

# THE EFFECT OF AN IRON OXIDE CATALYST (Fe<sub>3</sub>O<sub>4</sub>) ON THE CHARACTERISTICS OF WAXY OIL COKE

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## Introduction

Waxy Oil coke is produced by commercial delayed coking of Waxy Oil produced at Sasol Synfuels (Secunda, South Africa). The Sasol Synthol reactors produce hydrocarbons from synthesis gas (hydrogen and carbon monoxide) by the Fischer-Tropsch reaction; the distillation of which produces a heavy residue bottoms product namely Waxy Oil, which forms an anisotropic coke. The quality of the Waxy Oil coke is periodically affected by high catalyst content (Fe<sub>3</sub>O<sub>4</sub>) in the feed to the delayed coker. Increasing the iron oxide concentration has been reported to decrease the anisotropy of the coke either acting as a physical barrier or promoting oxidative polymerisation [1]. 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 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 disordered carbon [2; 3]. Increasing the iron oxide concentration in coke is also known to be a catalyst for carbon dioxide reactivity reducing the carbon yield during calcination [5-7]. The object of the investigation is to determine the effect of the catalyst on the Waxy Oil coke with reference to current and potential future applications

## Experimental

Four samples of Waxy Oil green coke (with varying catalyst content) were obtained from the Sasol Synfuels delayed coker in Secunda (South Africa). The four Waxy Oil green coke samples were thermally treated to 1400 °C (2-10 mm; approximately 350 g; nitrogen atmosphere in a muffle oven at 5 °C.min<sup>-1</sup>) to produce calcined coke and to 2000 °C (approximately 17 g; -2.0 mm; in an argon atmosphere using a medium frequency induction furnace) to produce pre-graphite.

Optical microscopy of the four calcined cokes was conducted by mounting the samples in epoxy resin and examined under 500x magnification (oil immersion) using a Leica DM4500P

petrographic microscope with polarised light but without a lambda plate.

All other analyses were conducted according to ASTM standard methods. The real density was conducted using a Micro-metrics AccuPuc 1330 pycnometer in helium using a coke size fraction of - 75 μm.

X-ray powder diffraction data was collected using a Phillips X'pert Pro multipurpose 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<sub>α</sub> 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 HighScore Plus version 2.2d PANalytical software.

Raman spectroscopy was conducted by placing the samples 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<sup>-1</sup> 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. 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.

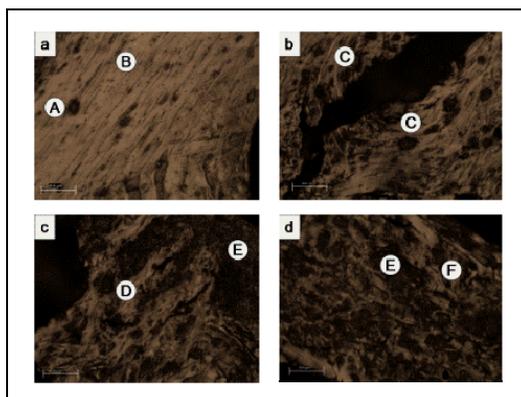
## Results and Discussion

Table 1 shows ash content and iron concentration of the calcined cokes. With increasing ash content, the CO<sub>2</sub> reactivity increases as previously reported as both iron and calcium act as catalysts [5-7]. The real density increases as the ash content increases showing an acceptable linear correlation coefficient (R<sup>2</sup>= 0.9862) due to the effect of the catalyst size (-78 μm), being retained in the particles.

**Table 1 Effect of the catalyst content on the ash content, iron content, CO<sub>2</sub> reactivity and Real density of Waxy Oil calcined coke**

Analysis	Units	Sample 1	Sample 2	Sample 3	Sample 4
Ash	Mass %	3.016	5.420	8.658	13.511
Iron	Mass %	1.8365	2.6882	3.7474	4.7624
Calcium	Mass %	0.0931	0.1380	0.1473	0.1521
CO <sub>2</sub> reactivity	Mass%. 100min <sup>-1</sup>	69.78	77.88	81.13	87.02
Real density	g.cm <sup>-3</sup>	2.1024	2.1087	2.1124	2.1220

The influence of the ash content on the microstructure of the calcined coke is shown in Figure 1.



**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. Magnification x500

The effect of an increase in the catalyst concentration is to decrease the overall anisotropy of the Waxy Oil calcined coke (Figure 1). Nomenclature used to describe the carbon microstructure has been sourced elsewhere [8]. The optical anisotropic texture decreases from acicular and elongated flow domains (Position B), to elongated coarse flow (Position C) to elongated medium flow (Position D) and finally to coarse grained mosaic (Position F). The density and size of the catalyst agglomerate increases from 6  $\mu\text{m}$  diameter (Position A) to irregular sizes of over 20-60  $\mu\text{m}$  (Position E).

The XRD trace of the calcined coke shows 3 overlapping peaks in the 002 region of the samples; identified as (i) disordered (ii) thermal and (iii) catalytic. Increasing the catalyst concentration decreases the interlayer spacing of the disordered (3.504 to 3.483  $\text{\AA}$ ) and thermal (3.441 to 3.409  $\text{\AA}$ ) graphitic peaks mentioned above which is in agreement with previous work [3]. The interlayer spacing of the catalytic 002 peak is higher for Sample 1 (3.376  $\text{\AA}$ ) however reducing and remaining stable (3.359 to 3.360  $\text{\AA}$ ) from Sample 2-4. Raman spectroscopy data also indicates an increase in the overall ordering of the crystallographic structure as the catalyst concentration increases ( $R_f$  ratio: 0.624 to 0.400). The  $R_f$  ratio of the four calcined coke samples is lower than for the needle coke (0.769) reference used which had significantly lower ash content, indicating a more ordered carbon.

The XRD trace for the pre-graphite showed the same three overlapping peaks as identified for the calcined coke. However, the interlayer spacing of the disordered and thermal graphite peaks with the lowest catalyst concentration was the lowest (3.371 and 3.360  $\text{\AA}$  respectively). As the catalyst concentration increased so did the interlayer spacing of both the disordered and thermal graphite peaks (3.422 and 3.396  $\text{\AA}$

respectively) until saturation was reached. The interlayer spacing of the catalytic graphite peak remain stable (3.354-3.357  $\text{\AA}$ ) irrespective of a catalyst increase. The Raman spectroscopy data indicates an increase in the  $R_f$  ratio from 0.206 to 0.225 as the catalyst concentration increased.

## Conclusions

Increasing the catalyst concentration of Waxy Oil calcined coke increases the carboxy reactivity and the real density. The anisotropic microstructure of the calcined coke is reduced by increasing the catalyst content, however due to the variance in the size, the catalyst acts more as of a physical barrier to mesophase development. The development of the crystal structure in the Waxy Oil calcined cokes is dominated by multiphase graphitisation, more specifically by the dominance of iron-based catalysis. The development of the Waxy Oil calcined coke 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 development of the crystal structure of the pre-graphite indicates both a dependence on thermal and catalytic ordering. In order to correlate the Waxy Oil coke with an anisotropic coke (e.g. needle coke) the catalyst would need to be removed prior to delayed coking.

## References

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