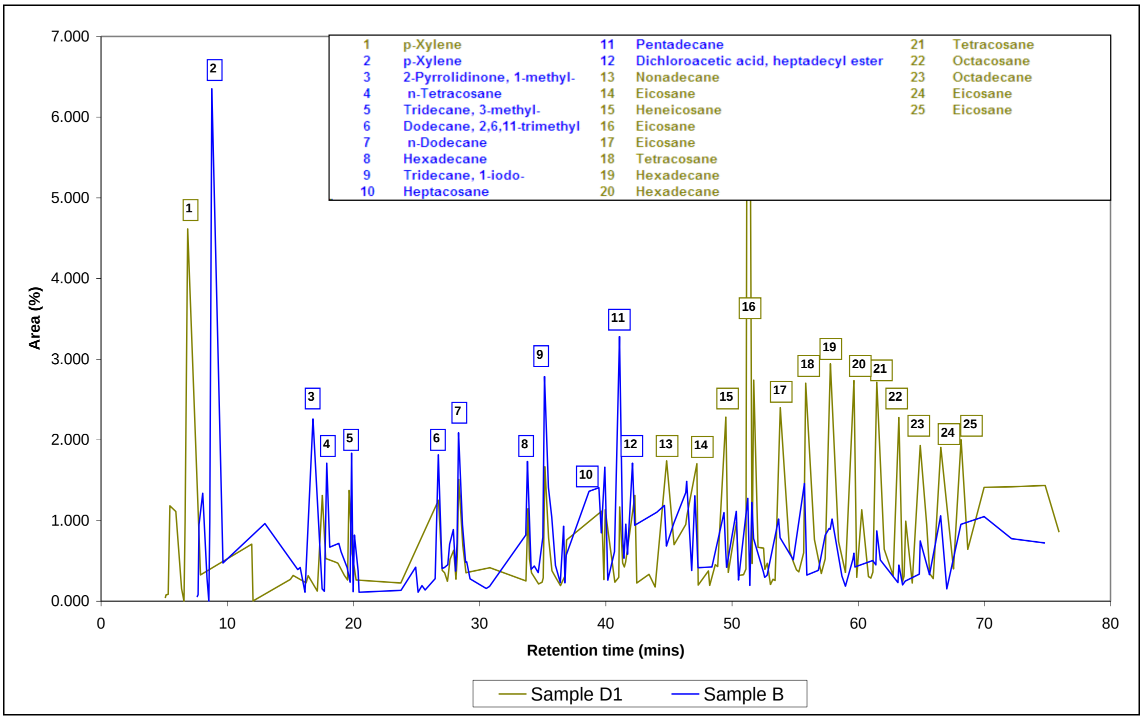

Figure 7-13 Gas Chromatography–Mass Spectroscopy (GCMS) of Samples D1and B residues

The major distinction of Sample D1 (compared with Sample B) is the emergence of a dominant "crest" pattern of stable normal alkanes, ranging from nonadecane (C_{19}) to octacosane (C_{28}) between peaks 13–25. As previously mentioned, these normal alkanes do not necessarily elute at exactly the same retention time, so it is not unexpected to see two peaks of the same normal alkane (e.g. eicosane, hexadecane and octacosane) at different retention times. This is the reason that the comparison of the GCMS traces is merely qualitative and does not have an exact quantitative value. Although in the first 40 min Sample B shows peaks with a comparatively higher area percentage, there is evidence of the lighter molecules in Sample D1; these are present due to the lower distillation coefficient.

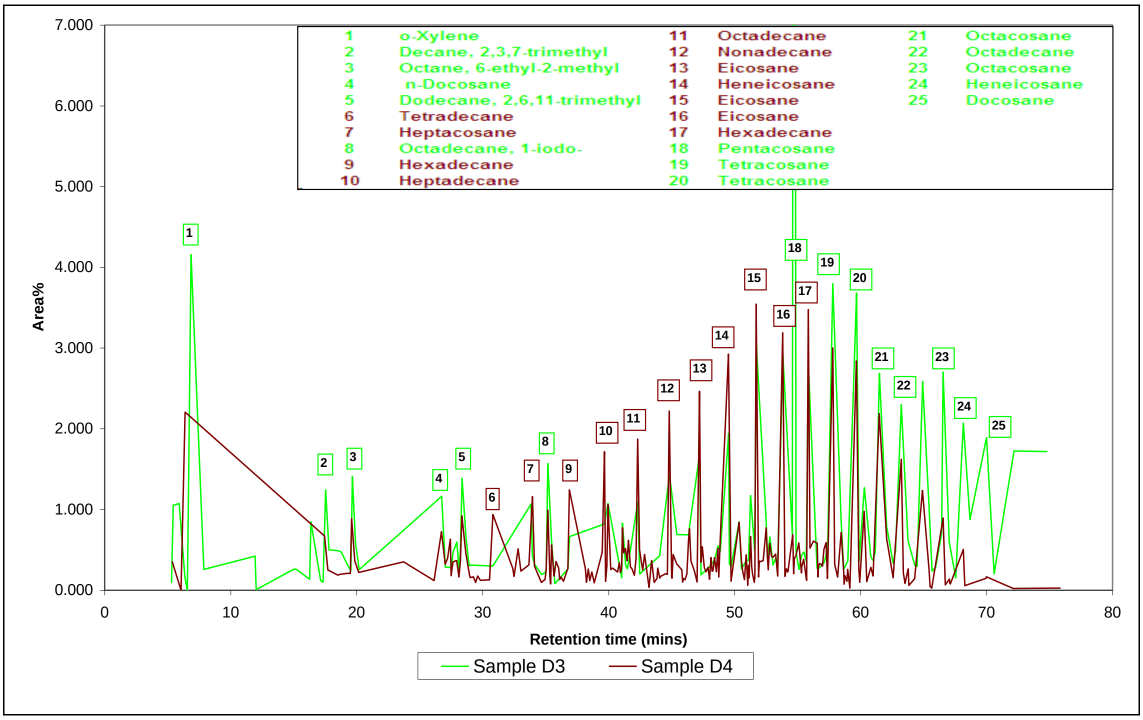

Figure 7-14 Gas Chromatography–Mass Spectroscopy (GCMS) of Samples D3 and D4 residues

When the GCMS traces of Samples D3 and D4 are compared, once again a dominant "crest" of normal alkanes is evident between 40 and 70 min (peaks 10–25). Surprisingly, Sample D3 indicates a higher area percentage of normal alkanes between 60 and 70 min, which is not consistent with an increase in thermal severity under ideal distillation conditions. The reason for this is the higher area percentage of lighter molecules within the initial retention time range (Sample D4), indicating a higher dilution factor in the lower temperature range.

In order to compare the GCMS traces of the distillates from Samples D1 and D3, they are plotted against one another in Figure 7-15. Similarly, the distillates from Samples D3 and D4 are compared in Figure 7-16.

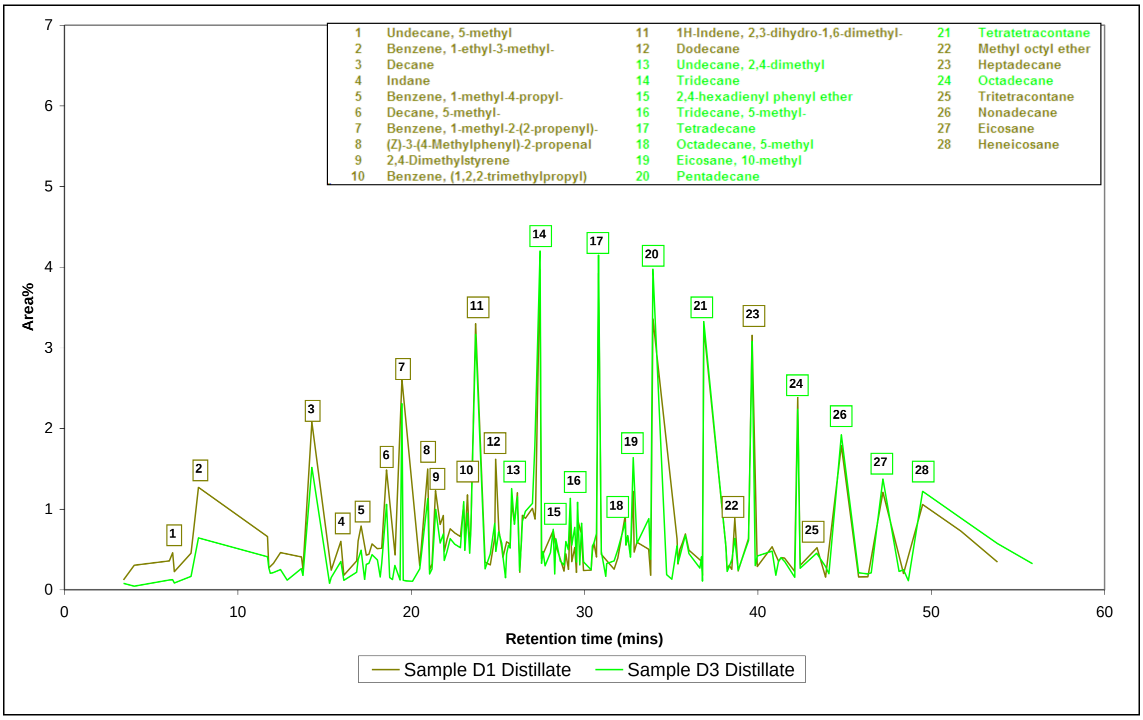

Figure 7-15 Gas Chromatography–Mass Spectroscopy (GCMS) of Samples D1 and D3 distillates

The GCMS traces of Sample D1 and D3 distillates appear similar. However, the elution of lighter molecules from Sample D1 appears to be more prominent in the first 20 min (peaks 1–7). Between 25 to 40 min, heavier molecules within Sample D3 distillate appear to have the greater area percentage, which is not unexpected given the higher reaction temperature.

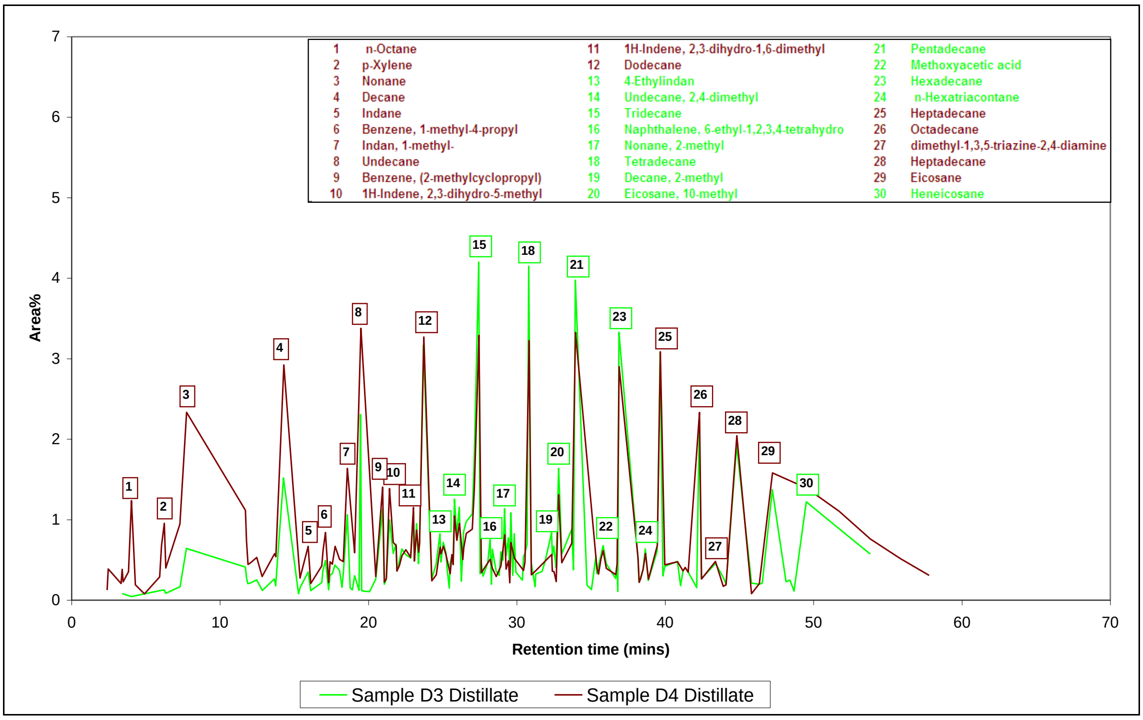

Figure 7-16 Gas Chromatography–Mass Spectroscopy (GCMS) of Samples D3 and D4 distillates

A comparison of the distillates of Samples D3 and D4 shows that Sample D4 distillate is composed of a greater percentage of lighter molecules which elute in the first 20 min (peaks 1–8). The distillate of Sample D4 (within the first 20 min) also shows the presence of pure lower normal alkanes (e.g. octane, nonane and decane) and alkylated homologues of benzene which are more than likely the stabilised products of the cracking reaction. The TGA (Figure 7–12) is proof of the lower distillation coefficient of lighter hydrocarbons, especially from Sample D4 residue. Under ideal distillation conditions the area percentage of molecules eluting in the initial retention time of 20 min would be higher than shown above.

As previously indicated, it is easier to determine the variation in the molecular composition of the thermal treatment residues when similar compounds are grouped, as shown in Table 7-10.

Table 7-10 Molecular compound groups in Sample D1, D3 and D4 residues

Molecules	Unit	Sample D1	Sample D3	Sample D4
Alkylated aromatics	**Area %**	5.37	5.42	6.18
Pure aromatics	**Area %**	0.00	0.71	0.57
Iso-alkanes	**Area %**	13.54	15.14	11.16
Normal alkanes	**Area %**	66.85	63.27	58.68
Oxygenates	**Area %**	1.71	1.57	2.85
Cyclo-alkanes	**Area %**	2.54	0.46	1.52

The percentage of normal alkanes produced decreases from Sample D1 to D4. Although this trend may initially appear to contradict the effect of thermal severity on the area percentage of higher molecular weight normal alkanes, this is not correct. The trend indicated is due to an increased percentage of lighter cracked hydrocarbons which form as the temperature increases. However, at 5 bar pressure the lighter hydrocarbons do not escape the residue, which in turn serves to dilute the area percentage of heavier normal alkanes.

Apart from the somewhat unexpected trend described above, one of the most important results is the reduction of the oxygenate concentration (1.71–2.85%) in the three thermally treatment residues (compared with Samples B: 13.12%; C1: 10.34%; and C2: 11.05%).

The concentrations of normal alkanes (C_{10}–C_{30}) in Sample D1, D3 and D4 residues are shown in Table 7-11.

Table 7-11 Normal alkanes (C_{10}–C_{30}) in Samples D1, D3 and D4 residue

Molecule description	Carbon number	Unit	Sample D1	Sample D3	Sample D4
Decane	**C10**	**Area %**	0.00	0.00	0.00
Undecane	**C11**	**Area %**	0.00	0.10	0.21
Dodecane	**C12**	**Area %**	4.32	1.96	1.94
Tridecane	**C13**	**Area %**	0.25	0.00	0.63
Tetradecane	**C14**	**Area %**	0.79	1.46	1.32
Pentadecane	**C15**	**Area %**	2.16	0.42	1.57
Hexadecane	**C16**	**Area %**	9.00	5.16	8.42
Heptadecane	**C17**	**Area %**	4.84	2.17	5.99
Octadecane	**C18**	**Area %**	4.27	7.09	5.18
Nonadecane	**C19**	**Area %**	3.61	3.78	6.92
Eicosane	**C20**	**Area %**	12.76	4.93	14.51
Heneicosane	**C21**	**Area %**	8.26	7.41	6.49
Docosane	**C22**	**Area %**	1.91	3.30	0.53
Tricosane	**C23**	**Area %**	0.00	0.42	0.00
Tetracosane	**C24**	**Area %**	5.42	9.67	0.00
Pentacosane	**C25**	**Area %**	3.32	3.95	1.02
Hexacosane	**C26**	**Area %**	0.88	2.04	0.26
Heptacosane	**C27**	**Area %**	1.12	3.78	2.42
Octacosane	**C28**	**Area %**	3.94	5.62	1.28
Nonacosane	**C29**	**Area %**	0.00	0.00	0.00
Contane	**C30**	**Area %**	0.00	0.00	0.00
TOTAL		**Area %**	**66.85**	**63.27**	**58.68**

The data presented in Table 7-11 are important in that they demonstrate the effect of the dilution factors on the area percentage of higher molecular weight normal alkanes. For comparing the results of normal alkanes within the residues of Sample D1 to D4, the data are of little value given the dilution factor involved. However, all three thermal treatment residues indicate an increase in the concentration of normal alkanes (C_{10}–C_{30}) compared with distillation (Sample C2) and mild thermal treatment (Sample C1).

The aromatics in Sample D1 are largely alkylated or oxygenated homologues of benzene (e.g. ortho- and para-xylene and benzaldehyde). At the maximum thermal treatment temperature, Sample D4 shows that the aromatic molecules are largely based on two to four benzyl ring structures (e.g. 1-(propenyl) naphthalene, 9-H fluorene, 1-methyl 9-H fluorene, 4-methyl phenanthrene and 1-methyl pyrene). This increases the probability that a certain amount of cyclisation of aliphatics, coupled with dehydrogenation, may have occurred. To some degree the increase in the size of the aromatic rings between Sample D1 and D4 decreases the problematic nature of accounting for alkylated aromatics previously mentioned. Furthermore, the ratio of alkylated aromatics to non-alkylated aromatics decreases from Sample D1 (3.2) to D3 (1.7) and finally D4 (1.5).

It could very well be argued that the presence of lighter molecular weight components within the thermal treatment residues would be of little consequence as they would be expected to distil off during carbonisation. However, as discussed in Chapter 8, they prove to have a substantial effect on the microstructure of the coke. In Chapter 7 the *actual reactivity* of the residue is of less importance than the *potential for reactivity* of the residue at carbonisation temperatures. The “potential for reactivity” is defined (in this study) as the quantitative identification of molecules (or families of molecules) with a known propensity to decrease the temperature of the onset of poly-condensation, producing semi-carbons which gravitate towards the bottom of the test tube and form mosaic microstructures.

Thermal treatment of filtered Waxy Oil (under pressure) very broadly produces two types of organic molecules in the residue: firstly, the lighter hydrocarbons (which did not escape) and secondly, the stabilised long-chain normal alkanes. To demonstrate the effect of lighter hydrocarbons as potential reactivity promoters, the residue of Sample D3 is analysed in greater detail.

It was noted in Figure 7-14 that the second peak of maximum mass loss rate of the DTG was at approximately 420 °C for Sample B and at 440 °C for Sample D3, thus implying that as the area percentage of heavier long-chain alkanes increases, the thermal stability also increases. However, it is important to note that this does not refer to the thermal stability of Sample D3 residue in its entirety, but only to the stabilised heavier normal alkanes, as the lighter molecules had already been distilled.

Thus in order to examine potential reactivity promoters, the GCMS for Sample D3 (Figure 7-16) can be split into two approximate regions. The first region (below 30 min retention time) is ascribed to lighter hydrocarbons and the second region (after 30 min retention time) to heavier normal alkanes as this is where the "crest" begins to show.

To identify potential reactivity promoters, the first region of lighter hydrocarbons is therefore examined. A breakdown of potential reactivity promoters in this region has been manually calculated from the GCMS data for Sample D3 and divided into groups of molecules as shown in Figure 7-17.

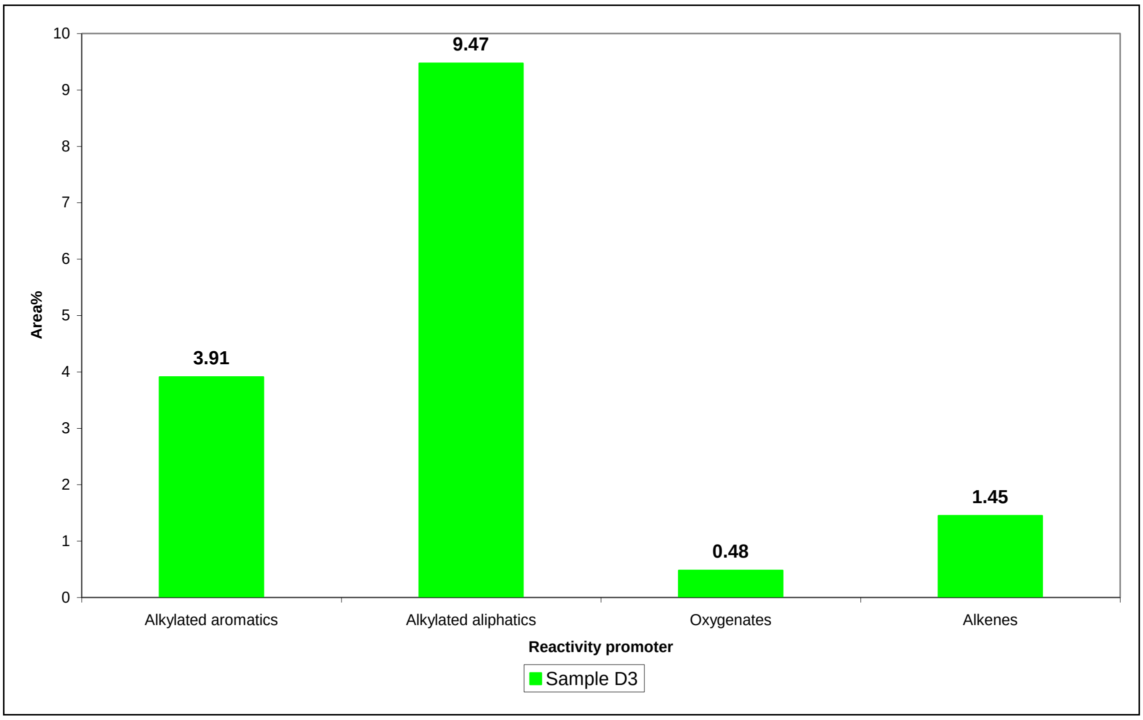

Figure 7-17 Histogram of potential reactivity promoters subdivided into groups of Sample D3 residue (eluting before 30 min according to Figure 7-16)

The dominant group of potential reactivity promoters is iso-alkanes (9.47%), which include methyl to tetra-methyl side chains on parent aliphatics from heptane to decane. Other substituents include a small amount of ethyl and propyl substituents on heptane. In order to substantiate the potential reactivity of hydrocarbons in this region, a comparison is made with the findings of Obara *et al.* (1981) who, while studying the reactivity of Ethylene Tar Pitch (ETP), noted the scission of aliphatic side chains at 400 °C and the formation of reactive radicals to lower the temperature of poly-condensation, thus promoting the formation of mosaic microstructures. This is further substantiated by Mochida *et al.* (1990), also investigating the thermal stability of ETP, who ascribed the higher reactivity to 1-methyl or ethyl substitutions to the aromatic ring.

In Sample D3 the area percentage of alkylated aromatics (3.91%) is lower than that of alkylated aliphatics. In order to differentiate between the thermal stability of pure and alkylated aromatics the results of Perez *et al.* (2002) may be studied. This research compared the variance of composition and reactivity of thermally treated petroleum residues with those of distilled petroleum residues. In this research physical distillation did not dealkylate the aromatics (due to resonance stabilised benzyl radicals), leading to a higher reactivity, compared with thermal treatment which did dealkylate the aromatics. Similarly, during a study of model compounds, Lewis *et al.* (1987) further argued for the activating effect of methyl substituents causing dimethyl naphthalene to carbonise at a faster rate than naphthalene. While the concentration of alkylated aromatics (3.91%) is certainly lower than that of the alkylated aliphatics, the same dealkylation mechanisms should apply to both, which makes Sample D3 relatively thermally unstable. Although the small percentage of alkenes (1.45%) is of comparatively less concern, Mochida *et al.* (1990) previously argued for the effect of olefins in increasing the reaction rate during carbonisation and inhibiting the formation of anisotropic microstructures.

As with the thermal treatment at 5 bar, there is no reason to believe that these lighter compounds would not be present in residue during “static” coking (also conducted at 5 bar). The time differential between the increase in typical thermal treatment temperatures (in this case 410 °C) and the onset of carbonisation (approximately 460 °C) is small. It is therefore concluded that the groups of compounds discussed above possess substantial potential to increase the reactivity of the residue during carbonisation and thus the formation of mosaic microstructures. The effect on the microstructure is further discussed in Chapter 8.

A similar exercise has been conducted with Sample E1b, from whose residue the lighter hydrocarbons were removed after thermal treatment by distillation. This is further discussed below in Section 7.4.2.3.

7.2.4.2 Waxy Oil thermal treatment at lower pressure

Given the challenges presented by the distillation coefficient of the initial thermal treatment experiments at 5 bar, it was decided to repeat the experiments at one of the temperatures (namely 410 °C, Sample D3), but to reduce the pressure of thermal treatment after 1 h from 5 bar to 1 bar (Sample E1a) and 0 bar (Sample E2) to determine the efficacy of removing distillate from the residue. The yields of the isothermal thermal treatment reactions are shown in Table 7-12 and compared with Sample D3 as a reference.

Table 7-12 Waxy Oil yields from thermal treatment reactions at lower system pressure

Experiment number	Temperature (°C)	Time [1] (h)	Pressure (bar)	Residue (%)	Distillate (%)	Distillation coefficient (%)
D3	**410**	**2**	**5**	58.7	41.3	62.2
E1a	**410**	**2**	**1 h at 5 bar; 1 h at 1 bar**	54.4	45.7	68.3
E2	**410**	**2**	**1 h at 5 bar; 1 h at 0 bar**	49.6	50.4	84.6

As expected, the yield of the thermally treated residues is reduced as the reaction pressure (after 1 h) is reduced. Similarly, because the reaction was conducted under isothermal conditions, the reduction in the residue yield is accompanied by an increase in the distillation coefficient.

In order to study the effect on the concentration of lighter hydrocarbons in the residues produced, the TGA and DTG for Samples E1a and E2 are shown in Figures 7-18 and 7-19 respectively. Samples B and D3 are included as references.

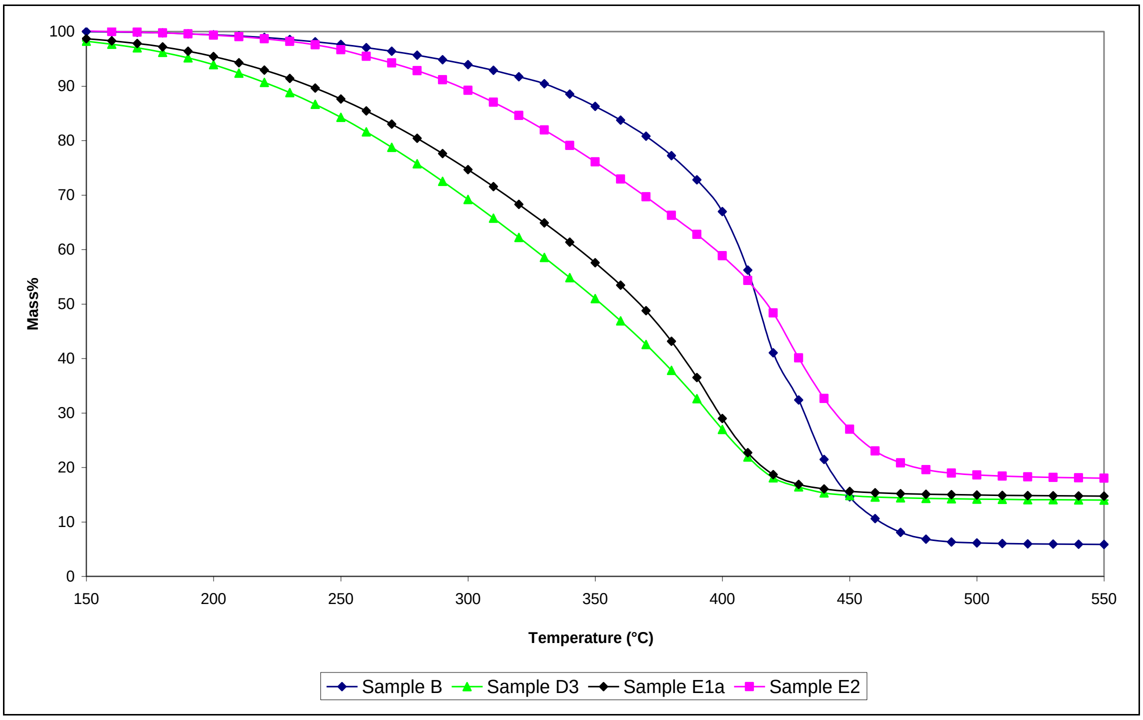

Figure 7-18 Thermogravimetric Analysis (TGA) of Samples B, D3, E1a and E2 residues

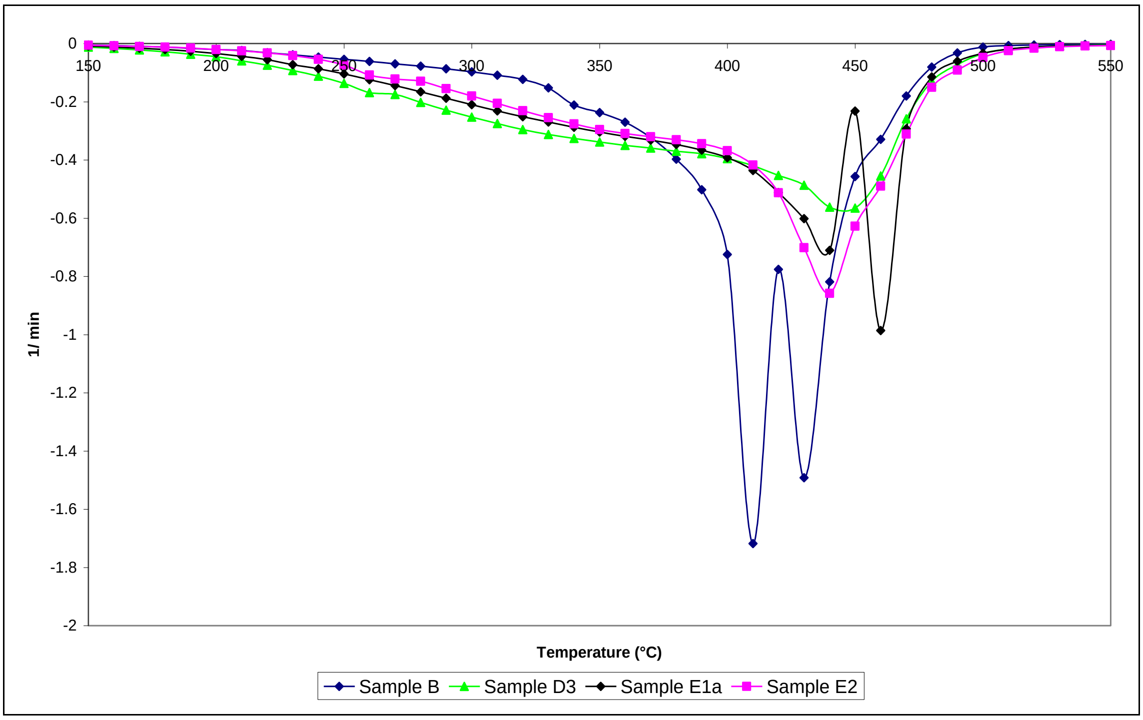

Figure 7-19 Differential Thermogravimetry (DTG) of Samples B, D3, E1a and E2 residues

As shown in Figure 7-18, reducing the pressure (after 1 h to 1 bar; Sample E1a) does not substantially reduce the amount of lighter cracked hydrocarbons in the residue, as indicated by the mass loss between 200 and 370 °C and compared with Sample D3. The efficiency with which lighter hydrocarbons are removed from the residue also serves to increase the residuum yield at 500 °C. However, a further pressure drop (to 0 bar for 1 h; Sample E2) does further reduce the amount of lighter hydrocarbons but retains almost 50% thereof.

The increased efficiency of lighter hydrocarbon removal in the 200–370 °C range promotes the shift of the second peak of maximum rate of mass loss to a higher temperature for Sample E2 (470 °C) compared with Sample D3 (440°C) as shown in Figure 7-21.

The GCMS trace of Sample D3 residue is compared with that of Sample E1a residue in Figure 7-20 and their distillates are compared in Figure 7-21.

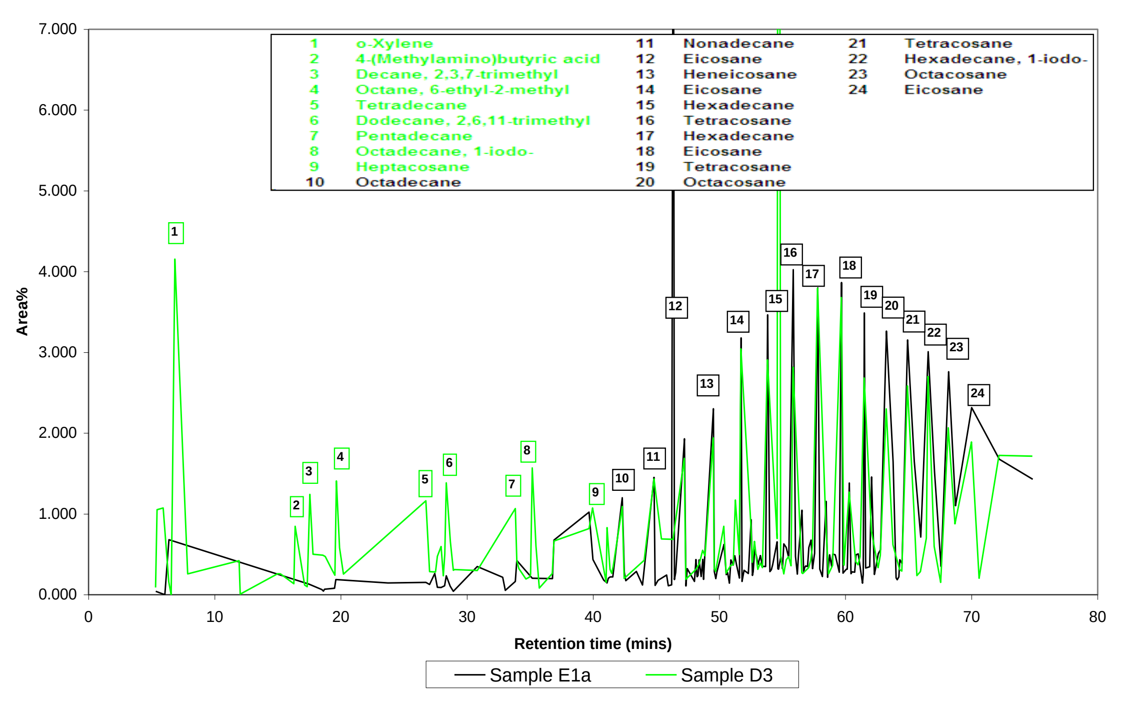

Figure 7-20 Gas Chromatography–Mass Spectroscopy (GCMS) of Samples D3 and E1a residues

As shown in Figure 7-20, there is a substantial reduction in lighter hydrocarbons eluted below a retention time of 35 min for Sample E1a residue compared with Sample D3 residue. The increase in the distillation efficiency involves the removal of ortho-xylene, alkylated and normal alkanes below C_{18} (peaks 1–8). There is a reciprocal increase in the area percentage of the stable normal alkanes after a retention time of 40 min (peaks 10–24).

The removal of lighter hydrocarbons from Sample E1a compared with Sample D3 is perhaps better described by comparing the GCMS traces of their respective distillates, shown in Figure 7-21.

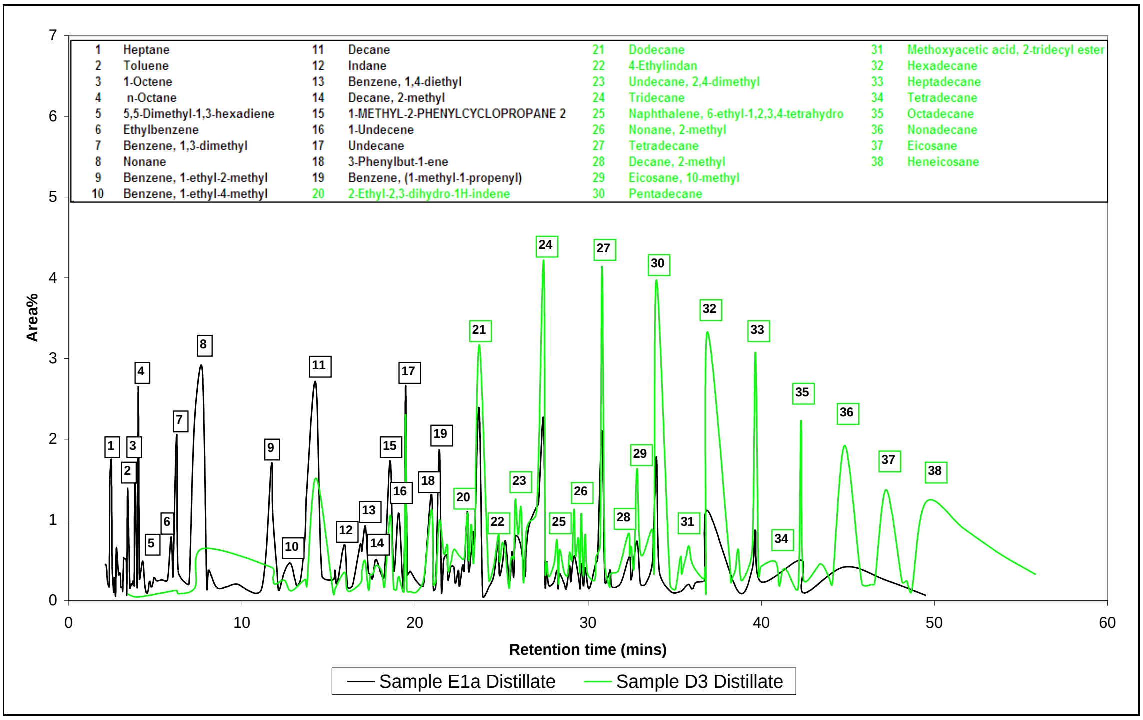

Figure 7-21 Gas Chromatography–Mass Spectroscopy (GCMS) of Samples D3 and E1a distillates

The distillate fraction of Sample E1a shows a higher area percentage of lighter hydrocarbons eluted in the first 20 min (peaks 1–17) compared with Sample D3. The lighter molecules in Sample E1a distillate include both alkylated homologues of benzene, lower molecular weight pure alkanes (e.g. octane, nonane, decane and undecane) and alkenes (e.g. 1-octene and 1-undecene) as the major peaks. Sample D3 distillate, in turn, shows a higher area percentage of higher molecular weight pure and alkylated aliphatics after an elution time of 25 min. This is merely a function of the greater concentration of lighter hydrocarbons reporting to the residue and not the distillate of Sample D3.

The effect on the comparative GCMS traces of Samples E1a and E2 residues of further reducing the system pressure (to 0 bar) is shown in Figure 7-22 and the effect on their respective distillates in Figure 7-23.

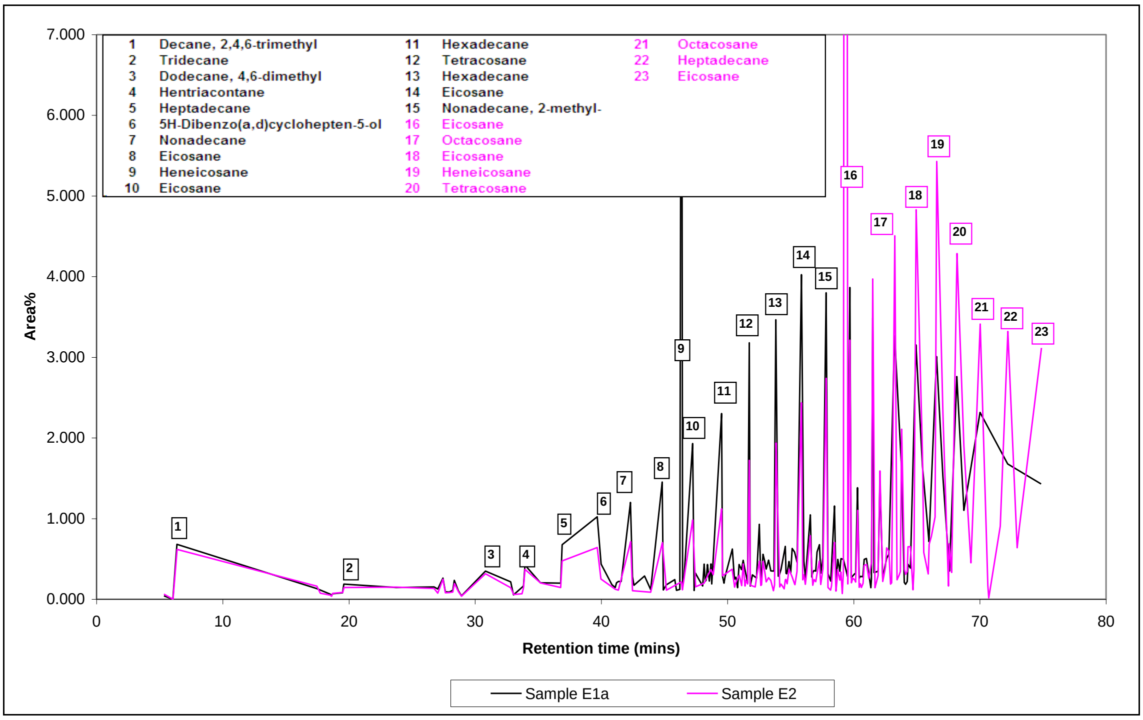

Figure 7-22 Gas Chromatography–Mass Spectroscopy (GCMS) of Samples E1a and E2 residues

Both Samples E1a and E2 residues show a similar elution trend for the first 35 min of retention time. However, between 35 and 55 min Sample E1a shows individual component peaks with a higher area percentage when compared with Sample E2 (peaks 7–14; C_{16}–C_{21}), with the exception of peak 12. The reciprocal effect is evident between an elution time of 60 and 70 min when Sample E2 yields peaks with a higher area percentage (peaks 16–23; C_{20}-C_{28} normal alkanes).

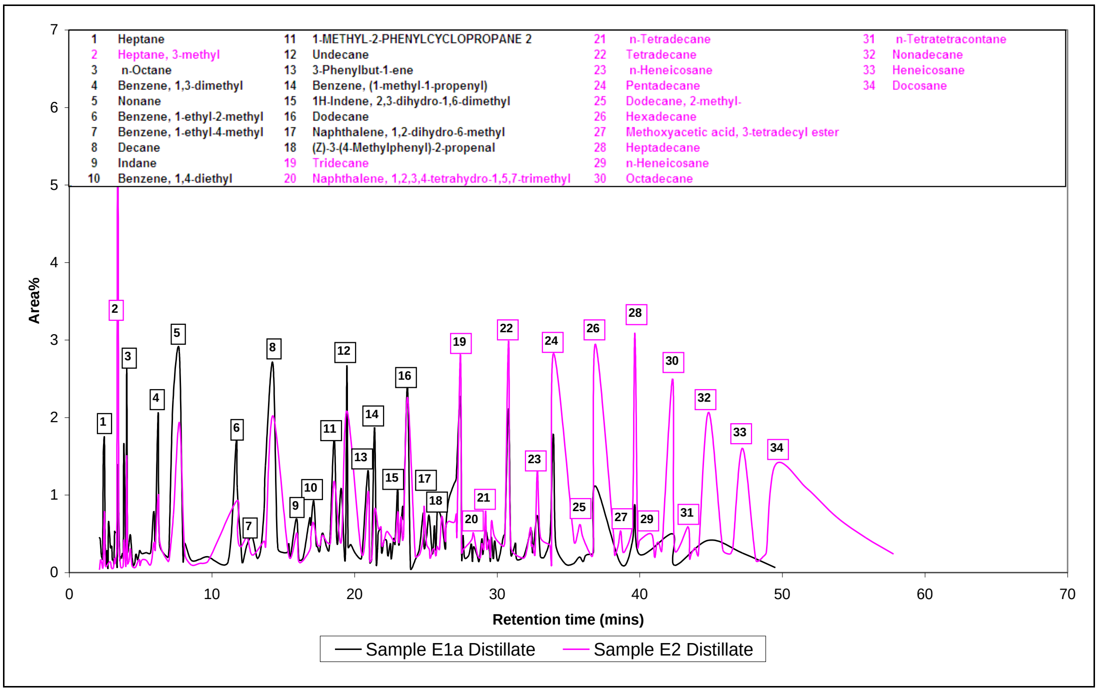

Figure 7-23 Gas Chromatography–Mass Spectroscopy (GCMS) of Samples E1a and E2 distillates

Sample E2 distillate is a heavier fraction than Sample E1a distillate, especially with regard to the “crest” of heavy normal alkanes shown in peaks 19–34 (C_{13}–C_{22}) which emerge within a retention time of 25–50 min. The reverse is true for the first 25 min when peaks 1–15 show a higher retention time for Sample E1a (with the exception of peak 2).

In terms of the groups or families of products for the three thermal treatments, a comparison is shown in Table 7-13.

Table 7-13 Molecular compound groups in Samples D3, E1a and E2 residues

Molecules	Unit	Sample D3	Sample E1a	Sample E2
Alkylated aromatics	**Area %**	5.42	2.71	3.60
Pure aromatics	**Area %**	0.71	0.29	1.19
Iso-alkanes	**Area %**	15.14	1.77	3.03
Normal alkanes	**Area %**	63.27	74.61	74.93
Oxygenates	**Area %**	1.57	1.38	2.28
Cyclo-alkanes	**Area %**	0.46	0.55	0.19

The removal of lighter cracked material is evident in the percentage increase of normal alkanes when Sample D3 residue is compared with Samples E1a/E2 residue. Both Samples E1a and E2 show a considerable decrease in the component percentage of iso-alkanes, with minimal difference in the oxygenate concentration. It is surprising that the component percentages of pure alkanes in Samples E1a and E2 are so similar. To evaluate this further it is necessary to consider the spread of normal alkanes (C_{10}–C_{30}) in the two samples, which is shown in Table 7-14.

Table 7-14 Normal alkanes (C_{10}–C_{30}) in Samples D3, E1a and E2 residues

Molecule description	Carbon number	Unit	Sample D3	Sample E1a	Sample E2
Decane	**C10**	**Area %**	0.00	0.00	0.00
Undecane	**C11**	**Area %**	0.10	0.08	0.08
Dodecane	**C12**	**Area %**	1.96	0.32	0.51
Tridecane	**C13**	**Area %**	0.00	0.26	0.25
Tetradecane	**C14**	**Area %**	1.46	0.35	0.57
Pentadecane	**C15**	**Area %**	0.42	0.29	0.45
Hexadecane	**C16**	**Area %**	5.16	12.11	5.39
Heptadecane	**C17**	**Area %**	2.17	1.42	6.53
Octadecane	**C18**	**Area %**	7.09	2.37	4.95
Nonadecane	**C19**	**Area %**	3.78	3.91	1.16
Eicosane	**C20**	**Area %**	4.93	21.20	29.28
Heneicosane	**C21**	**Area %**	7.41	6.04	8.26
Docosane	**C22**	**Area %**	3.30	3.34	1.04
Tricosane	**C23**	**Area %**	0.42	1.10	1.10
Tetracosane	**C24**	**Area %**	9.67	12.05	3.22
Pentacosane	**C25**	**Area %**	3.95	0.84	0.54
Hexacosane	**C26**	**Area %**	2.04	0.39	1.34
Heptacosane	**C27**	**Area %**	3.78	0.14	0.00
Octacosane	**C28**	**Area %**	5.62	8.39	10.26
Nonacosane	**C29**	**Area %**	0.00	0.00	0.00
Contane	**C30**	**Area %**	0.00	0.00	0.00
TOTAL		**Area %**	**63.27**	**74.61**	**74.93**

The probable reason for this similarity is the substantial influence of hexadecane in Sample E1a.

7.2.4.3 Waxy Oil filtration, thermal treatment and distillation.

As the sample quantities were limited, only Sample E1a could be distilled (by bubbling under nitrogen to 325 °C) to determine the effect of lighter hydrocarbon removal from the residue. The yields of residue and distillate are shown in Table 7-15. Sample E1a is shown for comparison purposes.

Table 7-15 Yields from the distillation of Sample E1a producing distillate and residue (named Sample E1b)

Experiment number	Temperature (°C)	Time [1] (h)	Pressure (bar)	Residue (%)	Distillate (%)	Distillation coefficient (%)
E1a	**410**	**2**	**1 h at 5 bar; 1 h at 1 bar**	54.4	45.7	68.3
E1b	**none**	**none**	**Sample E1a N_2 stripped to max. 325 °C**	43.0	57.0	93.2

The nitrogen-strip distillation of Sample E1a increased the distillate fraction, producing a heavier Waxy Oil residue (Sample E1b) accompanied by an increase in the distillation coefficient.

The TGA and DTG of these samples are shown in Figures 7-24 and 7-25 respectively.

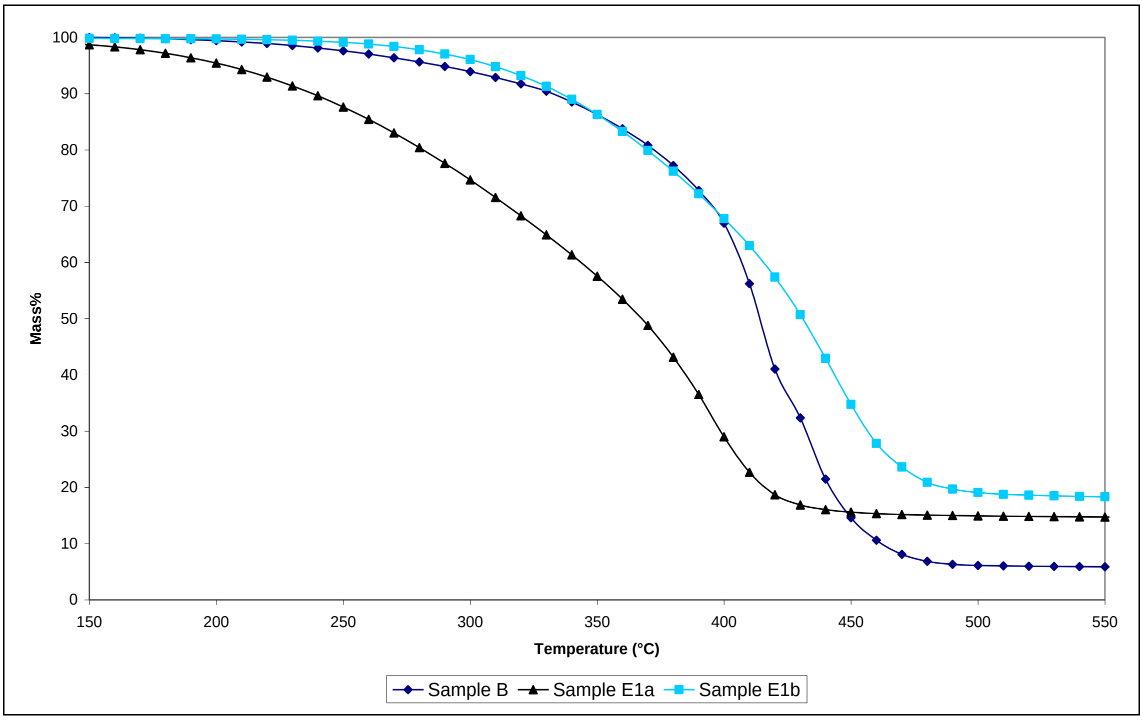

Figure 7-24 Thermogravimetric Analysis (TGA) of Samples B, E1a and E1b residues

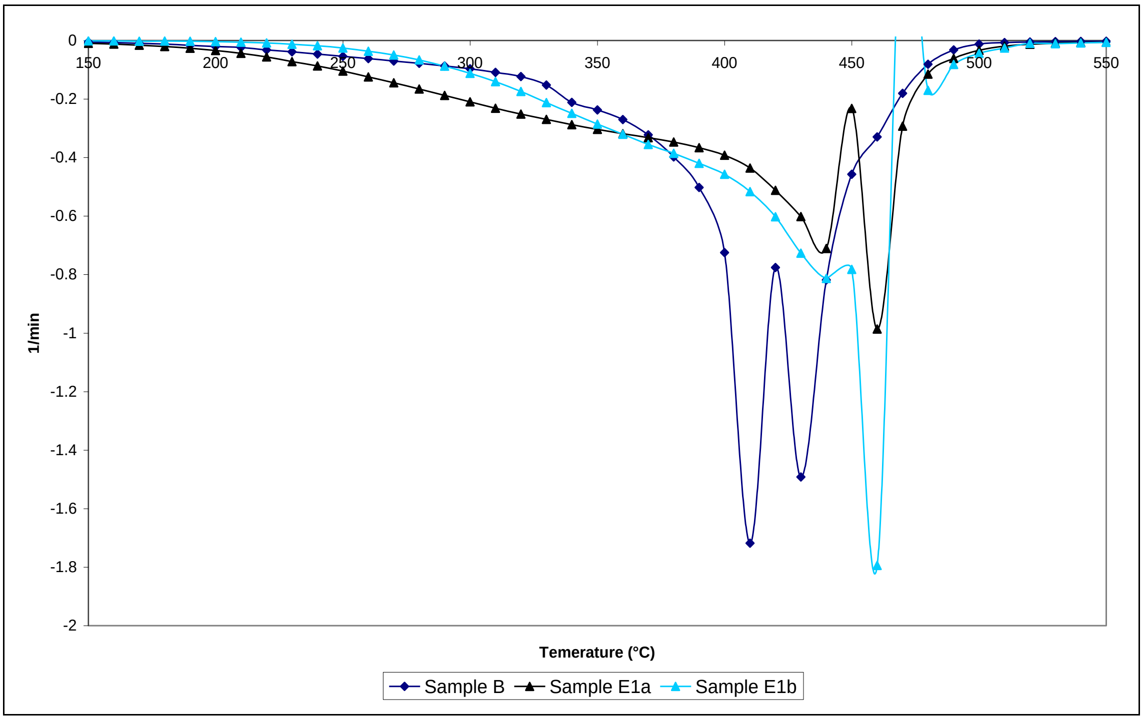

Figure 7-25 Differential Thermogravimetry (DTG) of Samples B, E1a and E1b residues

As shown in Figure 7-24, not only is the amount of lighter hydrocarbons in Sample E1b reduced (compared with Sample E1a), but there is a similar, if not lower, mass loss compared with Sample B within the 200–370 °C region of the TGA. The removal of lighter material from Sample E1a also serves to increase the residue of E1b (17%) compared with E1a (14%) and B (5%). The greater amount of carbon residue in Sample E1b is comparable to the reduction in mass loss in the initial region of the TGA. The distillation coefficient is also increased from 84.6% (Sample E1a) to 93.2% (Sample E1b) as shown in Table 8-17.

With regard to the DTG (Figure 7-25), Sample E1b shows a more intense (second) peak at a higher carbonisation temperature than either Samples B or E1a. The rate of mass loss between Samples E1b and B is similar between 200 and 370 °C. The higher temperature at which the second peak occurs (Sample E1b) again indicates an increase in the concentration of thermally stable heavier normal alkanes. However, what is very apparent is the substantial increase in the intensity of the second peak, indicating that a greater percentage of the residue is reacting at this temperature. This is not unexpected given the lower dilution factor. The effect of the distillation on the molecular composition of Sample E1b residue (compared with Sample E1a residue) is shown in Figure 7-26 and the effect on their respective distillates in Figure 7-27.

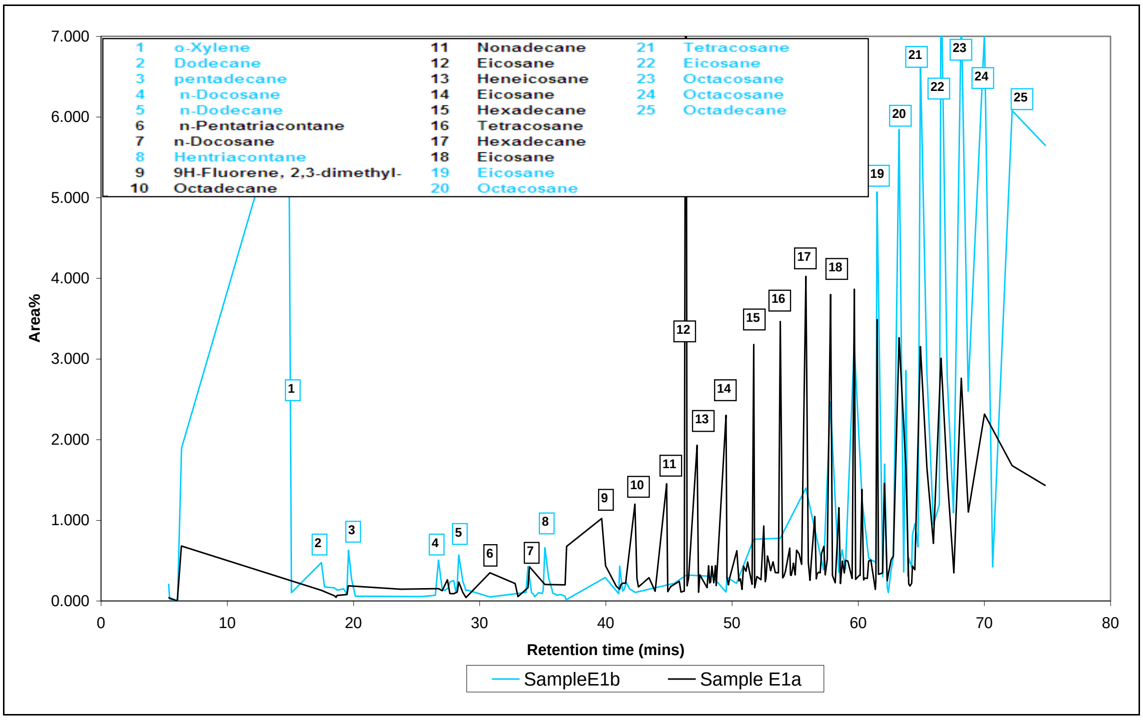

Figure 7-26 Gas Chromatography–Mass Spectroscopy (GCMS) of Samples E1a and E1b residues

While Sample E1b residue does show a slight increase of peaks 1–5, the greatest effect of distillation is to remove components with a retention time between 40 and 60 min, specifically molecules below C_{21} (peaks 10–18), and there is a reciprocal increase in the area percentage of higher molecular weight pure aliphatics (C_{20}–C_{28}; peaks 19–25).

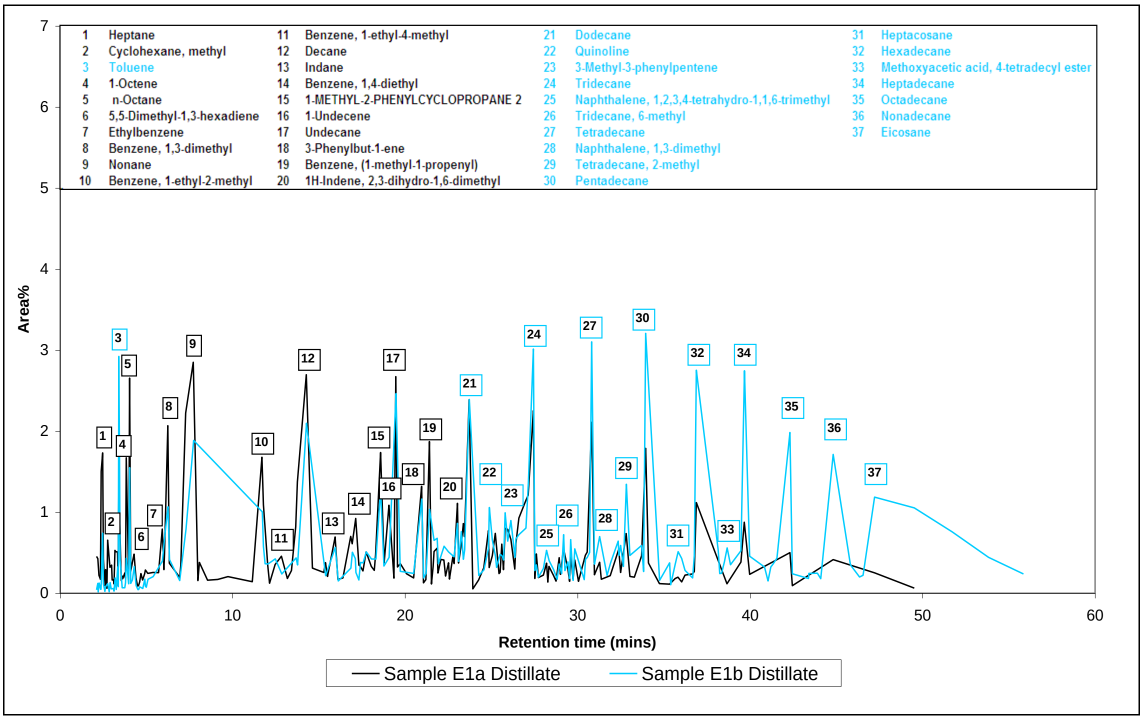

Figure 7-27 Gas Chromatography–Mass Spectroscopy (GCMS) of Samples E1a and E1b distillates

Compared with the distillate of Sample E1a, Sample E1b shows an increase in the concentration of heavier pure aliphatics, specifically C_{13}–C_{21} (peaks 21–37) and, on average, a decrease in the area percentage for the products eluting before 25 min retention time (peaks 1–20).

In terms of the groups or families of products for Samples E1a and E1b residues, a comparison is shown in Table 7-16.

Table 7-16 Molecular compound groups in Samples E1a and E1b residues

Molecules	Unit	Sample E1a	Sample E1b
Alkylated aromatics	**Area %**	2.71	1.89
Pure aromatics	**Area %**	0.29	0.83
Iso-alkanes	**Area %**	1.77	2.61
Normal alkanes	**Area %**	74.61	85.82
Oxygenates	**Area %**	1.38	1.31
Cyclo-alkanes	**Area %**	0.55	0.02

Sample E1b shows the highest concentration of normal alkanes of any of the modified Waxy Oil residues discussed in this chapter. It is suggested that, with minimal contributions from any of the other alkylated compounds and a low oxygenate concentration, Sample E1b should produce the highest coke yield and the greatest concentration of stable molecules; it is thought that this will promote flow domains in the coke.

In terms of the distribution of normal alkanes (C_{10}–C_{30}), Samples E1a and E1b residues are compared in Table 7-17.

Table 7-17 Normal alkanes C_{10}–C_{30}) in Samples E1a and E1b residues

Molecule description	Carbon number	Unit	Sample E1a	Sample E1b
Decane	**C10**	**Area %**	0.00	0.00
Undecane	**C11**	**Area %**	0.08	0.05
Dodecane	**C12**	**Area %**	0.32	1.93
Tridecane	**C13**	**Area %**	0.26	0.00
Tetradecane	**C14**	**Area %**	0.35	0.16
Pentadecane	**C15**	**Area %**	0.29	0.63
Hexadecane	**C16**	**Area %**	12.11	2.44
Heptadecane	**C17**	**Area %**	1.42	3.55
Octadecane	**C18**	**Area %**	2.37	14.35
Nonadecane	**C19**	**Area %**	3.91	0.00
Eicosane	**C20**	**Area %**	21.20	24.76
Heneicosane	**C21**	**Area %**	6.04	3.71
Docosane	**C22**	**Area %**	3.34	1.11
Tricosane	**C23**	**Area %**	1.10	1.63
Tetracosane	**C24**	**Area %**	12.05	6.71
Pentacosane	**C25**	**Area %**	0.84	0.43
Hexacosane	**C26**	**Area %**	0.39	2.31
Heptacosane	**C27**	**Area %**	0.14	0.00
Octacosane	**C28**	**Area %**	8.39	20.42
Nonacosane	**C29**	**Area %**	0.00	0.00
Contane	**C30**	**Area %**	0.00	1.63
TOTAL		**Area %**	74.61	85.82

The three molecules that are in the greatest concentration in Sample E1b are eicosane (C_{20}), octacosane (C_{28}) and octadecane (C_{18}), making up 59.53% of the total percentage of the sample. Sample E1b also shows a reduction in the area percentage contribution of molecules with a lower molecular weight than octadecane (C_{18}) compared with Sample E1a.

In the same way as lighter hydrocarbons in Sample D3 were shown to have the potential to act as reactivity promoters, the effect of their removal is considered when evaluating Sample E1b. Following the procedure used to determine the reactivity potential of Sample D3, the presence of lighter compounds eluting within the first 30 min is considered and shown in Figure 7-28.

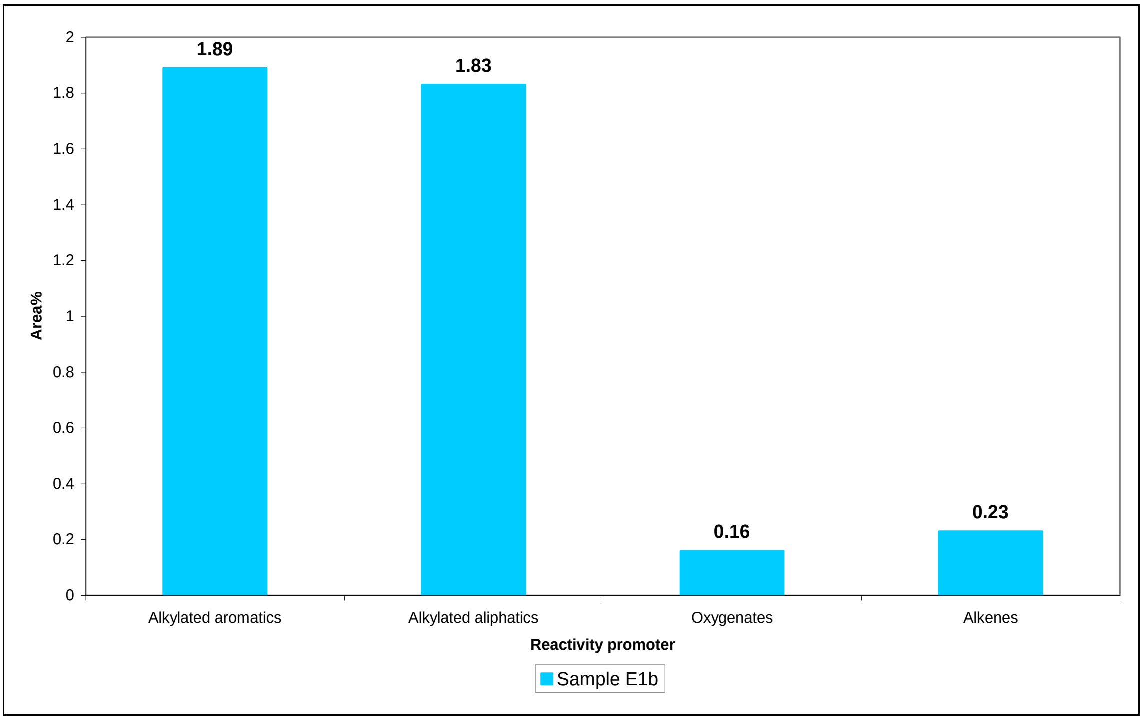

Figure 7-28 Histogram of potential reactivity promoters subdivided into groups of Sample E1b residue (eluting before 30 min according to Figure 7-28)

Compared with Sample D3 (Figure 7-19), Sample E1b shows a substantial reduction in the concentration of iso-alkanes and alkylated aromatics which were previously identified as potential reactivity promoters. Thus, it would be expected (if this theory is correct) that the coke residue formed from Sample E1b would thus be more anisotropic than that of Sample D3 coke. This is further discussed in Chapter 8.

7.3 Hydrogen (^{1}H) Nuclear Magnetic Resonance (NMR) and Aromatic Index (I_{ar}) of modified Waxy Oils

The research detailed in Chapter 7 showed GCMS evidence of a substantial increase in the concentration of normal alkanes, based on a series of experimental interventions. However, the question may well be asked whether the GCMS data are representative of the whole residue. In other words, were there heavier aromatics which did not elute? For this reason a comparison between the ^{1}H (aliphatic to aromatic ratio) and the Aromatic Index (I_{ar}) of the residues is shown in Table 7-18.

Table 7-18 Comparison between the ^{1}H (aliphatic to aromatic ratio) and the Aromatic Index [$I_{ar}=Abs_{3050}/(Abs_{3050}+Abs_{2920})$] of modified Waxy Oils

Residue	^{1}H (aliphatic to aromatic) ratio	Aromatic Index (I_{ar})
Sample B	26.50	*
Sample C1	18.62	0.0041
Sample C2	23.75	*
Sample D1	16.17	*
Sample D3	12.45	0.0046
SampleD4	8.58	0.0079
Sample E2	10.97	0.0110
Sample E1b	9.93	0.0118

*Data not detected

The data in Table 7-18 provide a general comparison between the ^{1}H Nuclear Magnetic Resonance (NMR) and Aromatic Index (I_{ar}) of modified Waxy Oils. In general, as the ^{1}H (aliphatic to aromatic) ratio decreases, there is an increase in the I_{ar}, which would be expected. Given the low aromaticity of the modified Waxy Oils, ^{1}H NMR is more of a quantitative analysis method due to the problems encountered in determining the absorbance of the FTIR band around 3500 cm^{-1}.

^{1}H NMR was preferred over ^{13}C NMR for two reasons. Firstly compared to coal-tar pitches, Waxy oil is not in the amorphous fused state at room temperature but is a liquid. Secondly, given the abundance of hydrogen compared to carbon, quantitative analysis was easier using ^{1}H NMR. While the aromatic index is a less quantitative measure of the aromaticity it is shown in Table 7-18 to indicate only a slight increase in the absorbance of the 3050 cm^{-1} band. this is relevant to show that thermal treatment does not induce substantial increases in the aromaticity due to a lack of activation energy

Samples B and C2 indicate a relatively high ^{1}H (aliphatic to aromatic) ratio since their preparation does not involve chemical cracking and dealkylation. As the severity of thermal treatment increases, so the ^{1}H (aliphatic to aromatic) ratio further decreases due to dealkylation with a corresponding increase in the I_{ar}. However, the results indicate that the slight increase in the I_{ar}, which corresponds to a reduction of the ^{1}H (aliphatic to aromatic) ratio, is related to the dealkylation of aromatics or aliphatics and not to the aromatisation of thermally stable normal alkanes. It is proposed that aromatisation of the stabilised normal alkanes in Waxy Oil would require a greater activation energy and would take place within the initial phase of carbonisation.

In order to put the I_{ar} for the modified Waxy Oils, which range from 0–0.012, into perspective, the I_{ar} of other feedstocks available from the cited literature (Sima *et al.*, 2003; (Perez *et al.*, 2002) are listed, namely coal-tar binder pitch (0.63), Ashland petroleum pitch (0.41), low-temperature gasification pitch (0.37), distilled petroleum vacuum residue (0.38) and thermally treated petroleum vacuum residue (0.45). Similarly, the ^{1}H (aliphatic to aromatic) ratio for the modified Waxy Oils ranges from 9 to 26, whereas that of other feedstocks available from the cited literature (Alcaniz-Monge *et al.*, 2001) is substantially lower, including that of thermally treated coal-tar pitch (0.25) and distilled coal-tar pitch (0.63).

7.3.1 The question of aromaticity

Although the literature cited in this chapter mostly confirms the dependence of anisotropicity on the increase in the concentration of aromatic compounds, in all the modified Waxy Oils the concentration of such compounds was found to be negligible. So the question must be asked: Were the optimum reaction conditions utilised? Thus, the thermal treatment temperature and duration need to be discussed.

As reported, Sample D2 showed small pieces of solid carbon at the bottom of the test tube after thermal treatment. Thus 420 °C is considered a maximum temperature.

In the same way, it may be possible to increase the aromaticity by extending the duration of thermal treatment, as suggested by Eser *et al.* (1989) who studied petroleum residues. While the author is in complete agreement with the work of Eser *et al*., Waxy Oil is a vastly different residue. During a failed experiment, increasing the duration of thermal treatment resulted in a heavy polymer gum forming and gravitating to the bottom of the test tube. This is probably due to dehydrogenation and polymerisation, which are not beneficial.

Although it is the author's opinion that the carbonisation of Waxy Oil does include an aromatisation step prior to mesophase formation, it is more than likely that this occurs at higher temperatures and thus close to the onset of carbonisation.

7.4 Influence of Waxy Oil modification on the distillate fractions of Samples C2, E1a and E1b

Inasmuch as the emphasis of this study is focused on the quality of the residue and subsequent coke formation, the influence of hydrocarbon distillates produced during Waxy Oil modifications cannot be ignored as they have a substantial influence on the revenue generated from the value chain. While it would have been possible to compare the distillate fractions of all the samples, the major difference between a distillation approach and a thermal treatment approach can be determined by studying the distillate fractions of two samples:

- **Sample C2 distillate:** This is the product of physical distillation and does not include chemical modification of Waxy Oil.
- **Samples E1a and E1b distillate:** This is the product of a chemical cracking reaction and the removal of lighter hydrocarbons. As the residue of Sample E1a was distilled to produce Sample E1b, the relative distillate fractions of both samples are added together to represent one combined fraction.

7.4.1 Intermediate[28] distillation fractions[29] of Samples C2, and E1a and E1b

The composition of product yields for Samples C2, and E1a and E1b are shown in Table 7-19.

Table 7-19 Distribution of product yields of Samples C2, and E1a and E1b

Sample	Unit	Distillate fractions			Residue
		Petrol intermediate	Diesel Intermediate	Heavy fuel oil	
Sample C2	**mass %**	0.4	5.1	0.2	94.3
Sample E1b	**mass %**	32.7	11.6	0.3	43.0

1 All distillate fractions are shown as a mass percentage of the filtered Waxy Oil.

2 The cumulative distillate fraction of Samples E1a and E1b are shown. The distillate fractions of Sample E1a have been corrected for a 15% mass loss due to the production of hydrocarbon gas.

As previously mentioned, Waxy Oil is the product of a flash distillation of SDO. Thus it contains a negligible naphtha (petrol intermediate) concentration but more coker oil (diesel intermediate). This is evidenced by the large temperature increase between the Initial Boiling Point (IBP) and the 5% distillate removal (179–311 °C), as shown in Chapter 3 (Table 3-1). The same relationship between distillation and low-temperature pyrolysis was noticed by Martinez-Escandell *et al.* (1999) in their study of long-chain aliphatic waxes. The study reported no distillates up to 360 °C, compared with distillates of lower molecular weight products of up to 59% when the wax was thermally treated.

Vacuum distillation to pre-cracking temperatures is a physical reaction in that it removes the small amount of lower molecular weight hydrocarbons remaining in the Waxy Oil given the inaccurate nature of flash distillation. Thus the petrol intermediate (0.4%) is negligible and the bulk of the distillate is composed of the diesel intermediate (5.1%), with a small contribution from the production of heavy fuel oil. As distillation is a *physical* reaction and not a *chemical* reaction, there is no need to account for hydrocarbon gas and thus the mass balance is complete.

Thermal treatment (at 410 °C) or low-temperature thermal pyrolysis[30] is a chemical reaction which increases the percentage of stable high molecular weight normal alkanes and of lighter molecular weight hydrocarbons, as well as producing gas. The production of 15% gas yield from the low-temperature pyrolysis of Waxy Oil is in general agreement with the results of Martinez-Escandell *et al.* (1999) who obtained similar gas yields when studying the low-temperature pyrolysis of aliphatic petroleum vacuum residues. The distillation of thermally treated residue thus substantially increases the distillate yield. There is also a larger percentage of petrol intermediates (32.7%) produced compared with that of the diesel

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[28] The term “intermediate” is defined in this study as a product produced in the refinery which requires further downstream processing before it can be sold.

[29] Manual calculation of the GCMS data was done to estimate the quantitative amount of various distillation fractions. The petrol fraction is based on molecules between C_4 and C_{12}. The diesel fraction is calculated based on molecules between C_{12} and C_{21}. The heavy fuel oil fraction is calculated based on molecules greater than C_{21}.

[30] For the purpose of this study thermal treatment at 410 °C is referred to as “low-temperature thermal treatment” compared with carbonisation at 480 °C which may be comparatively referred to as “high-temperature thermal treatment”.

intermediates (11.6%). As thermal treatment involves the production of hydrocarbon gas, this has been accounted for in the mass balance.

In summary, the production of a substantially higher percentage of petrol and diesel intermediates would be beneficial to the refinery in terms of the need for fuel additives and reducing the amount of residue as feed for carbonisation.

7.4.2 Molecular grouping of intermediate petrol distillation fraction of Samples C2, and E1a and E1b

As both the petrol and diesel distillate fractions are only intermediate products requiring downstream processing, a comparison with the typical molecular groupings of saleable fuel products is not applicable. However, what is apparent is the effect of low-temperature pyrolysis on the typical spectrum of the lower molecular weight breakdown products produced which report to the distillate fraction. Low-temperature pyrolysis of a complex mixture of organic molecules (e.g. Waxy Oil) has the potential for billions of individual reactions. By way of example, Domine *et al.* (2002) calculated 156 individual reactions for the pyrolysis of normal hexane alone. As Waxy Oil is composed predominantly of iso and normal alkanes, the typical reactions may be modelled on these groups of molecules.

Low-temperature pyrolysis of normal alkanes involves a myriad of potential reactions. However, starting from the most basic of cleavage mechanisms, the aliphatic C-C bond (bond enthalpy of 348 kJmol^{-1}) is more readily cleaved than the C-H bond (bond enthalpy of 412 kJmol^{-1}), as argued by Saunders (2003). Thus lysis of an alkane by a radical formation mechanism to form lower alkanes is slightly preferred to initial dehydrogenation. The process may be represented in the simplified reaction mechanism provided by Domine *et al.* (2002) shown in Figure 7-29. A similar reaction mechanism for the production of lower molecular weight intermediates during low-temperature pyrolysis has previously been reported by Rodriguez-Reinoso *et al.* (2001).

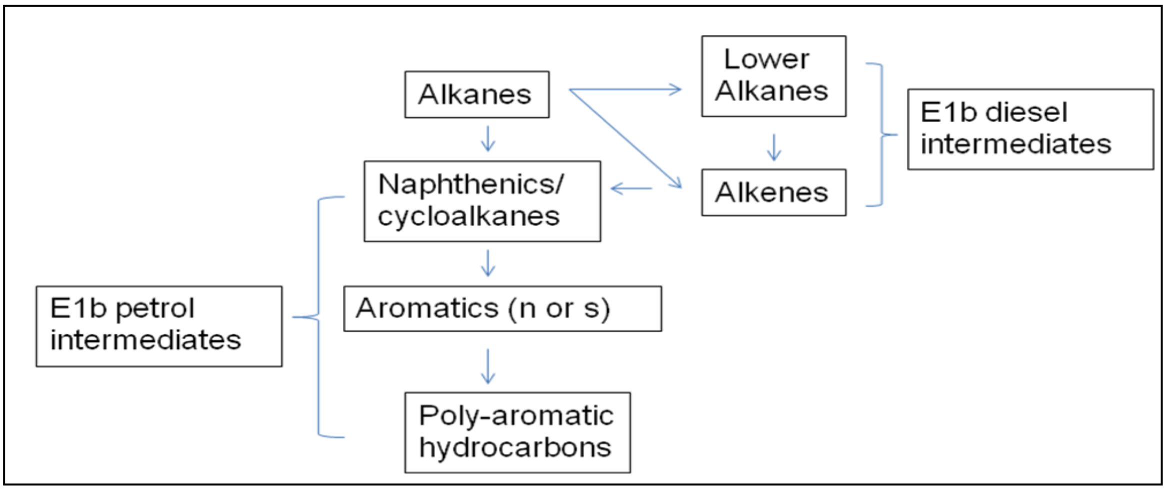

Figure 7-29 Simplified reaction model of exchanges between molecular families during thermal pyrolysis (modified from Domine *et al.*, 2002)

In line with the simplified reaction model shown in Figure 7-29, the percentages and types of molecular family shown in the product spectrum of the petrol intermediate distillate of Samples E1a and E1b can be described as shown in Figure 7-30.

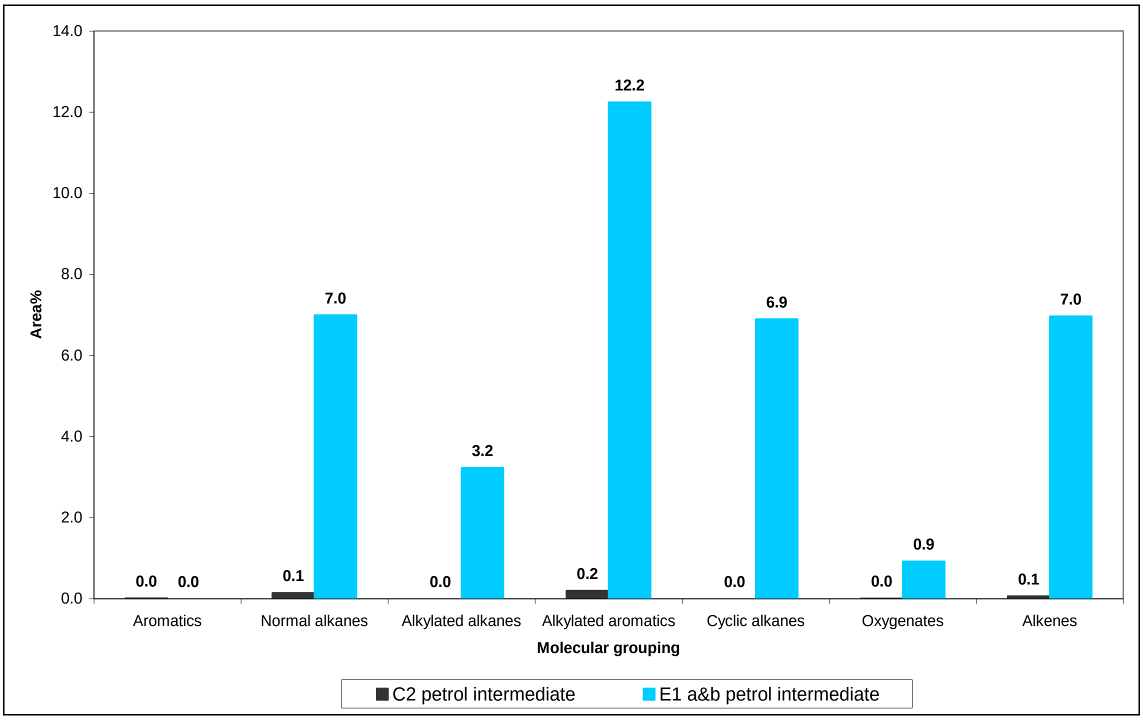

Figure 7-30 Quantitative analysis of molecular groups comprising the petrol fraction of Samples C2, and E1a and E1b distillates[31]

Low-temperature pyrolysis produces a host of different lower molecular weight families (Figure 8-32), dominated by alkylated aromatics (12.2%), normal alkanes (7.0%), alkenes (7.0%), cyclic alkanes (6.9) and alkylated alkanes (3.2%). The normal and iso-alkanes have a higher molecular weight compared with that of most of the other families and are probably relatively unreactive. The alkenes formed are the larger normal alkane fragments of C-C bond homolytic cleavage which have been dehydrogenated, in agreement with the study of pyrolytic cracking of *n*-hexadecane by Tsuzuki *et al.* (1999). The smaller alkane fragments are probably removed as hydrocarbon gases. However, there is also a substantial percentage of cyclic alkanes which are either the product of cyclo addition reactions or, more likely, due to self-condensation of normal alkanes as they mostly contain long alkyl substitutions on the alicyclic ring. This compounding effect of reactions has also been studied by Bounaceur *et al.* (2002) who described them as “H-transfer, decomposition by B-scission, radical isomerisation, addition and termination”. Although the formation of cyclic alkanes is a slow reaction, their dehydrogenation is rapid, which would explain the relatively high percentages of alkylated aromatics. The absence of oxygenates is probably due to lysis of the carbonyl or hydroxyl function and the formation of water.

The substantially higher percentage of lower molecular weight petrol intermediates compared with diesel intermediates (shown in Table 7-19) from low-temperature pyrolysis may also be affected by the distillation efficiency of the reactive system (as in Sample E1a). The longer the breakdown products remain in the reactor at temperature (as opposed to distilling off), the

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[31] All distillate fractions are shown as a mass percentage of the filtered Waxy Oil.

higher the percentage of lower molecular weight products, as also observed by Martinez-Escandell *et al.* (1999). This may also serve to explain the relatively high percentage of alkylated aromatics produced by the dehydrogenation of alkylated cyclic alkanes as shown in Figure 7-30.

7.4.3 Molecular grouping of intermediate diesel distillation fraction of Samples C2, and E1a and E1b

By means of comparison with Figure 7-30 the percentages and types of molecular family shown in the diesel intermediate distillate of Samples E1a and (E1) can be described as in Figure 7-31.

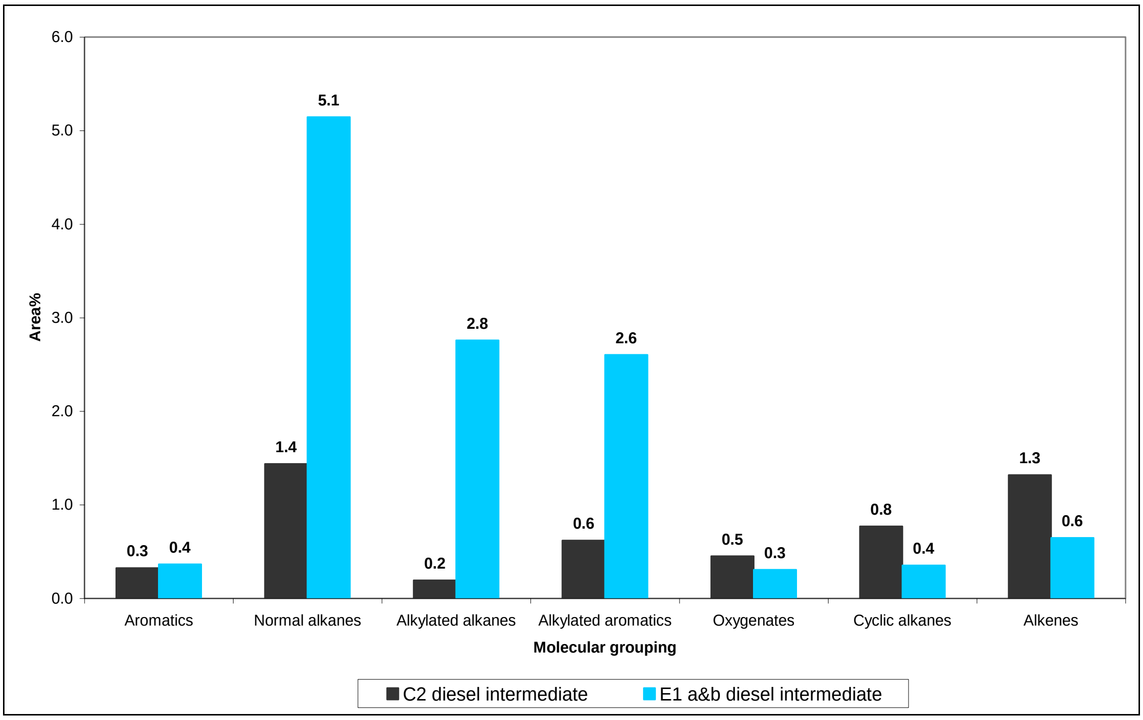

Figure 7-31 Quantitative analysis of molecular groups comprising the diesel fraction of Samples C2, and E1a and E1b distillates[32]

The diesel intermediate fraction presents a less “mature” spectrum of breakdown molecules (Figure 7-31) when compared with the petrol intermediate fraction (Figure 7-30). The “maturity” of the product spectrum is defined in this study as the distribution of intermediate products formed by low-temperature thermal pyrolysis as shown in Figure 7-29.

The product spectrum (Figure 7-31) of the diesel intermediate fraction is dominated by normal alkanes (5.1%), with smaller contributions from alkylated alkanes (2.8%) and alkylated aromatics (2.6%). The higher thermal stability of this fraction is based on the dominance of normal alkanes and the relatively low percentages of the primary breakdown products, namely cyclic alkanes (0.4%) and alkenes (0.6%).

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[32] All distillate fractions are shown as a mass percentage of the filtered Waxy Oil.

Compared with the petroleum intermediate fraction of Sample C2 distillates, the diesel intermediate fraction is composed predominantly of normal alkanes (1.4%) and alkenes (1.3%).

7.4.4 Importance of distillate breakdown products to the mechanism of carbonisation

The importance of a detailed discussion of the breakdown product spectrum from low-temperature thermal pyrolysis of Waxy Oil (described above) is that it sheds light on the probable reaction mechanism of the higher molecular weight normal alkanes during carbonisation (otherwise stated as high-temperature thermal pyrolysis).

The lower reactivity of higher molecular weight normal alkanes discussed above and proposed by Domine *et al.* (2002) explains the "crest" of normal alkanes (C_{21}–C_{30}) shown in the GCMS of Sample E1b residue (Figure 7-26). Low-temperature thermal pyrolysis of Waxy Oil does not induce thermal breakdown of these higher molecular weight normal alkanes and thus as the distillate is removed, their concentration increases due to a reduction in the dilution factor. In support of this, Bounaceur *et al.* (2002) also determined the increase in the activation energy required to breakdown *n*-tetradecane compared with *n*-hexane.

Throughout Chapter 7 it has been seen that the thermal stability of normal alkanes limits the concentration of aromatic molecules (be they pure or alkylated). However, to show that a small amount of aromatisation does occur (especially in the distillate fraction of E1b) a simple calculation is possible as shown in Table 7-20.

Table 7-20 Comparison of the total aromatics (including pure and alkylated aromatics) in Sample B (residue) and Sample E1b (residue and distillate)

Fraction	Unit	Sample B	Sample E1b
Aromatics in distillate	**Area%**	0.0[1]	15.2[3]
Aromatics in residue	**Area%**	10.0[2]	1.2[4]
Total aromatics	**Area%**	**10.0**	**16.4**

- Sample B does not have a distillate fraction.
- Cumulative value of both alkylated and pure aromatics in Sample B as given in Table 8.3
- Cumulative value of both alkylated and pure aromatics in petrol and diesel intermediates calculated from Figures 8-23 and 8-33 respectively
- Cumulative value of both alkylated and pure aromatics in Sample E1b residue corrected by the residue yield factor of 0.43

The total area percentage of aromatics in the filtered Waxy Oil (Sample B) is 10.0%. If Sample B is used as a reference, then by calculating the total aromatic area percentage of Sample E1a residue and distillate (16.4%), it is determined that a small amount of aromatisation has occurred. It is further evident that the aromatics are the product of low temperature as the greater percentage thereof is present in the distillate fraction of Sample E1b. This essentially proves that aromatics are formed according to the product breakdown mechanism shown in Figure 7-29.

Both thermal treatment at 410 °C (low-temperature thermal pyrolysis) and carbonisation at 480 °C (high-temperature thermal pyrolysis) are the same types of reaction; it is only that the latter has a higher energy input. At carbonisation temperatures, the normal alkanes (C_{21}–C_{30})

will react by much the same reaction mechanism, forming substituted cyclic alkanes and then substituted aromatics. Complete or incomplete lysis of alkyl substitution on the aromatic ring increases the percentage of pure aromatics which provide the primary "building blocks" for poly-condensation to form poly-aromatic hydrocarbons.

7.5 Conclusions – Waxy Oil modification

This chapter presents data showing the effect of Waxy Oil modification on the molecular composition.

The conclusions drawn are as follows:

- Waxy Oil filtration to less than 0.5 µm is effective in removing the required amount of catalyst to meet the needle coke specification. The lower the micron aperture of the sintered metal filter, the lower the ash content of the Waxy Oil.
- Filtration would be better conducted on the SDO and not the Waxy Oil.
- Distillation of the Waxy Oil would be better conducted at higher vacuum pressure to allow the removal of a greater volume of lighter molecules prior to cracking.
- Distillation (even at higher vacuums) is, however, not considered a viable option due to the distribution of oxygenates throughout the molecular weight range of Waxy Oil. Furthermore, a substantial increase in the molecular weight of the diesel intermediate fraction may present quality problems.
- Thermal treatment at 400–420 °C is effective in the partial destruction of iso-alkanes aliphatic and aromatics, as well as of oxygenates.
- An increase in the thermal treatment temperature serves to increase the cracking severity. However, the experimental set-up used does not promote efficient removal of lighter hydrocarbons from the residue, especially noticeable at 5 bar pressure.
- Reducing the system pressure after 1 h during thermal treatment does increase the removal of lighter hydrocarbons from the residue.
- Lighter cracked molecules remaining in the residue may act as reactivity promoters during carbonisation.
- Distillation of thermally treated residues is the most effective method for removing lighter cracked hydrocarbons from the residue. By using this method it is possible to increase the concentration of normal alkanes to 85% in the residue. This is also effective in reducing the yield of the residue to 45%, based on the virgin filtered Waxy Oil.
- The modification techniques used are not dissimilar to those in the cited literature on aromatic coal tar or petroleum-based residues. However, while dealkylation and the destruction of oxygenated molecules are common goals, the stabilisation of Waxy Oil includes the concentration of long-chain normal alkanes as opposed to aromatics.
- Another difference is that the carbonisation of Waxy Oil will involve an extra aromatisation step.
- Thermal treatment induces the formation of pre-carbonisation products which decrease as the molecular weight increases, thus explaining the stability of the high molecular weight normal alkanes in Waxy Oil.

7.6 Recommendations – Waxy Oil modification

Based on the evidence provided in this chapter, the following recommendations are made:

- The modified Waxy Oils produced should be subject to “static” carbonisation in a test tube to determine the effect of Waxy Oil modification on the anisotropy of the carbon.
- “Static” carbonisation will further test the theory that distillation after thermal treatment is necessary to remove reactivity promoters and thus reduce the anisotropicity of the carbon.
- “Static” carbonisation will promote a layered coke deposition with mosaic microstructures (formed from the more reactive components) at the bottom of the test tube, and flow domains (from the more stable components) higher up the test tube.
- The anisotropicity of the cokes produced will be determined using optical microscopy.