THE EFFECT OF AN IRON OXIDE CATALYST (Fe_3O_4) ON THE CHARACTERISTICS OF WAXY OIL COKE

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Abstract

A study was conducted on four commercial Waxy Oil green cokes with varying catalyst (Fe_3O_4) concentrations (ash content: 1.84-11.18%), to determine the effect thereof on the structural characteristics of calcined (1400 °C) and pre-graphitised (2000 °C) cokes. An increase in the catalyst content of the coke shows a substantial detrimental affect on the overall anisotropy of the carbon microstructure. The catalyst (with a particle size distribution between 0.5 µm and 78 µm) was found to present a physical barrier around which the anisotropic flow domains formed. At higher catalyst concentrations the catalyst dominates the carbon microstructure; however, there is still evidence of flow patterns albeit with a shorter range. XRD powder data and Raman spectroscopy provide evidence of multiphase graphitisation in both the calcined coke and pre-graphite. The crystal development of the calcined coke is dominated by catalytic graphitisation and that of the pre-graphite showed a greater dependence on thermal graphitisation. This is the first scientific study of the effect of catalyst concentration on the characteristics of this novel coke and proves the disingenuous comparability thereof with a highly anisotropic coke (e.g. needle coke).

Introduction

Waxy Oil coke is produced by commercial delayed coking of a distilled heavy residue produced by Sasol Synfuels (Secunda, South Africa). The Fischer-Tropsch reaction produces a syncrude hydrocarbon mixture from synthesis gas (hydrogen and carbon monoxide); the distillation thereof producing a heavy residue namely Waxy Oil which is used as a delayed coker feedstock. Unlike either coal-tar or petroleum residues the Waxy Oil does not contain stable heteroatoms originating from the origin as compared with coal or crude oil.

Calcined Waxy Oil coke is unique to Sasol Synfuels and is sold into high quality recarburiser applications as a trimming addition (due to the low nitrogen and sulphur content). The quality of Waxy Oil coke is periodically affected by high concentrations of the catalyst (Fe_3O_4) in the feed to the delayed coker. However, apart from the effect of this ash on the fixed carbon content (in respect of the recarburiser application), no scientific study has previously been conducted to determine the effect thereof on the structural characteristics of the coke. Waxy Oil coke is anisotropic and in this respect is most suitable for artefact markets (anode or electrode), but the high ash content is a problem. The study aims to prove why these cokes cannot be directly compared with other anisotropic cokes (e.g. needle coke)

The effect of iron oxide powders has previously been reported to disrupt mesophase development by catalytic dehydrogenation of hydrocarbons resulting in premature solidification producing mosaic microstructures [1]. However, while previous work has studied the effect of fine iron oxide powders (0.1-1.0 μm) on the microstructure, the current study evaluates the effect of a commercial catalyst with a larger particle size distribution (0.5-78 μm) on the carbon microstructure. This study also considers the effect of the comparatively large catalyst size in presenting a physical barrier to the development of flow domains within the carbon microstructure (as has been reported in studies evaluating the effect of other solids on the microstructure), specifically primary QI [2] and alkali metal carbonates [3].

Increasing iron or iron oxide concentration in coke reduces the temperature at which graphitisation is initiated serving to decrease the interlayer spacing (d_{002}) and increase the coherence length (L_c) [1]. However, this presents a challenge as due to the low ash content of commercial needle coke, the crystal structure is entirely dependant on the anisotropy and thermal treatment. Here we compare the development of the crystal structure by thermal and catalytic graphitisation in Waxy Oil cokes thermally treated to both 1400 °C (termed calcined coke) and to 2000 °C (termed pre-graphite).

The partial reduction of iron oxide (in calcined coke) [4] or complete reduction to elemental iron [in thermally treated (1800 °C) cokes] [5], promotes multiphase graphitisation which is characterised by the development of both thermally and catalytically derived graphitic XRD peaks [1]. A third broad peak has also been identified at a lower 2θ angle attributed to more disordered carbon [6]. The effect of catalytic

graphitisation is reported to be dependant on the degree of contact between the carbon and elemental iron [5] and the fact that once carbon has been graphitised it is unlikely to be graphitised further by the same catalyst even at higher thermal treatment temperatures [1,7]. The mechanism for catalytic graphitisation is reported to involve either the dissolution of carbon in the molten metal (until super saturation is reached after which carbon precipitates in the form of crystalline graphite) or the formation of a metal carbide intermediate which decomposes to form crystalline graphite [8].

The study further evaluates the effect of increasing the catalyst concentration on both the real density and the carboxy reactivity of the calcined coke.

Experimental

Waxy Oil green coke

Four samples of high ash Waxy Oil green coke were obtained from the Sasol Synfuels delayed coker in Secunda (South Africa). The samples (30-60 mm) were crushed, dried and sieved to obtain a particle size fraction of 0-10 mm. The samples were ascribed random names (Sample 1 to Sample 4) and were differentiated in accordance with their respective ash contents: Sample 1 (ash content: 1.841%); Sample 2 (ash content: 4.223%); Sample 3 (ash content: 7.471%) and Sample 4 (ash content: 11.186%).

Thermal treatment (1400 °C)

The four Waxy Oil green coke samples (2-10 mm; approximately 350 g) were calcined to 1000 °C in a muffle oven with a nitrogen flux at a heating rate of 5 °C.min^{-1}. The temperature was further increased to 1400 °C at approximately 2 °C.min^{-1} and held for 80 minutes, then cooled to room temperature under nitrogen flux. The product termed **'calcined coke'** was weighed to determine the yield.

Thermal treatment (2000 °C)

A medium frequency induction furnace was used to graphitise the four Waxy Oil green coke samples to a pre-graphitisation temperature of 2000 °C (which was maintained for 5 minutes). The green coke (approximately 17 g; -2.0 mm) was placed in a cylindrical graphite crucible with a graphite lid. The crucible was wrapped with an inner layer of graphite wool insulator and an outer layer of alumina wool. The insulated sample was wedged in-between the copper coil. The reactor was closed and a vacuum pump evacuated the reactor to -0.8 bar. The reactor was then connected to an argon line and the pressure was kept constant at -0.6 bar. The product termed **'pre-graphite'** was weighed to determine the yield.

Optical microscopy

Samples of the four green and calcined cokes (+20 mm) were mounted in epoxy resin and polished using ISO 7404-2 (1985) as a guideline. The samples were examined under 50x

magnification (oil immersion) using a Leica DM4500P petrographic microscope with polarised light but without a lambda plate.

Chemical analyses

The ash content, metals, volatile carbon matter, carbon, hydrogen, nitrogen, sulphur, Hardgrove Grindability Index (HGI), bulk density, carboxy reactivity were conducted in accordance with ASTM standard methods. The real density was conducted using a Micro-metrics AccuPyc 1330 pycnometer in helium using a coke size fraction of –75 μm.

Thermo-gravimetric Analysis (TGA)

TGA was used to determine the proximate analysis for the Waxy Oil pre-graphite (-150 μm). The analysis was conducted using a Mettler TGA1/DSC1 thermo-gravimetric instrument. The following programme was used:

- Nitrogen flow of 150 ml.min^{-1}
- Equilibrated at 30°C for 3 min
- 30°C to 110°C rate 50°C.min^{-1}
- 110°C for 3 min
- 110°C to 900°C rate 50 °C.min^{-1}
- 900°C for 7 min
- Switched to air flow (150 ml.min^{-1}) and held at 900°C for 20 min

X-ray Diffraction (XRD)

X-ray powder diffraction data were collected using a Phillips X-pert Pro multi purpose diffractometer equipped with the X'Celerator detector at a scanning speed of 0.014 °2θ/s with a step size of 0.017 °2θ. Samples were irradiated with iron filtered cobalt (Co) K$_{\alpha}$ X-rays emitted from a sealed tube source. Crystalline phases present in the sample were identified by searching the powder diffraction file database (PDF-4+ 2008) using the X'Pert High Score Plus version 2.2d PANalytical software. The powder samples were packed using the back loading technique to minimise preferred orientation.

Raman spectroscopy

Samples were placed on a microscope slide and measured using the inVia Raman system, utilising the 514.5 nm line of a 5.3 mW (at the sample) Ar-ion ion laser beam that was focused with a Leica microscope using a x20 long focus objective. Data was obtained for the region 200 – 4000 cm^{-1} for 60 seconds, scanned 5 times using a laser power of 100% with a 75% defocused beam. Four to five separate spectra were obtained for each sample and then averaged to obtain the final spectrum used for analysis. Wire Version 2, service pack 8 software was used for data capturing and instrument control. The Raman band of pure Si was measured before data accumulation commenced for calibration purposes. Normalisation and band deconvolution was done using OPUS Software, Version 6 using

the Levenberg-Marquardt algorithm. Deconvoluted band shapes were described using pseudo-Voigt functions.

Results

Analysis of green and calcined cokes

Analysis of the four Waxy Oil green cokes is shown in Table 1.

Table 1 Analysis of Waxy Oil green cokes

	Units	Sample 1	Sample 2	Sample 3	Sample 4
Carbon	Mass%	90.20	90.80	89.20	85.60
Hydrogen	Mass%	3.68	3.68	3.52	3.63
Nitrogen	Mass%	0.05	0.03	0.08	0.02
Sulphur	Mass%	0.005	0.004	0.006	0.007
Ash content	Mass%	1.84	4.22	7.47	11.19
Volatile Carbon Matter (VCM)	Mass%	8.11	8.69	8.97	11.65
Fixed Carbon[1]	Mass%	90.05	87.09	83.56	77.19
Inherent moisture	Mass%	0.20	0.19	0.19	0.23
Real density (-75 µm; Helium)	g.cm^{-3}	1.3879	1.4237	1.456	1.4792

[1] Fixed Carbon = 100% - (ash + VCM)

The ash content of the Waxy Oil green cokes increases from Sample 1 to Sample 4 (1.84-11.19% respectively), with a reciprocal decrease in the fixed carbon content (90.05-77.167%). The Volatile Carbon Matter (VCM) of Samples 1-3 (8.11-8.97%) is within the normal commercial range (6-9%) while that of Sample 4 (11.65%) is slightly higher.

Both the nitrogen (0.030-0.083%) and (0.004-0.007%) sulphur content of Samples 1-4 are comparatively lower than most green cokes produced either from petroleum crude oil or coal-tar origins [13-15], which typically have nitrogen contents of 1-2% (for coal-tar calcined cokes) and sulphur contents of 1-6% (for petroleum derived calcined cokes.

Based on the values shown in Table 1 there is a linear correlation ($R^2 = 0.9655$) between an increase in the ash content and an increase of the real density.

Analysis of the four Waxy Oil calcined cokes is given in Table 2. The data are compared to those from a typical calcined needle coke.

Table 2 Analysis of Waxy Oil calcined cokes vs. calcined needle coke

	Units	Sample 1	Sample 2	Sample 3	Sample 4	Needle coke
Calcined coke yield	**Mass%**	90.6	90.5	89.4	86.5	-
Carbon	**Mass%**	97.11	95.86	94.34	92.88	98.85
Hydrogen	**Mass%**	0.13	0.11	0.13	0.12	0.06
Nitrogen	**Mass%**	0.02	0.02	0.02	0.02	0.68
Sulphur	**Mass%**	0.017	0.024	0.032	0.056	0.174
Real density (-75 μm; Helium)	**g.cm^{-3}**	2.1024	2.1087	2.1124	2.1220	2.2168
Volatile Carbon Matter (VCM)	**Mass%**	0.57	0.47	0.38	0.59	0.18
Fixed Carbon	**Mass%**	96.41	94.11	90.96	85.90	99.77
CO_2 reactivity	**Mass%. 100 min^{-1}**	69.78	77.88	81.13	87.02	8.34
Ash content	**Mass%**	3.02	5.42	8.66	13.51	0.06
Metal content:						
Calcium (Ca)	**Mass%**	0.0931	0.1380	0.1473	0.1521	0.0026
Iron (Fe)	**Mass%**	1.8365	2.6882	3.7474	4.7624	0.0038
Silicon (Si)	**Mass%**	0.0308	0.0437	0.0535	0.0800	0.0011
Vanadium (V)	**Mass%**	0.0001	0.0001	0.0001	0.0001	0.0001
Nickel (Ni)	**Mass%**	0.0005	0.0001	0.0001	0.0001	0.0001
Total metals in coke	**Mass%**	1.9671	2.8755	3.9533	4.998	0 0136

While the VCM for the four calcined cokes is relatively consistent it does indicate slight under calcining. As expected the ash content increases from Sample 1 to Sample 4, in agreement with the ash contents of the green coke. Compared to the Waxy Oil coke, the ash and metals content of the calcined needle coke is substantially lower.

The calcined coke yield decreases (from Sample 1 to Sample 4) with a correlation to the VCM of the respective green cokes. The decrease in the yield also serves to increase the ash content of calcined coke by between 39% (Sample 1) and 17% (Sample 4). Apart from the partial loss of volatiles, the partial reduction of the catalyst (which increases from Sample 1-4), producing carbon monoxide could contribute to the yield loss. Of course the fact that the ash increase is far larger in Sample 1 (39%) vs. Sample 4 (17%) is based on the relative amount of carbon available given ash content in the original green cokes.

The carboxy reactivity of the calcined coke increases from Sample 1 to Sample 4 (69.78-87.02% respectively). Research conducted with petroleum sponge cokes (in the aluminium industry) confirms the catalytic effect of sodium and calcium on the carboxy reactivity of calcined coke [16]. The increase of the iron (1.8365-4.7624%) and calcium (0.0931-0.1521%) content as indicated by an increase in the ash content (3.02-13.51%) correspond with an increase in the carboxy reactivity. Indeed the catalytic effect of calcium and iron on the carboxy reactivity of petroleum cokes, coals and chars has previously been established [9-11]. By means of comparison the carboxy reactivity of a commercial needle coke was 8.34% partially based on the lower ash (0.058%), calcium

(26 ppm) and iron (38 ppm) contents. The influence of the ash content on the carboxy reactivity does not negate influences of porosity.

The nitrogen and sulphur content of the Waxy Oil coke are far lower than the needle coke for reasons discussed previously.

As described for the Waxy Oil green coke, there is a linear correlation between the ash content and the real density of the calcined coke ($R^2 = 0.9862$). The correlation is slightly better than described for the green coke; due to the lower variation of the VCM. Based on the correlation, a Waxy Oil needle coke with no ash would have an extrapolated real density of 2.0974 g.cm^{-3}. The fact that real density increases with the ash content masks any influence of the carbon microstructure. In most anisotropic cokes with a low ash content (e.g. needle or anode coke) the real density increases with the degree of optical anisotropy of the coke [19]. In the Waxy Oil cokes this relationship is reversed (based on the effect of catalyst content on the carbon microstructure shown in Figure 1).

Proximate analysis of the pre-graphite

As the amount of pre-graphite produced did not produce enough sample for a conventional ash analysis (as given in Table 2), an indication of the ash content was derived by thermo-gravimetric proximate analysis. The proximate analysis for the pre-graphites is shown in Table 3.

Table 3 Proximate analysis and yield for the Waxy Oil pre-graphite

	Units	Sample 1	Sample 2	Sample 3	Sample 4
Yield	mass%	82.0	83.3	84.6	85.4
VCM	mass%	0.6	0.8	0.6	0.4
Fixed carbon	mass%	97.5	95.2	93.0	88.4
Ash content	mass%	1.9	4.0	6.4	11.2

The yield of pre-graphite (based on green coke) is lower than for the calcined coke (Table 2). As thermal treatment was conducted in an inert argon atmosphere, the yield loss is attributed to the loss of volatiles and carbon monoxide produced by the complete reduction of the catalyst to iron. The yield increase from Sample 1 to Sample 4 is based on the relative amount of ash and VCM in the green coke.

Optical Microscopy calcined cokes

Optical microscopy was conducted on the calcined cokes to establish the effect of increasing catalyst content on the carbon microstructure. Microscopy conducted on the green cokes did not yield clear images of the catalyst. Nomenclature used to describe the microstructure of the Waxy Oil calcined coke microstructures has been described elseware [3].

The micrographs of the four Waxy Oil calcined cokes are shown in Figure 1 a-d.
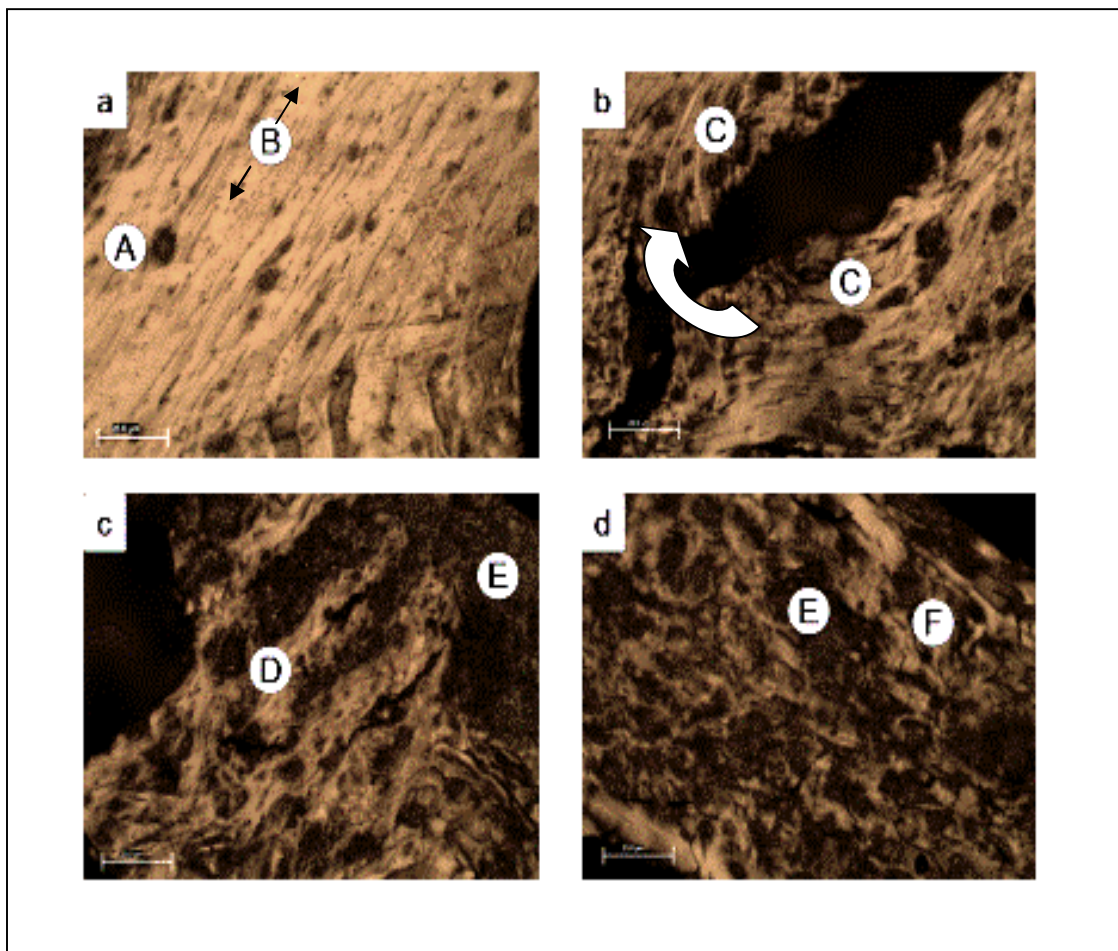
Figure 1 Micrographs of Waxy Oil calcined cokes showing the effect of ash content on the carbon microstructure, (a) Sample 1,,(b) Sample 2, (c) Sample 3, (d) Sample 4

The coke with the lowest ash content (Sample 1; Figure 1a) shows a microstructure dominated by both acicular and elongated flow domains (Position B). The catalyst agglomerates (Position A) appear as a physical barrier, around which the mesophase develops long range flow domains.

Figure 1b shows an increase in the density of slightly larger catalyst agglomerates with a shrinkage fissure perpendicular to the domain flow (as indicated by the arrow, Position C).

As the ash content increases (Figure 1 a-d), the predominantly oval shaped agglomerates (1-6 μm; Position A) increase in size forming long range irregular shaped occlusions (of over 20 μm in length and width; Position E). The matrix of catalyst agglomerates appears to increasingly dominate the micrographs, occluding the spatial availability for the development of the carbon microstructure. Thus, the effect of an increase in the catalyst concentration is to decrease the overall anisotropy of the Waxy Oil calcined coke. The optical texture shows an anisotropic decrease from acicular flow domains and elongated

flow domains (Position B, 70-90 µm x 4-5 µm), to elongated coarse flow (Position C, 20-60 µm x 4-5 µm) to elongated medium flow (Position D, < 20 µm x 4-5 µm) and finally to coarse grained mosaic (Position F, 10-12 µm x 7-8 µm).

X-Ray diffraction on Waxy Oil calcined coke and pre-graphite

Evaluation of the catalyst form in the calcined coke and pre-graphite

XRD powder traces of the calcined coke (Figure 2) and pre-graphite (Figure 3) show the variance in the form of the catalyst in response to thermal treatment.
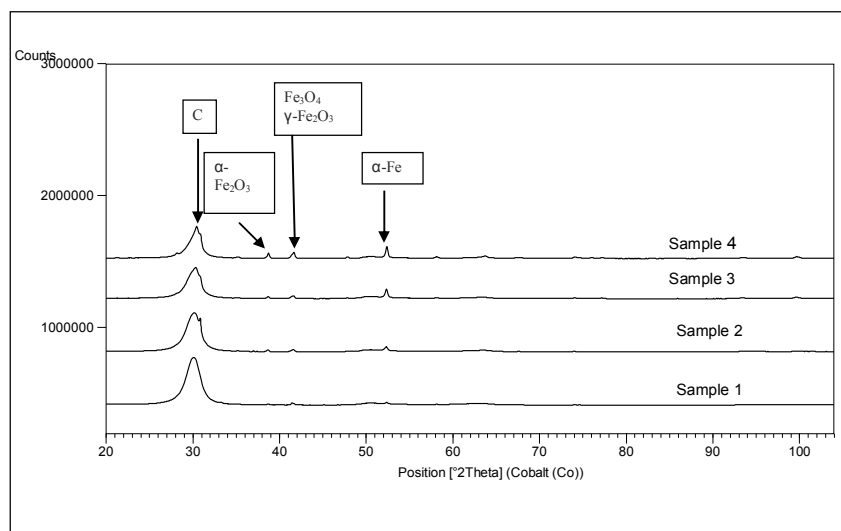
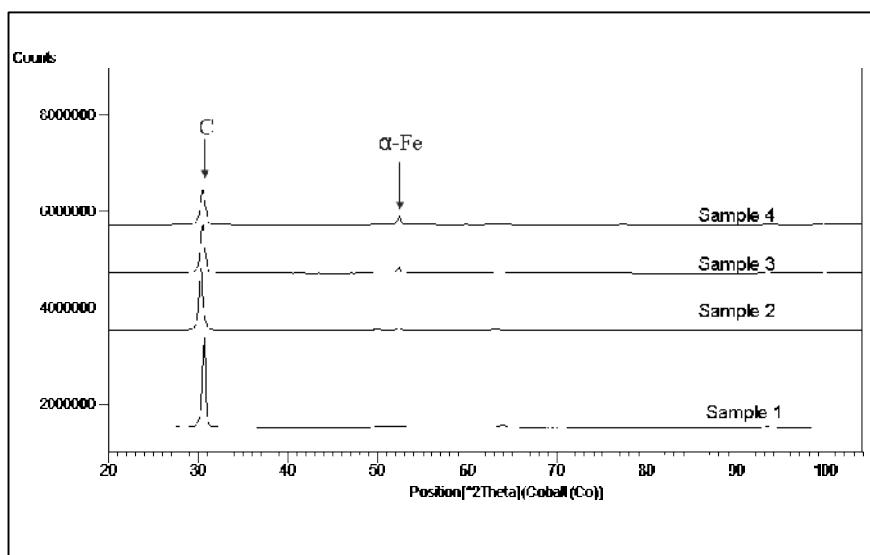**Figure 2 XRD trace (20-100 °2θ) of Waxy Oil calcined coke showing forms of the iron catalyst**

Figure 3 XRD trace (20-100 °2θ) of Waxy Oil pre-graphites showing the form of the iron catalyst

Waxy Oil calcined coke (Figure 2) shows evidence of a mixture of catalyst phases (Fe_3O_4, Fe_2O_3 and Fe), which indicates partial reduction of the catalyst from green coke (Fe_3O_4). This is in agreement with previous research on other calcined cokes [4]. The Waxy Oil pre-graphite (Figure 4) only shows the presence of elemental iron (Fe) in accordance with previous work [5] due to thermal treatment at 2000 °C in a reducing atmosphere. Apart from the effect of catalyst concentration on the carboxy reactivity and as a graphitisation catalyst, it is also noted that given the unusually large catalyst concentration; complete reduction would liberate oxygen which would be emitted as carbon monoxide. It can be calculated that the carbon monoxide loss due to the catalyst reduction would vary between 0.89-2.25% (based on the iron content in shown in Table 2).

Evaluation of the crystal development in the calcined cokes and pre-graphites

An expanded XRD trace of the 002 region for both the calcined cokes and pre-graphites is shown in Figures 4 and 5 respectively. The insert provided in both figures shows the deconvolution of overlapping peaks. Three independent peaks were identified, [denoted as G1 (turbostatic or disordered carbon [6]); G2 (thermally derived carbon peak [1, 6]) and G3 (catalytic graphite peak [1, 6])], with different interlayer spacings.
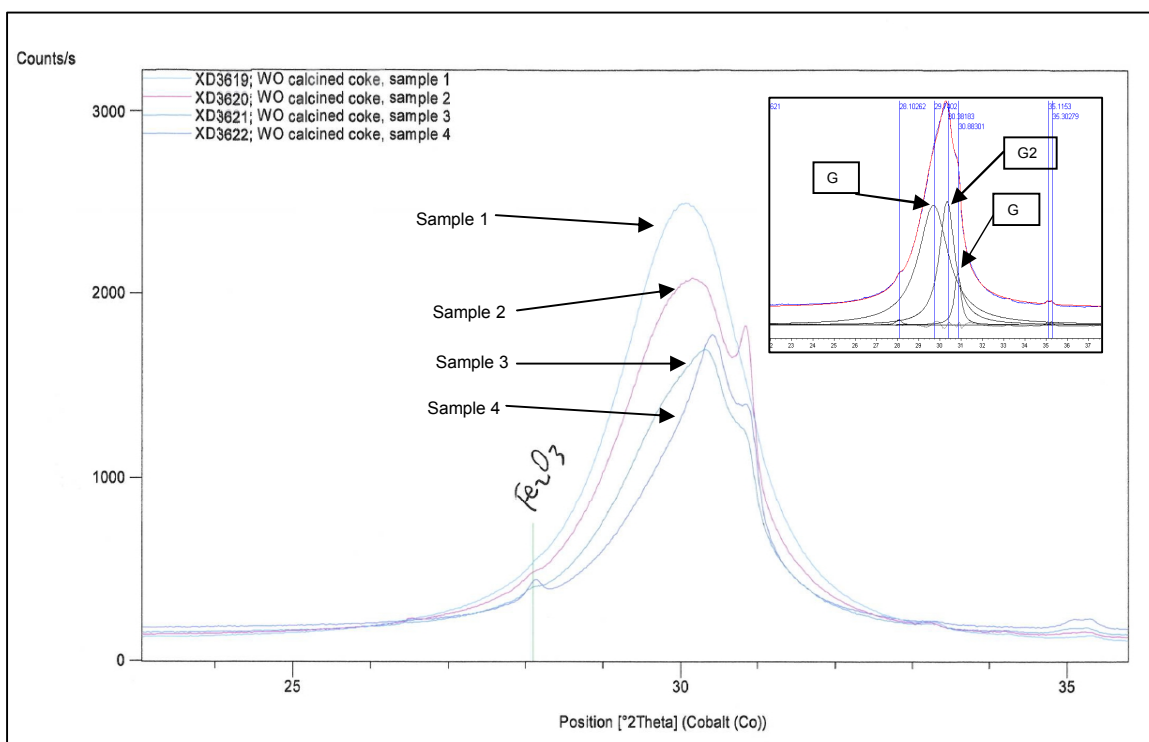

Figure 4 XRD trace showing peaks between a 2θ angle of 25 and 35° in the Waxy Oil calcined cokes. The insert shows the split of 3 overlapping peaks (indicated as G1, G2 and G3)
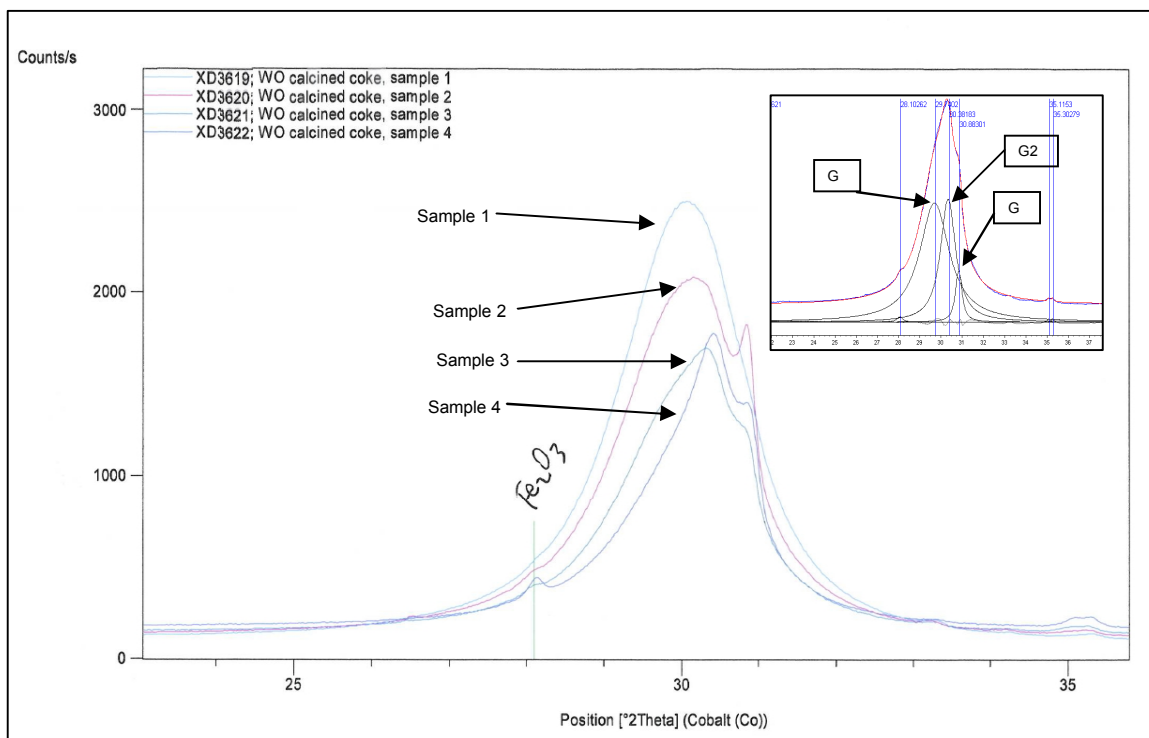
Figure 5 XRD trace showing peaks between a 2θ angle of 28 and 34° in the Waxy Oil pre-graphites. The insert shows the split of 3 overlapping peaks (indicated as G1, G2 and G3)

A description of the peaks to which random numbers **(G1, G2 and G3)** were ascribed uses terminology described in previous research [1, 6]:

- **Turbostatic or disordered graphite peak (G1):** This peak appears at a 2θ angle of 29.74 ° for the Waxy oil calcined coke vs. pre-graphite which appears at a higher 2θ angle of 30.31°. As G1 appears at the lowest 2θ angle of the three peaks and is the broadest it is thought to be a disordered carbon peak as previously reported [6]. Furthermore the interlayer spacing for the G1 peak of both the calcined coke and pre-graphite (Tables 4 and 5 respectively) is comparatively higher than for the G2 and G3 peaks which is in agreement with previous research [6]

- **Thermal graphite peak (G2):** This peak appears at a 2θ angle of 30.38 ° for the Waxy Oil calcined coke vs. the pre-graphite which appears at a higher 2θ angle of 30.55°. The thermal peak is indicative of the development of the crystal structure based on thermal treatment and dependant on the original anisotropy of the carbonised coke (450-500 °C) [18]. In terms of the interlayer spacing (d_{002}) of the G2 peak, (Tables 4 and 5 respectively) it appears lower than the G1 (d_{002}), which is ascribed to the higher anisotropic order, yet higher than the (d_{002}) for the G3 peak [6]

- **Catalytic graphite peak (G3):** This peak appears at a 2θ angle of 30.88° for the Waxy oil calcined coke vs. the pre-graphite which appears higher 2θ angle of 30.92°. As this peak is the sharpest yielding the lowest d_{002} interlayer spacing (Tables 4 and 5

respectively), it is suggested that it is due to catalytic graphitisation (as a result of the iron or iron oxide [1] content in the coke) which has previously been reported [1,6]

The slight increase of the 2θ angle and narrowing of the peaks (shown in the insert of Figures 4 and 5) from the calcined coke to the pre-graphite for G1, G2 and G3 is in agreement with previous research [6] and as a result of higher thermal treatment.

As a reference an XRD trace showing graphite peak between a 2θ angle of 20 and 40° in calcined needle coke is given in Figure 6. The insert shows the split of 3 overlapping graphite peaks (indicated as G1, G2 and G3).
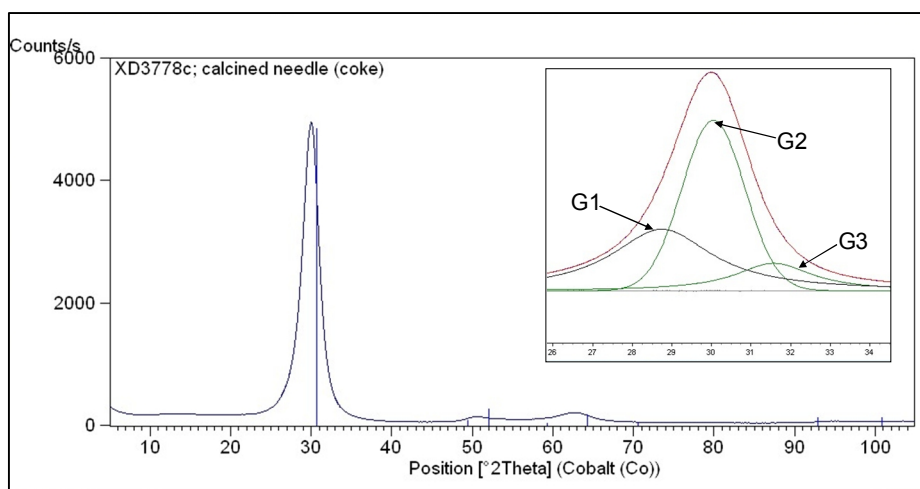

Figure 6 XRD trace showing peak between a 2θ angle of 20 and 40° in calcined needle coke. The insert shows the split of 3 overlapping peaks (indicated as G1, G2 and G3

The needle coke reference sample exhibits clear G1 and G2 peaks with a broad G3 peak, ascribed to the fact that the ash content is 0.058% and the iron content is 38 ppm.

A comparative table of the interlayer spacing (d_{002}) of the three graphite peaks (G1, G2 and G3) for Waxy Oil calcined cokes and the needle coke reference is shown in Table 4.

Table 4 Interlayer spacing (d_{002}) for peaks G1, G2 and G3 in the calcined coke

	Units	Sample 1	Sample 2	Sample 3	Sample 4	Needle coke
(G1) d_{002}	Å	3.504	3.488	3.485	3.483	3.650
(G2)d_{002}	Å	3.441	3.418	3.414	3.409	3.490
(G3) d_{002}	Å	3.376	3.359	3.360	3.359	3.330

Å= 1x10-10 m

The interlayer spacing of the G1 and G2 are higher in the needle coke reference than reported for any of the Waxy Oil calcined cokes. The interlayer spacing for the G3 peak is however lower than the Waxy Oil cokes. The interlayer spacing of G1 and G2 in the graphite region of the Waxy oil calcined coke decreases slightly with increasing catalyst content (Sample 1 to Sample 4; Table 4). It has previously been reported that the

presence of iron or it's oxides lowers the temperature at which graphitisation is initiated [5] lowering the interlayer spacing of the turbostatic (G1), thermal (G2) peaks irrespective of the microstructure [1,5-6], until saturation has been reached, which is agreement with the current results.

There is a decrease in the catalytic interlayer spacing (G3 d_{002}) from Sample 1 (3.376 Å) to Sample 2 (3.359 Å), after which the interlayer spacing of Sample 3 (3.360 Å) and Sample 4 (3.359 Å) essentially remain constant.

While the decrease in the interlayer spacing (G3 d_{002}) due to catalytic graphitisation has been linked to an increase in the concentration of iron in the carbon [1, 5], it is suggested that this may be highly dependant on the PSD of the catalyst and thus by default the surface area available for reaction. Previous research [1] does support the mechanism of an increase in catalytic graphitisation as a function of iron concentration, although it should be noted that that the iron oxide powder used was well dispersed and the PSD was 0.1-1.0 μm. This varies from the current study which indicates a heterogeneous dispersion of the catalyst with a lower surface area.

While the presence of inert obstructions to mesophase development is known to increase the interlayer spacing, specifically primary QI [2] and alkali metal carbonates [3], the influence of the catalyst barrier in the current study varies in that the iron acts as a graphitisation catalyst thus lowering the interlayer spacing.

A comparative table of the interlayer spacing (d_{002}) of the three graphite peaks (G1, G2 and G3) for Waxy oil pre-graphite is shown in Table 5.

Table 5 Interlayer spacing (d_{002}) for peaks G1, G2 and G3 in the pre-graphite

	Units	Sample 1	Sample 2	Sample 3	Sample 4
(G1) d_{002}	Å	3.371	3.429	3.417	3.422
(G2) d_{002}	Å	3.360	3.404	3.390	3.396
(G3) d_{002}	Å	3.355	3.357	3.354	3.357

Å= 1x10-10 m

In the pre-graphite, the interlayer spacing of the turbostatic graphite peak (G1 d_{002}) and the thermal graphite peak (G2 d_{002}) increase with an increase in the catalyst content from Sample 1 to Sample 2, after which (Samples 3 and 4), the interlayer spacing is lower, yet still higher than Sample 1.

The substantial decrease in the G1 and G2 interlayer spacing for Sample 1 compared with Samples 2-4, is related to the comparatively greater anisotropy and the effect of thermal treatment.

Raman spectroscopy on Waxy oil calcined coke and pre-graphite

The Raman spectra trace of the calcined cokes are shown in Figure 7 and the calculated ratios (R_1; R_1' and R_2) are shown in Table 6.
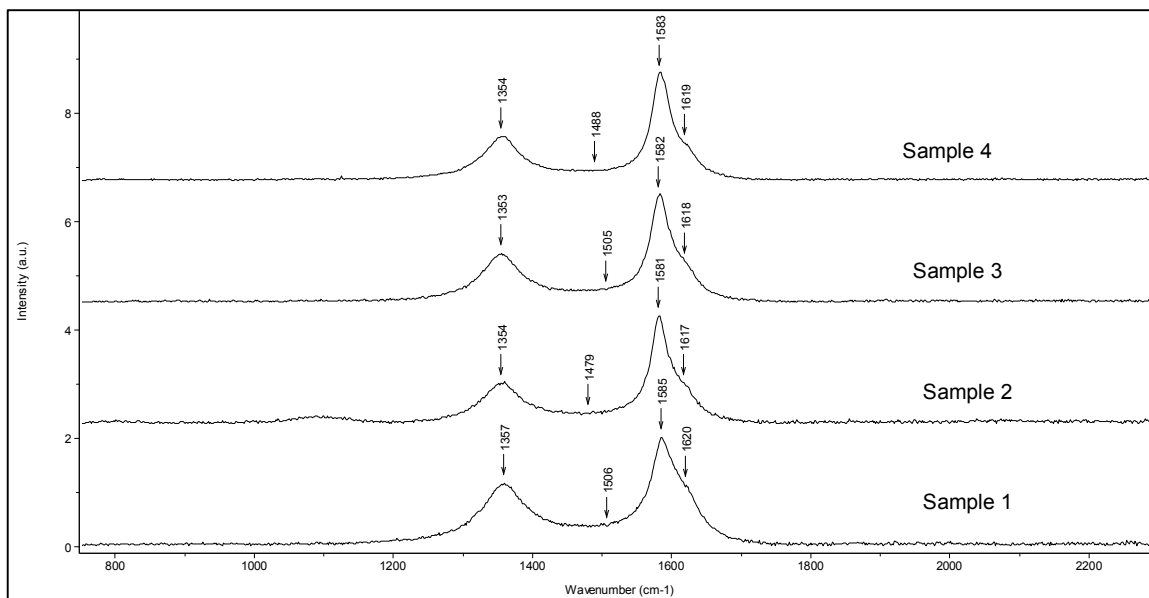
Figure 7 Raman spectra of Waxy Oil calcined cokes

Table 6 Comparative table of Raman spectrographic ratios (R_1, R_1' and R_2) for Waxy Oil calcined cokes

Ratio	Calcined coke				Reference carbon	
	Sample 1	Sample 2	Sample 3	Sample 4	Needle coke	Graphite
R_1	0.624	0.357	0.452	0.4	0.769	0.062
R_1'	0.332	0.203	0.195	0.169	-	-
R_2	0.319	0.229	0.275	0.255	0.435	0.058

R1 = *ID1/IG*

R1' = *ID2/IG*

R2 = *ID1/(ID2 + IG)*

The calcined coke samples all have large R_1 values (0.400-0.624), but "appear" more ordered in crystallographic structure than the calcined needle coke (used as a reference) which has the largest value of 0.769 (as shown in Table 5). As the R_1 ratio gives an indication of the overall crystallographic order and taking into consideration the low ash and iron content of the needle coke (Table 6), the effect on the general crystal ordering of the coke is evident. The trend towards lower R_1 ratios as the catalyst content increases is in agreement with the trend of the interlayer spacing for the deconvoluted peaks in the 002 region for the calcined coke. The graphite reference sample has effectively infinite graphitic domains as no D2 band was observed. For the calcined needle coke no separate D2 band could be observed and the broad band at 1602 cm^{-1} probably represents both the G and D2 band of calcined needle coke. Confident deconvolution was not successful due to the broadness of the band.

The Raman spectra of the pre-graphites is shown in Figure 8 and the calculated ratios (R_1; R_1' and R_2) are shown in Table 7.
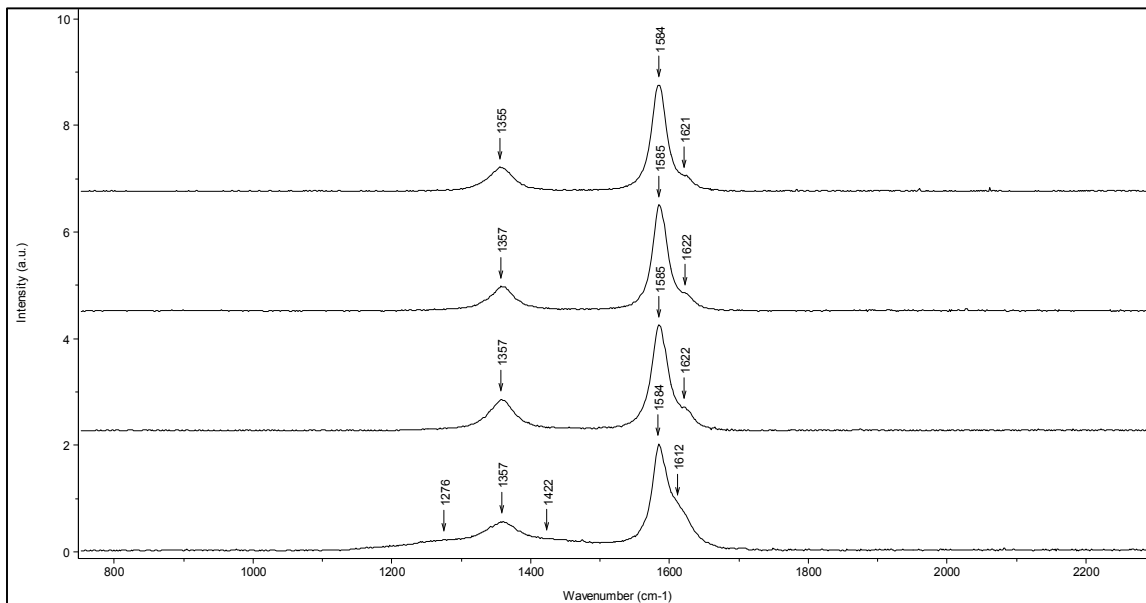

Figure 8 Raman spectra of Waxy Oil pre-graphites

Table 7 Comparative table of Raman spectrographic ratios (R_1, R_1' and R_2) for Waxy Oil pre-graphites

	Pre-graphite				
Ratio	Sample 1	Sample 2	Sample 3	Sample 4	Graphite
R_1	0.206	0.284	0.225	0.225	0.062
R_1'	0.321	0.118	0.086	0.074	-
R_2	0.135	0.203	0.172	0.173	0.058

$R_1 = I_{D1}/I_G$

R_1' $= I_{D2}/I_G$

$R_2 = I_{D1}/(I_{D1} + I_{D2} + I_G)$

The R_1 and R_2 ratio for the pre-graphites indicates a relative thermal ordering of the compared to the calcined cokes [17]. The highest crystallographic order is given by Sample 1, followed by a substantial decrease in Sample 2. The trend is in agreement with the trend of the interlayer spacing for the deconvoluted peaks in the graphite region for the pre-graphite (Table 5).

The same substantial decrease in the R_1 and R_2 value for Sample 1 vs. Sample 2-4 corroborates XRD evidence and is due to a higher temperature on the thermal and turbostatic graphite peaks.

The R_1 ratio indicates the same value, and the R_2 ratio indicates a slight decrease in the ordering of the crystal structure (Sample 3 compared to Sample 4). This again is related to possible saturation.

Discussion

The results of the study indicate that the effect of increasing catalyst content in the Waxy Oil coke is detrimental in terms of the microstructure, carboxy reactivity, ash content but not to the development of the crystal lattice. It also shows the difficulties in comparing the high ash Waxy Oil cokes with other anisotropic cokes (e.g. needle coke).

While an increase of the catalyst content reduces the anisotropy of the carbon microstructure, the variance of the catalyst particle size (0.5-78 µm) produces both a calcined coke and pre-graphite with a heterogeneous microstructure. The physical barrier presented to flow domains reduces the spatial vicinity within which the carbon microstructure is able to develop.

However, it is only when viewed from an industrial viewpoint that the significance of the catalyst content in the Waxy Oil coke can truly be appreciated. Highly anisotropic cokes (e.g. needle coke) rely on the thermal development of the crystallographic lattice, dependant on the microstructure. While the ash content of Waxy Oil coke is not only far in excess of the specified value for needle coke (0.2%) [12], the crystal ordering is dependant on an increase of the catalyst content. Both Raman spectroscopy and XRD results indicate that both the thermal and turbostatic graphite peaks of the calcined needle coke are less developed than the Waxy Oil calcined cokes. Thus, the graphatisability of the Waxy Oil calcined cokes is higher than the needle coke reference sample and is for the most part independent of the anisotropy of the coke.

In the calcined form, the crystal development of Waxy Oil coke is dominated by catalytic graphitisation, reducing the interlayer spacing and crystal order of the thermal and turbostatic peaks, which is in contrast to the dependence of crystal development on the anisotropy and thermal history of a coke with low ash needle or anode cokes [19]. It is only with increased thermal treatment that the crystal development of the Waxy Oil coke appears to revert to a dependence on the microstructure with lower ash contents. It is furthermore important to consider the effect of the larger PSD of the catalyst of the Waxy Oil by increasing the ability to affect the order at higher catalyst contents due to a lower surface area. Therefore it is understandable that while previous authors have reported the effect of iron on catalytic graphitisation to be saturated at 1% [5], it should be noted that the PSD of the iron was considerably smaller (0.1-1.0 µm) and thus had a much higher surface area. It is thus only possible to compare a Waxy Oil coke with a needle coke were the catalyst removed before coking.

In respect of the real density, the high ash Waxy Oil cokes negate the effect of microstructure which is in direct contradiction of the effect of anisotropic order on the real density in needle cokes. The carboxy reactivity of the cokes is one of the reasons for

the lower calcination yield of the Waxy Oil coke due to the catalytic effect of calcium and iron.

Conclusions

Conclusions drawn from the current study of commercial Waxy Oil coke include:

- The microstructure of Waxy Oil calcined coke is dominated by elongated flow domains at lower catalyst concentrations. With increasing catalyst content the carbon microstructure is occluded by the matrix of catalyst agglomerates. The catalyst provides a barrier around which the domains form thus reducing the anisotropy
- The development of the crystal structure in the Waxy Oil calcined cokes is dominated multiphase graphitisation, more specifically by dominance of iron based catalysis
- The development of the crystal structure of the pre-graphite indicates both a dependence of thermal and catalytic ordering.
- The development of the Waxy Oil crystal structure cannot be directly compared with low ash anisotropic cokes (e.g. needle coke) due to the substantial variance by which the crystallographic structure is developed
- The carboxy attack on the Waxy Oil calcined coke increases as a function of an increased catalyst content due the catalytic effect of iron and calcium
- The partial reduction of the catalyst in the calcined coke and complete reduction in the pre-graphite further increase the carbon loss by reaction with released oxygen to form carbon monoxide
- The real density of the green and calcined Waxy Oil coke is dependant on the ash content. The real densities of the Waxy Oil coke (dependant on the ash content) and that of needle coke (dependant on the microstructure) can thus not be compared
- In order for the Waxy Oil coke to be compared to a needle coke, the catalyst would need to be removed prior to delayed coking
- The anisotropy and low heteroatom content of the Waxy Oil cokes would be beneficial in the development of artefact cokes provided that the ash content could be reduced.

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