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DELAYED COKING OF SOUTH AFRICAN PETROLEUM HEAVY RESIDUES FOR THE PRODUCTION OF ANODE GRADE COKE AND AUTOMOTIVE FUELS

John Graham Clark

A dissertation submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, in fulfilment of the requirements for the degree of Master of Science in Engineering

Johannesburg, 2008

DECLARATION

I declare that this dissertation is my own unaided work. It is being submitted to the Degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University

……

(Signature of Candidate)

……. day of …… year……
(day) (month) (year)

ABSTRACT

A laboratory scale delayed coking process was used to produce petrol precursors, diesel precursors, methane rich gas, green and calcined coke from five previously untested South African heavy petroleum residues.

The ash content of the heavy petroleum residues was found to be detrimental to the microstructure of the green coke and Coefficient of Thermal Expansion (CTE) of the calcined coke. The sulphur content of the calcined cokes produced was found to be in-line with typical global anode grade cokes. De-ashing of the feedstock would be necessary to produce anode grade fillers for the aluminium industry. The local production of anode grade coke would serve to reduce imports and supply the aluminium smelters on the east coast of South Africa.

The heavy petroleum residues (also known as heavy fuel oil) are currently used as bunker fuel in the shipping industry and are responsible for substantial air pollution. Delayed coking of these residues could extend the production of petrol and diesel per barrel of imported crude oil and reduce the effect on South Africa's balance of payments deficit and impact the environment in a beneficial manner with respect to carbon dioxide and sulphur emissions.

The research also evaluated the replacement of heavy fuel oil with marine diesel produced by delayed coking of the former. Marine diesel was found to emit less sulphur oxides and have a higher energy density per unit of carbon dioxide emitted. While seawater scrubbing of the heavy fuel oil would be more cost effective in reducing the sulphur oxide emissions, it would not contribute to carbon dioxide reductions. The research created a hypothetical scenario to determine the required value of Clean Development Mechanism credits for a marine diesel replacement, were shipping to be incorporated under the Kyoto Protocol in future.

DEDICATION

Dedicated to my wife

Karen Clark

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LIST OF SYMBOLS AND ACRONYMS

Technical abbreviations	Description	Units
mm	Millimetres	$x10^{-3}m$
µm	Micrometres	$x\ 10^{-6}m$
Å	Angstrom	$x10^{-10}m$
d_{002}	Graphite interlayer spacing	$x10^{-10}m$
L_c	Graphite layer height	$x10^{-10}m$
L_a	Graphite layer width	$x10^{-10}m$
ppb	Parts per billion	µg/kg
ppm	Parts per million	mg/kg
MJ	Mega Joules	$1\ x\ 10^{6}$ Joules
GJ	Giga Joules	$1\ x\ 10^{9}$ Joules
TJ	Terra Joules	$1\ x\ 10^{12}$ Joules
Apparent Density (Hg)	Apparent Mercury density	$g.cm^{-3}$
Real (He) Density	Real Helium Density	$g.cm^{-3}$
VCM	Volatile Carbon Matter	mass %
OTI	Optical Texture Index	
CTE	Coefficient of Thermal Expansion	$x\ 10^{-6}$ / ºC
QI	Quinoline Insolubles	Mass %
TI	Toluene Insolubles	Mass %
MSP	Mettler Softening Point	º C
Bbl	Barrel (Crude Oil)	159 Litres
Mbbl	Mega Barrel	$1\ x\ 10^{6}$ Barrels
XRD	X-Ray Diffraction	Å

NOMENCLATURE

Financial Acronyms	Description
Capex	Capital Expenditure
IRR	Internal Rate of Return
PPI	Producer Price Index
V.R.O.O.M	Very Rough Order Of Magnitude
ZAR	South African Rand

Miscellaneous Acronyms	Description
ASTM	American Society for Testing and Materials
CDM	Clean Development Mechanism
DEAT	Department of Environmental Affairs and Tourism
DNA	Designated National Authority
EIA	Environmental Impact Assessment
GC-MS	Gas Chromatography - Mass Spectrometry
HFC	Hydro Flouro Carbon
HGI	Hard Grove Index
HPLC	High Performance Liquid Chromatography
IMO	International Maritime Organisation
ISO	International Organisation of Standardisation
MDC	Mini Delayed Coker
MERC	Mobile Emission Reduction Credits
PFC	Per Flouro Carbon
SEM	Scanning Electron Micrograph
WAI	World Aluminium Institute
WHO	World Health Organisation

CONFIDENTIALITY NOTICE

The research for this dissertation was conducted by John Clark (Sasol Synfuels Marketing) and Sasol Technology (Research and Development) Division. Ownership of the research and all intellectual property pertaining to the research has been transferred to Leswikeng Carbon.

In terms of the confidentiality agreement the author is not permitted to make specific reference to the concerned refineries or feed streams used during the course of this research, unless said information is already a matter of public knowledge.

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1 Introduction

1.1 Background to the investigation

The global demand for sustainable sources of energy to "fuel" the growth of the automotive transportation sector has necessitated a search for viable alternative sources for the production of both petrol and diesel. While significant advances have been made in the conversion of natural gas, coal and biomass into liquid fuels, South Africa is and will remain (at least for the foreseeable future) a net importer of crude oil.

Crude oil is composed of various hydrocarbon fractions and is distilled to recover valuable products according to a range of molecular weights (e.g. petrol and diesel). The heavier bottom fraction of crude oil is usually sold into the burner fuel or bunker fuel market (for shipping) as a Heavy Fuel Oil (HFO). Thus only a fraction of the crude oil refined can be distilled to serve the automotive fuel market. It is however possible using a process called delayed coking to crack the heavy petroleum residues to lighter products, thereby supplementing the production of automotive fuels and producing a solid carbon called coke.

The potential also exists for delayed coking to supply the South African aluminium industry with a local source of anode coke, which is used for the electrolytic reduction of alumina.

A delayed coking plant may be operated in two modes:

- ***White product*** mode: The delayed coker is operated under conditions that would maximise the production of petrol and diesel precursors and produce a fuel grade green coke. These conditions would include higher feed rate, higher temperature and lower pressure. Fuel grade coke is used as a solid burner fuel and thus not calcined. Fuel grade coke is discussed in Chapter 2.3.1
- ***Carbon*** mode: The delayed coker is operated under conditions that would promote the formation of a sponge coke (for use in the aluminium industry) producing less petrol and diesel precursors. These conditions would include lower federate, lower temperature and higher pressure. Sponge coke is discussed in Chapter 2.3.1

Heavy petroleum residues are currently sold as bunker oil into the shipping industry and are responsible for significant Sulphur Oxide (SO_x) and Carbon Dioxide (CO_2) emissions. The shipping industry will in future be forced to reduce the sulphur content of the bunker oil to comply with international maritime regulations (Einemo, 2007; Hammingh, 2007).

1.2 Problem statement

The South African economy is largely dependant on the availability of automotive fuels to service the significant growth of the automotive industry. The number of

registered motor vehicles on South African roads has increased from 6.5 million (in the year 1994) to 8.5 million (in the year 2006) (Botha, 2008). Crude oil imports have put significant strain on the balance of payments (current account) and there are plans to build a new refinery in Port Elizabeth (Reuters, 2007) to sustain the supply of liquid fuels.

The capital estimate for this refinery which will produce 200 000 barrels per day is estimated at 39 billion ZAR (Reuters, 2007). Given the trend towards higher oil prices, it is evident that South Africa will need to utilise her natural resources (e.g. coal) and extend the production of automotive fuels per tonne of crude oil, in a manner which would promote self sustainability.

A similar crisis looms within the aluminium industry on the East coast of Southern Africa. South Africa presents an attractive investment opportunity for aluminium smelters due to the competitive cost of electricity and labour. As a result, the Southern African demand for anode coke has grown significantly to 490 000 tonnes with potential growth to 800 000 tonnes per annum (Milne, 2007). This demand presents challenges, given the state of the global anode coke supply market. The most serious challenges pertain towards an alarming trend of increasing sulphur and vanadium contents in the coke (Meier, 2006). Coupled to this are increased sea freight charges (relating to the increase of the crude oil price).

As much of the calcined coke is sourced from the Gulf of Mexico, climatic phenomena (e.g. Hurricane Katrina) within the region have severely disrupted continuous supply. The result of all these challenges is seen in an escalation of the production cost of aluminium and thus conversely a reduction of the profit margins. As is common within commodity carbon price cycles, the increase in the price of aluminium has further resulted in an increased price for imported anode coke.

The quality of any coke produced by delayed coking in the ***Carbon*** mode is inherently dependant of the quality of the feed material, thus only certain petroleum heavy residues can produce anode grade quality coke. This coke quality is dependant on the molecular composition and ash content of the delayed coker feed which in turn governs the kinetics of the coking reaction and the coke microstructure. The coke microstructure controls the electrochemical and mechanical characteristics of the coke inclusive of the Coefficient of Thermal Expansion (CTE). Coupled with the ash and sulphur content, this determines the potential for any candidate anode coke in the aluminium industry. As the reaction chemistry of the five petroleum residues has previously not been tested, the quality of the delayed coker products is unknown.

Meanwhile, in a related petroleum industry, South African refineries currently produce significant quantities of heavy residues which are sold into the bunker fuel market for use in the shipping industry. Quite apart from the fact that the combustion of these residues is energy inefficient, the sulphur content of crude oil is known to concentrate in the heavier residues and thus is released into the atmosphere as SO_x, serving to further exacerbate the environmental challenges especially over global shipping waters (Einemo, 2007).

1.3 Hypothesis

The author proposes a hypothesis that South Africa is not exploiting the potential of the heavy petroleum residues available and that delayed coking will in part serve to **unlock** the value of these resources to service local demand for anode coke and automotive fuels.

1.4 Objectives of the investigation

1. Five heavy petroleum residues were obtained from South African refineries. A process called delayed coking with calcining was used to convert these residues into:

    - Methane rich gas
    - Naphtha (petrol precursor)
    - Coker gas oil (diesel precursor)
    - Calcined anode coke

2. The major objective of this dissertation was to evaluate the calcined coke produced as a candidate for the anode coke market

    Given the significant increase in the crude oil price over recent years, economics would dictate that the ***White product*** mode is adopted. As the drive behind this dissertation was to evaluate the quality of calcined coke which may command a value of $ 250-350 per tonne (Mannweiler, 2008a) for the anode market, experiments were conducted in the ***Carbon*** mode.

3. As the five heavy residues varied with respect to their origins, an objective was to evaluate the effect that feedstock variables (cited in literature) have on the quality of the coke and how this pertains to the anode coke industry. These variables include:

    - The effect of the ash content on the green coke microstructure (Obara and Marsh, 1985; Junji, 1993)
    - The catalytic effect of vanadium and nickel contents in the presence of sulphur, on the green coke microstructure (Oi and Onishi, 1978)
    - The effect of liquid and gas yields on the porosity of the green coke
    - The effect of macro-pore morphology on the CTE value of the calcined coke (Hulse, 2000)
    - The effect of green coke microstructure on the calcined coke CTE (Stadelhofer, 1981; Clark and Chang, 2001)

4. One of the objectives was to graphitise the green coke and study the development of the crystal structure and a reduction of the sulphur content. Delayed coking in the ***Carbon*** mode could be more financially viable were the resultant cokes produced of a quality to be placed into value added markets.

5. It is the author's opinion that the contribution of any technical research concerning delayed coking of high sulphur petroleum residues would be flawed were it not to mention the potential affect on the environment. The research thus examines the potential of delayed coking firstly, to act as a sulphur "sink" and proposes a novel idea whereby diesel produced by delayed coking of the heavy residues could be used to reduce the sulphur content of bunker fuels. The research further introduces the potential of this practice to reduce CO_2 emissions in the shipping industry to be registered as a CDM project.

6. As there is only one delayed coker and calciner in South Africa, a comprehensive understanding of this branch of science is not widespread. In order for the research presented to have relevance to a wider audience, the introductory chapters explain the theory behind this technology. Furthermore, in order to evaluate the potential contribution of the delayed coker petrol and diesel to South Africa's fuel pool, the state of automotive fuel production in South Africa is examined in detail.

1.5 Scope of the investigation

The scope of the dissertation is limited to industries which would be directly affected by the delayed coking of the available heavy residues.

A detailed scope of the investigation includes:

- Delayed coking : A historical perspective
- A description of the tar value chain
- An empirical description of industrial delayed coking and calcining
- A description of the chemistry associated with delayed coking, calcining and graphitisation
- An analysis of the demand market for automotive fuels in South Africa
- An analysis of crude oil imports into South Africa and the effect on the balance of payment deficit
- A market analysis for anode grade coke within Southern Africa
- Global supply and demand trends for anode grade coke
- Global trends with respect to the quality of anode grade coke
- A description of the experimental procedures utilised to produce delayed coke
- Discussion of the experimental results as they pertain to the **process and product chemistry:**
    - The quality of the feedstock
    - The delayed coker and calciner yields
    - The influence of feedstock chemistry and microstructure on the physical characteristics of calcined coke
    - Quality evaluation of the petrol and diesel precursors
    - Quality evaluation of the methane rich gas
    - The influence of blending feedstocks on the coke chemistry
    - The influence of graphitisation on the coke microstructure and chemistry

- A discussion of the experimental results as they pertain to **industry**:

    - A hypothetical estimation of the expected commercial product yields
    - The hypothetical economics of delayed coking, calcining and particle graphitisation based on a model developed
    - A sulphur balance over the delayed coking process
    - An examination of bunker fuels used in the shipping industry with respect to environmental CO_2 and SO_x emissions
    - The potential role of diesel produced by delayed coking in increasing the energy density per unit CO_2 emitted as compared to combustion of the heavy petroleum residues
    - A reduction in the SO_x emissions from bunker fuels by utilising delayed coker diesel as opposed to combustion of the heavy petroleum residues.
    - The use of a hypothetical future scenario which examines the economic validation of a fuel switch mechanism based both on CO_2 and SO_X reduction

2 DELAYED COKING AND CALCINING

2.1 Delayed coking – a historical perspective

Petroleum coke was first reported to have been produced in North-Western Pennsylvania in the 1860's. Utilising what by modern standards would seem somewhat primitive methods, petroleum oils were boiled in wood fired iron stills to recover kerosene. As the reaction cooled, coke was removed from the bottom of the reaction vessel (Ellis, 1998)

The 1920's saw the introduction of a tube furnace with distillation columns. This mode of coking was in operation until after World War II. The removal of coke from the still was arduous with labourers having to use picks, shovels and wheel barrows.

It should be realised that crude oil refining was also to a degree in its infancy (the process of de-salting had not yet been refined) and as all the ash components reported to the coke, the ash content thereof was typically high (1%) as compared with today's standards (0.2%).

Delayed coking during these "infancy periods" was used exclusively for the production of lighter more valuable oils and the coke was considered a waste product which had nominal value as a solid heating fuel (Ellis, 1998). Delayed coking in the ***White product*** mode is still guided by much the same paradigm.

The first use of vertical drum delayed coking was developed between 1912 and 1935 by Standard Oil for conversion of heavy gas oil to gasoline (petrol and diesel). The challenge of cutting coke from the coke drum was exacerbated by the fact that friction could cause a fire and thus was a safety hazard. This hazard was negated in the 1930's when the procedure of cutting the coke with a water jet was invented by Roy Dewoky (Ellis, 1998).

Through a myriad of technical improvements including the control of pressure, temperature and the use of various drums, the delayed coking process gained popularity leading to a surge of construction in the period between 1955 and 1975. Delayed coking was also the preferred process for inland petroleum refiners where the transport costs of the heavy residue (bunker fuels for the shipping industry) was not economical (Ellis, 1998).

It is indicative of the sentiment relating to delayed cokers, that with the advent of fluid and flexi coking the future of the delayed coker was seen to be in demise. The drive for the production of cracked oils from heavy residues, with little heed paid to the quality of the coke, drove the fluid / flexi coking industry, due to the fact that the lighter oils were recovered and the coke was gasified (Onder, 1997).

However, delayed coking today survives as the only commercially viable method of maximising the value of heavy petroleum residues both for the production of distillate oils and anode coke.

Delayed cokers that operate with the express purpose of producing both needle and sponge cokes are in the distinct minority. This historical practice has been driven by the fact that, apart from needle coke, it was and still is more economically viable to maximise ***White product*** production.

2.2 Understanding of the tar value chain

A working knowledge of the tar value chain is essential to understand the nature of delayed coker products and their respective markets. A basic description is given below with a corresponding schematic in Figure 2-1.

Within a petroleum refinery, crude oil is distilled to recover valuable diesel and petrol fractions. The bottoms fraction of these residues (referred to as HFO, pitch or bottoms) contain significant concentrations of aromatic macro molecules, whose use is, for the greater part, limited to burner and bunker fuel markets. It is however possible to further modify these aromatic macro molecules for the production of lighter organics (petrol and diesel) and a solid organic matrix (green coke) utilising the process of delayed coking conducted at a temperature range of 460-500 °C.

The origin, chemical and physical nature of the heavy residue has a significant affect on the structure and performance of the green or calcined coke. The calcination of green coke usually occurs at 1300 to 1400 °C and removes entrained lighter organic compounds as well as modifying the microstructural order of the carbon lattice. Calcined coke can (depending on quality) be sold to the aluminium market. The methane rich gas produced by delayed coking may be used to fire the calciner.

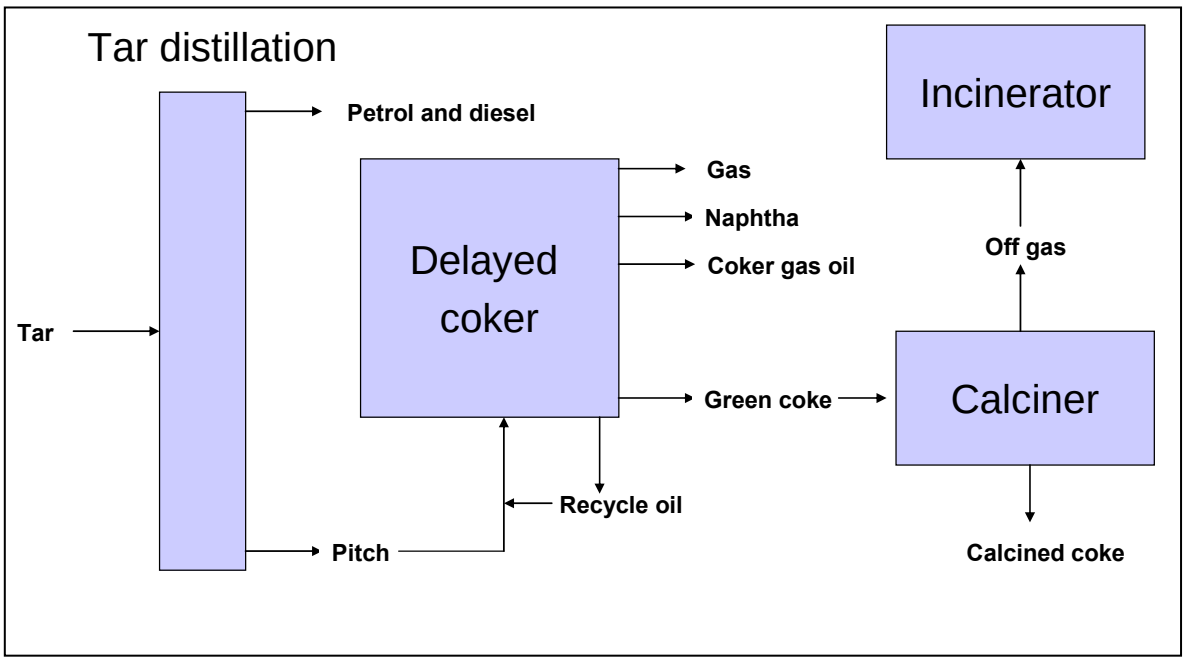


Figure 2-1: Schematic of the basic tar value chain

2.3 Commercial delayed coking and calcining

Delayed coking is described as:

"…an important refinery process which can economically upgrade the bottom of the barrel pitch material" (Marsh, 1997)

Delayed coking (460-500 ºC) is a refinery process that converts heavy residue streams into:

- White products - petrol and diesel precursors
- Methane rich gas
- Green coke

Delayed coking describes the upgrading "bottom of the barrel material" or "refinery waste" and has been commercially practiced since the early 20th century to "squeeze" the last "drops of value" from refinery bottoms. The kinetics of the delayed coking reaction are affected both by the quality of the crude oil and the nature of refinery processes which modify the component composition of a particular heavy residue stream. Given in Figure 2-2 is a simplified schematic flow diagram of a petroleum refinery.

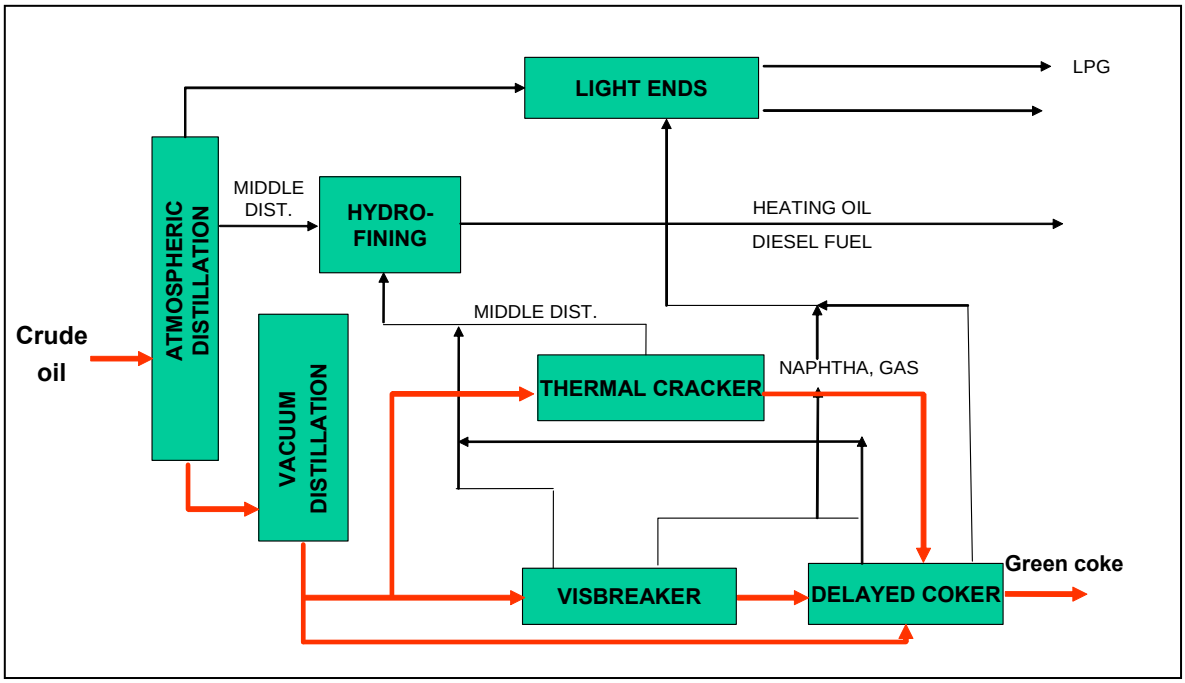


Figure 2-2 Simplified flow diagram of a petroleum refinery (Meier, 2006)

2.3.1 Types of commercial delayed cokes:

Green coke is the descriptive name for any type of coke produced in a delayed coker. If a coke is calcined it is usually named according to either its visual appearance or market in which it is utilised:

Fuel grade green coke:

Fuel grade green coke comprises the majority of global green coke production (68 million tonnes per annum) (Driscoll, 2007). This coke is not calcined as it contains an elevated sulphur and metals content. It is used as a fuel and thus any volatiles increase the calorific value thereof.

Fuel grade coke is typically produced when the delayed coker is run in the ***White product*** mode, meaning that the delayed coker process is run to maximise the production of petrol and diesel products. The delayed coker is operated at high feed throughput rates, high temperature (to maximise the cracking of distillate components), low recycle rates and low system pressure. One of the major uses for this grade of coke is as a fuel in cement production.

Green shot coke:

The production mechanism of shot coke is not fully understood. It is the product of coking heavy asphaltic residues, low recycle ratios and forms as small hard round pellets, although the diameter thereof has been known to exceed 30 cm. The name is believed to derive from the term “buck shot”, which describes hard round pellets used as ammunition in a specific type of rifle. If a cross-section is taken of shot coke it reveals an onion like structure. It usually forms at the bottom of a coke drum and is a safety hazard when opening the reactor.

It has a negligible value although it is used as filler in the furnace beds of aluminium plants and as a catalyst in titanium dioxide plants. The microstructure of this coke is highly isotropic and it is extremely hard. Shot coke usually forms within the matrix of either sponge or fuel coke and not as a separate entity, thus assigning it a market value is difficult.

Calcined sponge coke:

Sponge coke is given its name due to its visual resemblance to a sponge. The coke has a large visible amount of macro-porosity and is usually sold to the aluminium industry as filler for anodes. All the five samples (A–E) evaluated during the current research project produced sponge coke. The green sponge coke is generally sold to calciners for devolatilisation and densification. Sponge coke is anisotropic with a market value of approximately $ 250-350 per tonne (Mannweiler, 2008a).The market value is highly dependant on the ash content, sulphur content and freight costs.

Calcined needle coke:

Needle coke is so named by virtue of its visual resemblance to a set of vertically aligned needles. It is by far the highest value coke and is usually produced from highly aromatic feedstock inclusive of Fluidised Catalytic Cracker Decant Oil (FCCDO), coal tar pitches or synthetic pitches (produced in ethylene crackers). The two main criteria for these cokes are the Coefficient of Thermal Expansion (CTE) (below $1x10^{-7}$/°C) and the sulphur content (less than 0.3%). It is used in the production of graphite electrodes for steel production furnaces. Needle coke is highly anisotropic and has a market value which is equal to approximately two to three times the value of anode coke.

2.3.2 Commercial delayed coking

The terminology "delayed" refers to the fact that there is a delay between the time of onset of the coking reaction in the heater tubes and when coke laydown actually occurs in the coke drums. An empirical flow diagram is given in Figure 2-3. A delayed coker may be split into three functional areas

- Storage – Storage tanks for heavy residues
- Reaction unit – Heat exchangers and the heater furnace
- Recovery unit – Recovery of coke in the reactor drums and white products in the fractionator (distillation column)

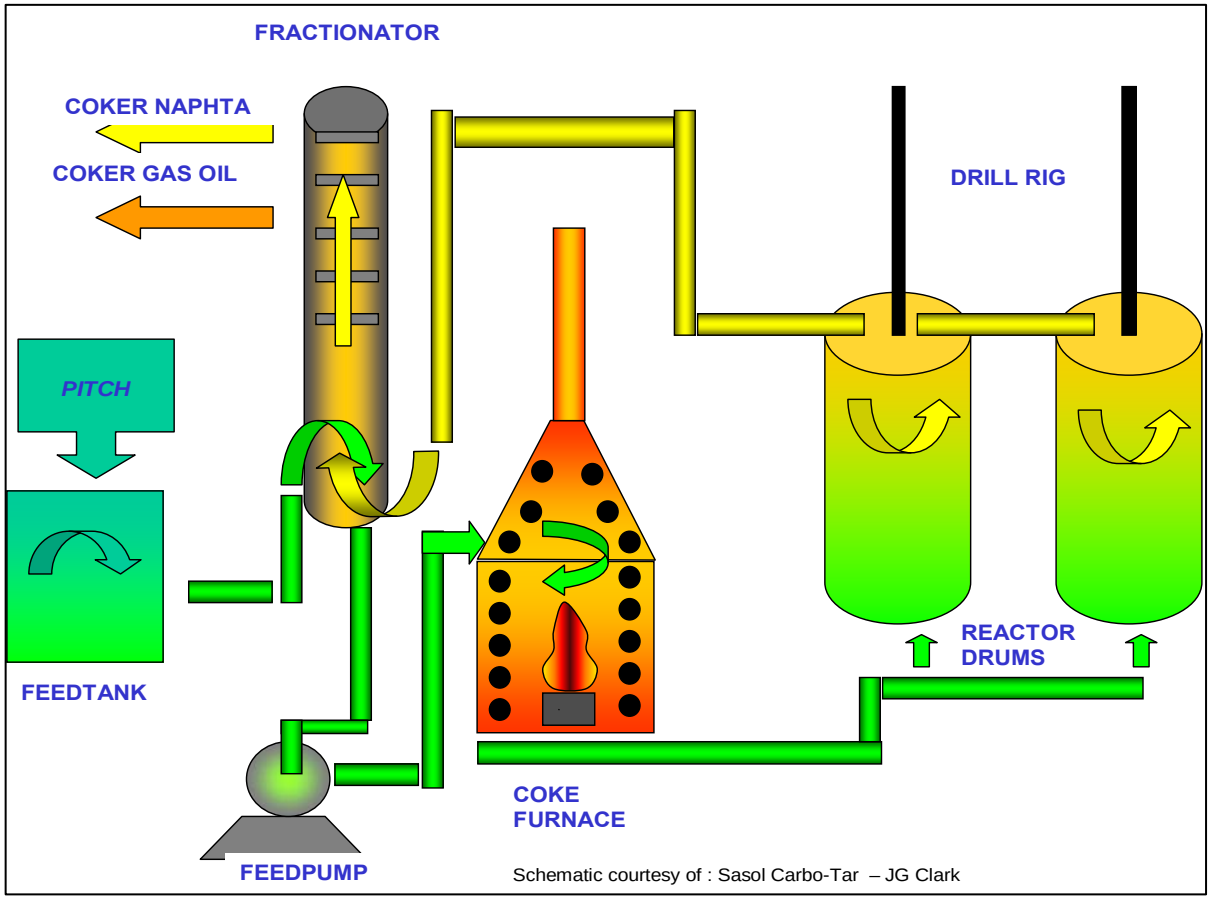


Figure 2-3 Empirical flow diagram of a delayed coker (Clark, 2005)

The heavy residue is stored at a temperature where it is a fluid, but not susceptible to significant volatile loss or cracking. The holding or “pump around temperature” is dependant on the viscosity of the heavy residue. It is fed through a series of pre-heaters into the fractionator, through to heater tubes (in the furnace) where the onset of the coking reaction occurs. Due to the velocity with which the heavy residue moves though the heater tubes the onset of coke laydown is only realised in the reactor drums.

The drums usually operate on a semi-batch mechanism, so that while one is being filled the coke is being cut out of the other. As coke laydown takes place in the drum, the lighter volatiles (cracked products) are removed at the top of the drum, cooled and condensed in the fractionator. It is here where the petrol and diesel precursors are produced. The heavy overheads are cooled and mixed in with the fresh feed (thus the term Recycle Ratio: the ratio of fresh feed to recycled material).

At the end of a cycle the coke is cooled by means of steam / water and cut using a water jet. It falls into a coke pit and is picked up onto a belt (using an overhead crane), where it is sized using a combination of crushers and sieves. The green coke is then left to dewater on a pad before calcining.

The term “green or raw coke” refers to the fact that it is not ready for commercial use in an aluminium smelter until it has been calcined. Green cokes that do not meet the specification (Table 2-1) are often downgraded and sold as solid fuels or low value carbon raisers.

Given in Table 2-1 is a typical specification for green coke that would produce acceptable anode coke filler for the aluminium industry. Important to note is the maximum Volatile Carbon Matter (VCM) content of the green coke (9-11%), if the VCM is much higher than 13% it could cause significant instability in the calciner, as will excessively high water content.

The Hard Grove Index (HGI) is a measure of the relative hardness of the coke and is used to determine the desirable Particle Size Distribution (PSD) of the final calcined product. During calcination the green coke may loose up to 25% of its weight (due to volatile loss and combustion reactions) and thus the ash content will increase, as will the relative concentration of metals.

Table 2-1 Typical anode grade green coke properties (Meier, 2006)

Properties	Method	Units	Typical range
Water content	ISO 11412	%	5-12
VCM	ISO9406	%	9-11
Hgi	ISO 5074I		70-90
Grain size:			
>16 mm	ISO 12984	%	25-35
>4 mm	ISO 12985	%	45-60
<0.25 mm	ISO 12986	%	10-15
Ash content	ISO 8005	%	0.10-0.13
Elements (XRF)			
S	ISO12980	%	0.5-3.5
V	ISO12981	ppm	50-350
Ni	ISO12982	ppm	40-240
Si	ISO12983	ppm	20-300
Fe	ISO12984	ppm	50-400
Na	ISO12985	ppm	30-120
Ca	ISO12986	ppm	20-100

2.3.3 Commercial calcining

Although there are many processes available to calcine green coke, one of the most common is the counter current rotating kiln, shown in Figure 2-4. The green coke is fed into a "day bin" using a conveyer belt and into a gas fired kiln through a weigh feeder which regulates the rate (tonnes per hour). As the green coke passes into the kiln, the temperature is in the range of 500 to 600 °C. At this temperature dehydration (loss of water through evaporation) occurs. As the green coke moves down the angled rotating kiln (which is lined with refractory bricks) the average temperature increases. The coke then passes though a zone of the kiln where rapid devolatilisation occurs (600-900 °C) and then moves through a zone where micro-molecular densification and rearrangement occurs (1100-1400 ºC). The calciner is fed with both air and plant hydrocarbon gas.

The coke then leaves the kiln at a maximum temperature of 1350-1400 °C. The coke enters a cooler where it is sprayed with water and distributed to the silo using a conveyer belt. There is a significant reduction in the average PSD due to attrition (between the coke particles and against the refractory walls) and thermal degradation (stress cracks which form within the matrix of the coke and result in planes of weakness).

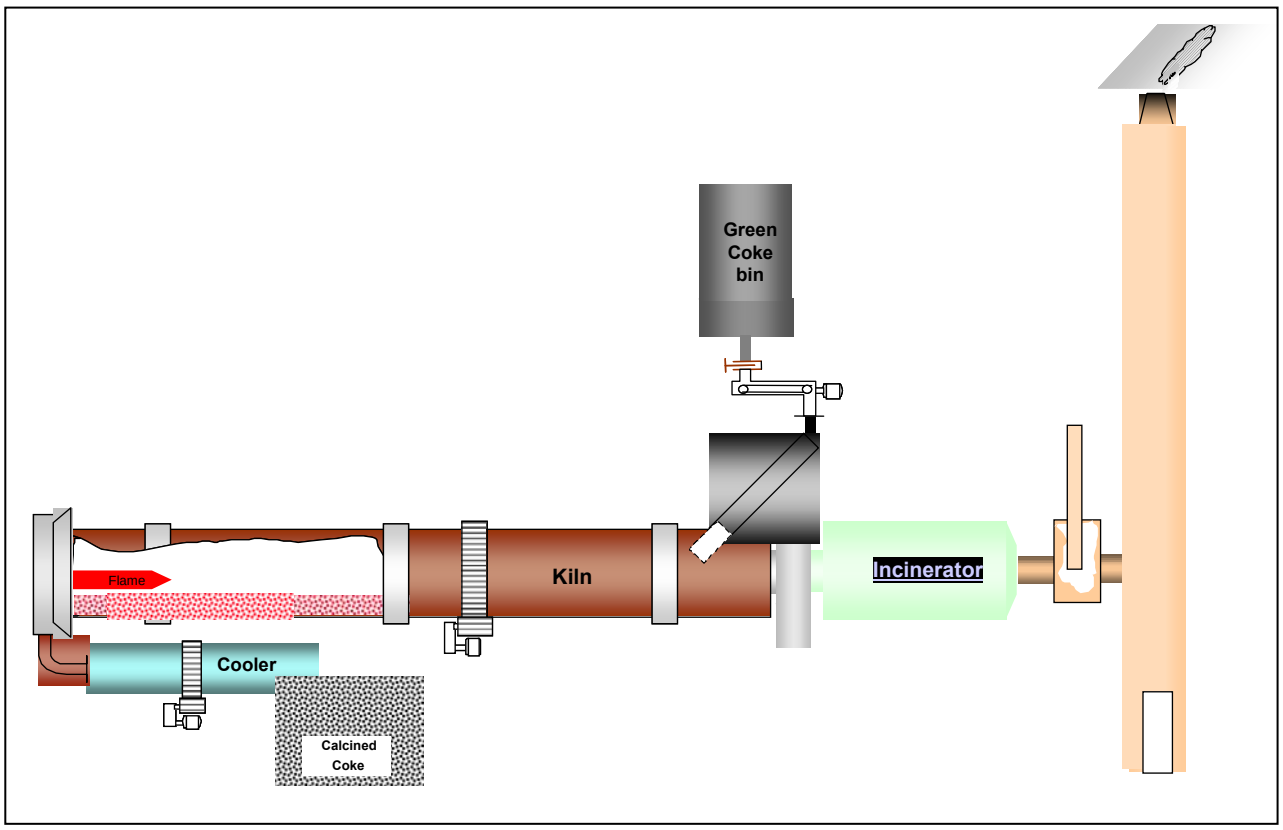


Figure 2-4 Schematic of a rotary kiln calciner (Clark, 2005)

A typical anode coke specification used in the aluminium industry is given in Table 2-2. The grain size of calcined coke is important as pre-baked anodes are produced using a "recipe" of various coke sizes. The Grain Stability (GS) is to calcined coke what the HGI is to green coke; it is a measure of the hardness of the carbon and is important as the smaller size fractions of the coke are ground to form a dust and coke that is too hard, could cause damage to the ball mill. As aluminium production is an electrolytic process, the Specific Electrical Resistance (SER) of the coke is of prime importance. This is governed on a micro-molecular or even atomic scale and the value describes with what level of difficulty current will pass through the carbon.

The desirable reaction for the carbon that is used as filler for pre-baked anodes is to reduce the divalent oxygen cations (O^{-2}) to Carbon Dioxide (CO_2). However, there are certain undesirable side reactions that may occur, namely CO_2 reactivity with coke, leading to the formation of Carbon Monoxide (CO) and air reactivity with coke, leading to the formation of CO_2. The minerals that are known catalysts for Air reactivity include vanadium and nickel, while those for CO_2 reactivity include sodium and Calcium (Hulse, 2000).

Table 2-2 Typical anode grade calcined coke specification (Hulse, 2000)

Property		Method	Units	Range
Density in Xylene		ISO 8004	kg/dm3	2.05-2.10
Specific Electrical Resistance		ISO DIS 10143	µΩm	460-540
CO_2 Reactivity Loss (1000ºC)		ISO N 802	%	3-15
Air Reactivity at 525ºC		ISO N 803	%/min	0.05-0.3
Crystallite Size (L_c)		-	Å	25-32
Ash Content		ISO 8005	%	0.10-0.20
Elements	Sulphur	ISO N 837	%	0.5-3.5
	Vanadium	ISO N 837	ppm	30-350
	Nickel	ISO N 837	ppm	50-220
	Silicon	ISO N 837	ppm	50-250
	Iron	ISO N 837	ppm	50-400
	Aluminium	ISO N 837	ppm	50-250
	Sodium	ISO N 837	ppm	30-120
	Calcium	ISO N 837	ppm	20-100
	Magnesium	ISO N 837	ppm	10-30

Consistency is the most important quality factor for coke used in the aluminium industry. This will be an important factor to note with respect to the current research, especially with the need to blend five different and variable feedstock streams.

The Coefficient of Thermal Expansion (CTE) specification is not listed in Table 2-2. It is generally accepted that petroleum green cokes which are considered calcinable (with reference to their ash and sulphur content) possess both a macro and microstructure which will naturally accommodate thermal shock without cracking. The other reason is due to the variance of methods by which thermal shock is measured. This is unfortunately a regrettable omission from a specification sheet as candidate cokes produced from coal tars tend to be more isotropic than petroleum cokes and thus have a higher CTE.

2.4 Mesophase chemistry

Factors affecting the quality of calcined coke for utilisation as fillers in the aluminium industry have a significant effect on the price and the market value. The physical characteristics of calcined coke are governed by the kinetics of the delayed coking reaction and the resultant microstructure.

Without a basic understanding the coking reaction (mesophase chemistry), coupled with a guide to understanding how to interpret polarised light micrographs, (shown in this dissertation), this research loses much of its value. This sub chapter by no means attempts to examine the chemistry of delayed coking in any detail but rather attempts to describe in general terms how heavy residues are transformed to coke and the various influences on the microstructure.

Heavy residues may result from various processes within a refinery and may vary in their suitability for delayed coking. Heavy residues have an appearance which varies

from that of syrup to an amorphous solid at room temperature. They are almost always blackish brown in appearance and have a characteristic refinery odour.

2.4.1 Molecular composition

The residues are a complex mixture of 5 000 to 10 000 organic compounds which vary in molecular weight, size and composition. The intricacies of mesophase chemistry become apparent when approached from the latter angle and not describing pitch as a "black waste". The most basic of the aromatic compounds that are present are naphthalene and quinoline, shown in Figure 2-5.

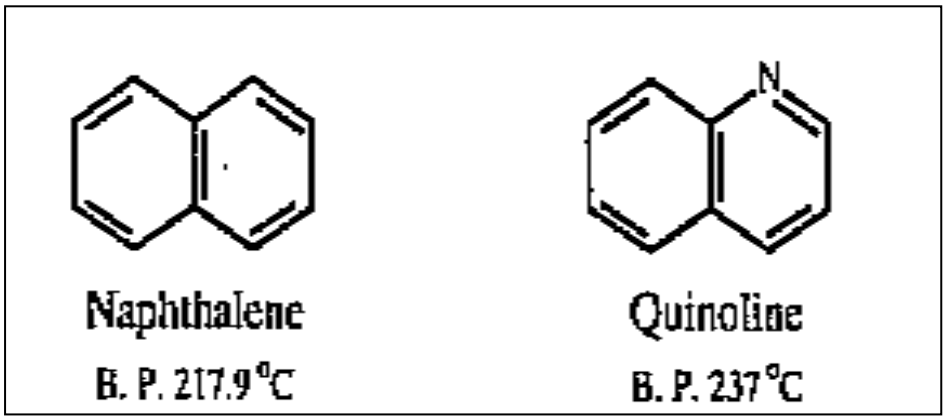


Figure 2-5 Molecular structure of naphthalene and quinoline (Marsh, 1997)

As the weight of these organic compounds increase so does their molecular size, for example benzo alphafluoranthrene (a five membered ring) and coronene (a seven membered ring structure) as given in Figure 2-6. These aromatic structures are the basic building blocks of the eventual coke structure.

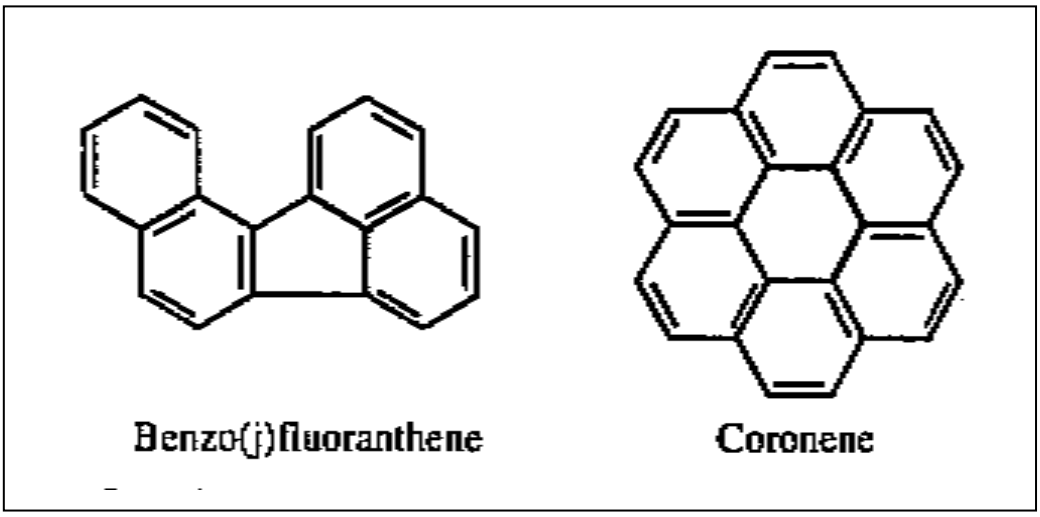


Figure 2-6 Molecular structure of benzo(a)flouranthene and coronene (Marsh, 1997)

Although heavy residues originating from petroleum and coal tar sources vary with respect to the way their different component fractions are described (solvency groupings), all heavy residues essentially contain lighter oils (reduction of the

viscosity), Beta resins (may be thought of as dimers or organic glue's) and macro-molecules (which provide the bulk of material that transforms into coke). It is the varying percentage of these three groupings that determine a heavy residue's softening point and its eventual coke yield.

Oxygen, nitrogen and sulphur present within the aromatic structure of the macro molecule are called heterocyclics, for example quinoline shown in Figure 2-65. These heteroatoms usually survive the delayed coking and calcining process steps and are present in the calcined coke. These heteroatoms may also be bound by weaker bonds to the parent aromatic compound as is the case with Thiols (Ar-SH) and Phenols (Ar-OH). In this case the heteroatoms are usually cracked off during the delayed coking process and can be found in the gas or liquid phase.

2.4.2 The delayed coking reaction

The delayed coking process includes heating residues in a tube furnace to a temperature of 430–500 °C to initiate the cracking (breaking down) of certain compounds and the poly-condensation (building up) of others.

The formation of coke is concerned with poly-condensation reactions. As the larger molecules condense with each other, the average molecular weight increases and very disordered planes of "benzene sheets or graphene layers" are formed. The compounds produce small spherules which coalesce with each other to form larger spherules. This process continues until the viscosity of the system is so great that no further movement of these macro-molecules is possible and so the coke "blueprint" (or solid carbon backbone) is formed. The coalescence of these spherules is called the mesophase (meaning intermediate phase) and it is driven by mesogens (macro molecules which generate the mesophase).

An understanding of mesophase chemistry makes analysing the Optical Texture Index (OTI) of the coke far easier. The coalescence of mesophase spherules is illustrated by the set of photo micrographs given below (Figure 2-7; Figure 2-8 and Figure 2-9).

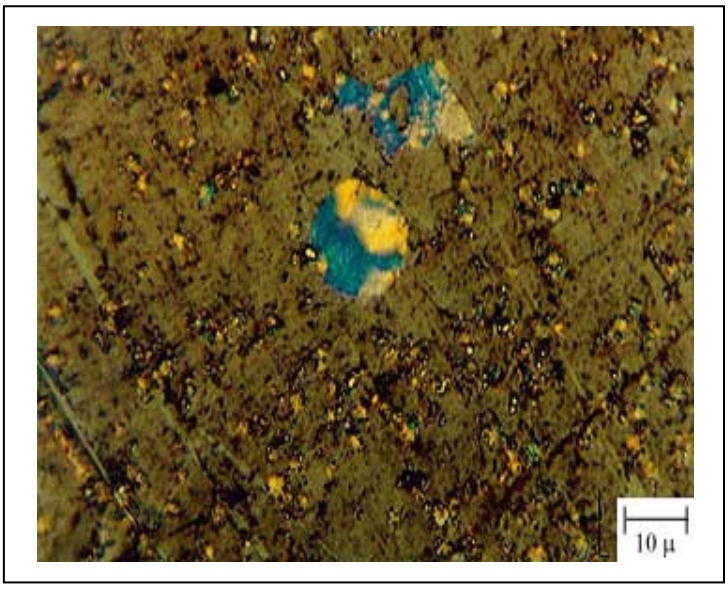


Figure 2-7 Polarised light micrograph showing development of embryonic mesophase spherules (Magnification x 50 in oil) (Crelling, 1990)

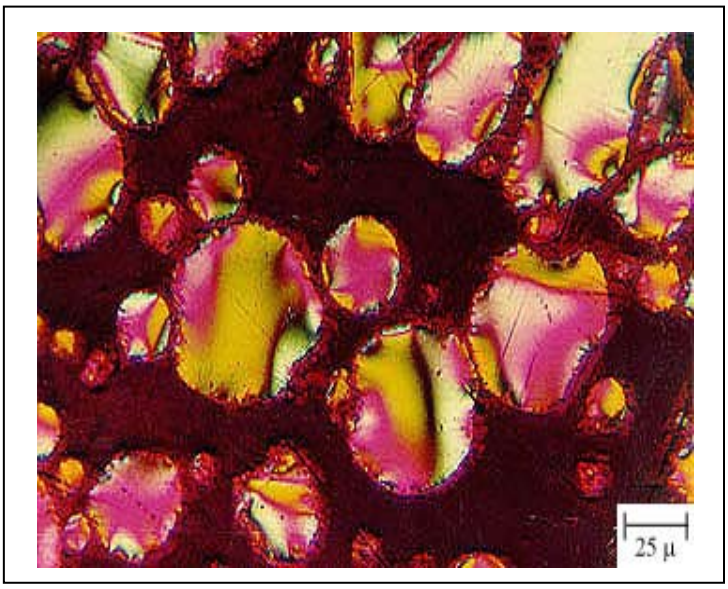


Figure 2-8 Polarised light micrograph showing coalescence of mesophase spherules (Magnification x 25 in oil) (Crelling, 1990)

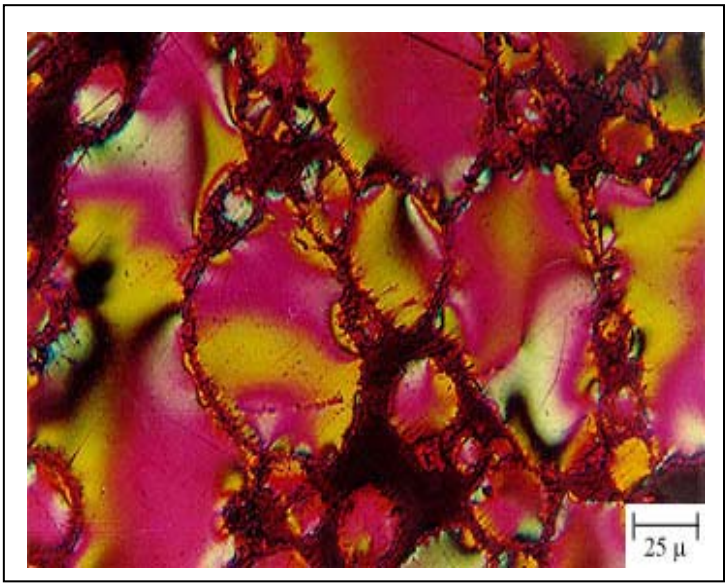


Figure 2-9 Polarised light micrograph of fully coalesced mesophase showing ash concentration at the grain boundaries (Magnification x25 in oil) (Crelling , 1990)

The development of the mesophase is highly dependent on the nature of the feedstock and the process conditions. Feedstock dependant factors include:

- Oxygen / nitrogen / sulphur content of the feedstock
- Asphaltene content of the feedstock
- Alkyl side chains bound to the parent aromatic compound (s)
- The ash concentration in the feedstock
- The Quinoline Insoluble (QI) content of the feedstock. This may include semi coke
- Viscosity or API Gravity of the feedstock
- The aromaticity of the feedstock specifically the abundance of aromatic hydrogen donors

Any one, or a combination of these factors listed above, will affect the kinetics (or the rate) at which the heavy residue is transformed into coke. If the mesophase "cures" too quickly, (dependant of certain reaction kinetics), the viscosity of the mesophase will prevent further coalescence of the mesogens. By doing so coalescence will be retarded and this gives rise to the family of microstructures known as MOSAICS, which include:

- Fine mosaic
- Medium mosaic
- Coarse mosaic

These appear as a "collection of balls" of varying sizes. This type of material is termed ISOTROPIC (without order) as may be seen under low magnification in Figure 2-10, but it is more apparent as a "collection of balls" under higher magnification in Figure 2-11.

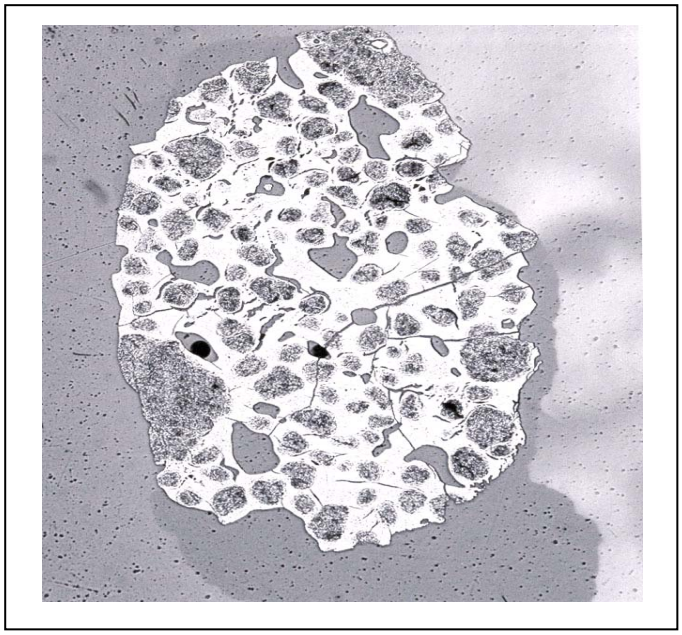


Figure 2-10 Bright Field Micrograph (Magnification x 10) of Isotropic coke structure (Clark, 1996)

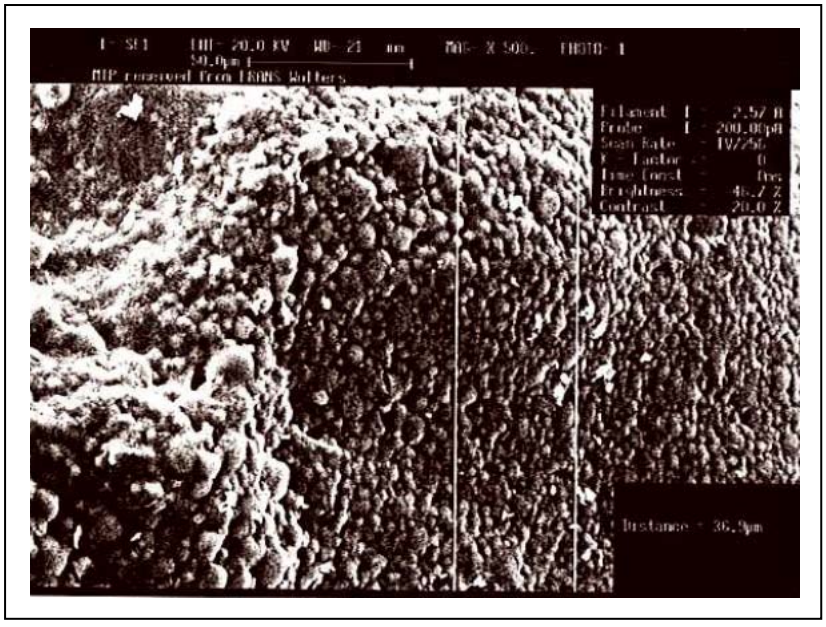


Figure 2-11 Scanning Electron Micrograph (SEM, Magnification x 3000) of an Isotropic coke showing fine mosaic "ball" structures (Clark, 1996)

A simple analogy would be to consider small round chocolates. If kept in a fridge they would retain their shape, however if placed into the sun, they would melt and flow (coalesce) into one another. Exactly the same happens within the mesophase, if the mosaics (balls) have enough energy they will coalesce.

If the mesophase kinetics allow for coalescence of the matrix, a flow pattern is evident. FLOW patterns include:

- Coarse
- Granular
- Laminar

These thus appear as a collection of elongated domains and are common in higher order sponge and needle cokes. These cokes are typically referred to as ANISOTROPIC (with order) as given under low magnification in Figure 2-12 and under higher magnification (
Figure 2-13 and Figure 2-14), which show the appearance of stacks of graphene sheets.



Figure 2-12 Polarised light micrograph of needle coke in a binder matrix showing elongated flow patterns (Magnification x 25 in oil) (Crelling, 1990)

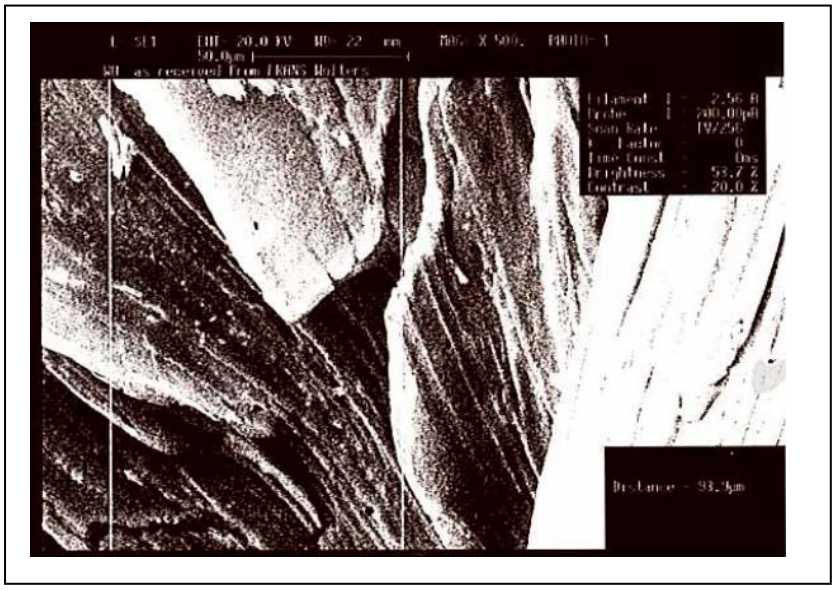


Figure 2-13 Scanning Electron Micrograph (SEM, magnification x 500) of graphene sheet clusters in highly ordered anisotropic petroleum coke (Clark, 1996)

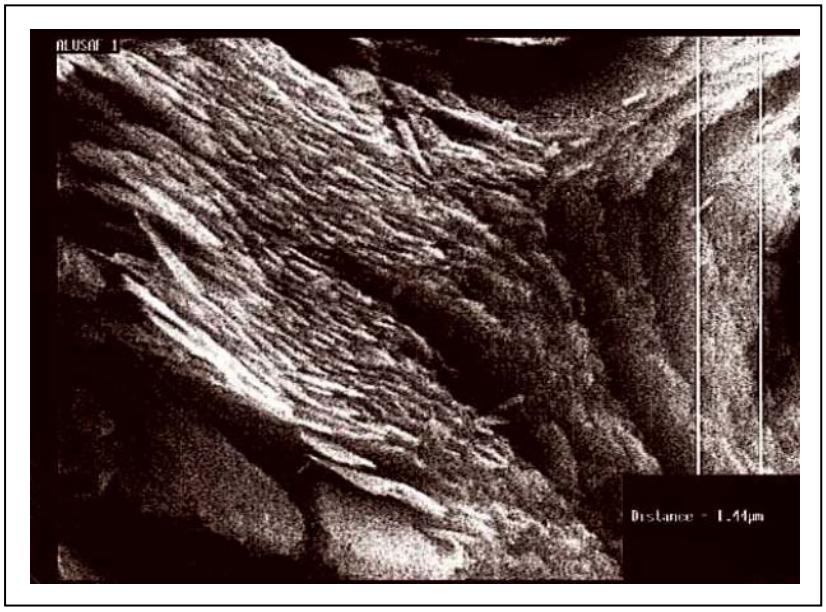


Figure 2-14 Scanning Electron Micrograph (SEM, magnification x 7000) of a graphene sheet cluster in a highly ordered anisotropic petroleum coke (Clark, 1996)

The difference between anisotropic and isotropic carbon relates to the order with which the graphene sheets align with one another as given in Figure 2-15, coupled with the range of that order.

Historically one of the most reliable methods for evaluating the microstructure of cokes and the expected quality of the carbon is the OTI. The procedure entails polishing the flat surface of a piece of carbon with fine alumina powder and then setting the carbon in an epoxy resin mould. The polished surface of the carbon is then examined under a light microscope at low magnification within a drop of oil. Under

magnification the carbon reveals “shapes or structures” which are point-counted to determine an “index value” and reveal the relative anisotropy / isotropy of the material. The OTI table is given in Table 2-3. The higher the OTI factor, the more ordered or anisotropic the coke will be.

Table 2-3 Determination of the Optical Texture Index (OTI) (Marsh, 1997)

Category	Description	OTI Factor
Fine Mosaics	Small circular < 0.8 μm in diameter	0
Medium Mosaics	Circular > 0.8 μm < 2.0 μm in diameter	1
Course Mosaics	Large circular > 2.0 μm < 10 μm in diameter	3
Granular Flow	> 2.0 μm in length and > 1 μm in width	7
Course Flow	> 10.0 μm in length and > 2 μm in width	20
Lamellar Flow	> 20.0 μm in length and > 10 μm in width	30

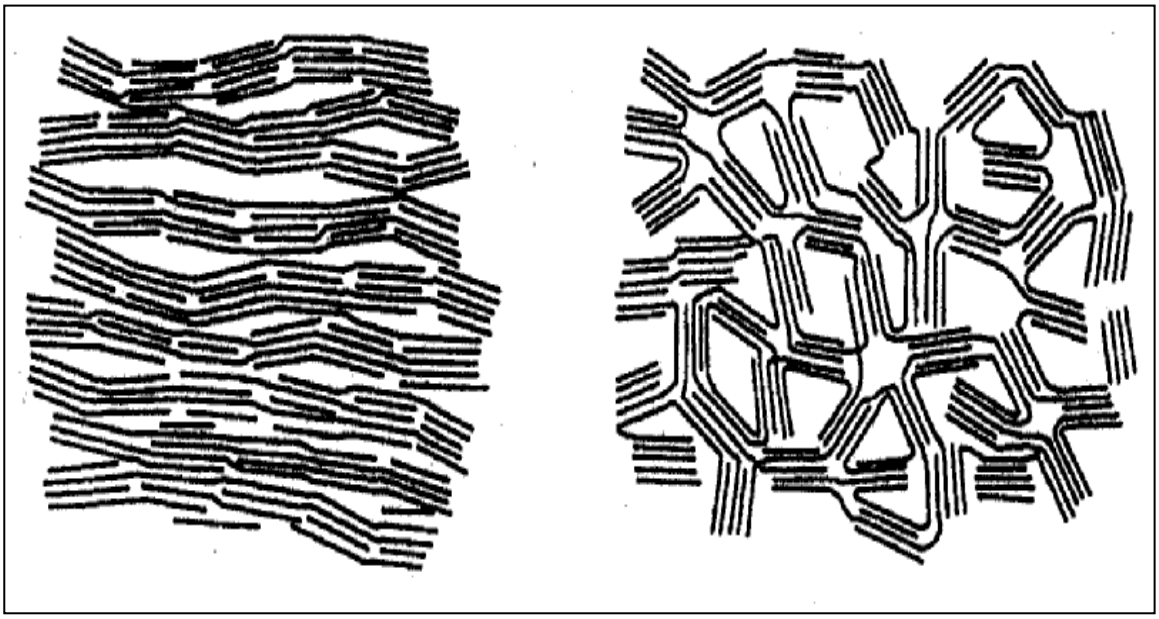


Figure 2-15 Descriptive diagram of Anisotropic (left) and Isotropic (right) carbon microstructures (Burchell, 1999)

2.4.3 Calcination

Coke is calcined (1350–1400 °C) to remove the remaining volatile matter and further promote molecular organisation of the graphene layers. The slightly disordered benzene layers organise into aligned graphene sheets as given in Figure 2-16.

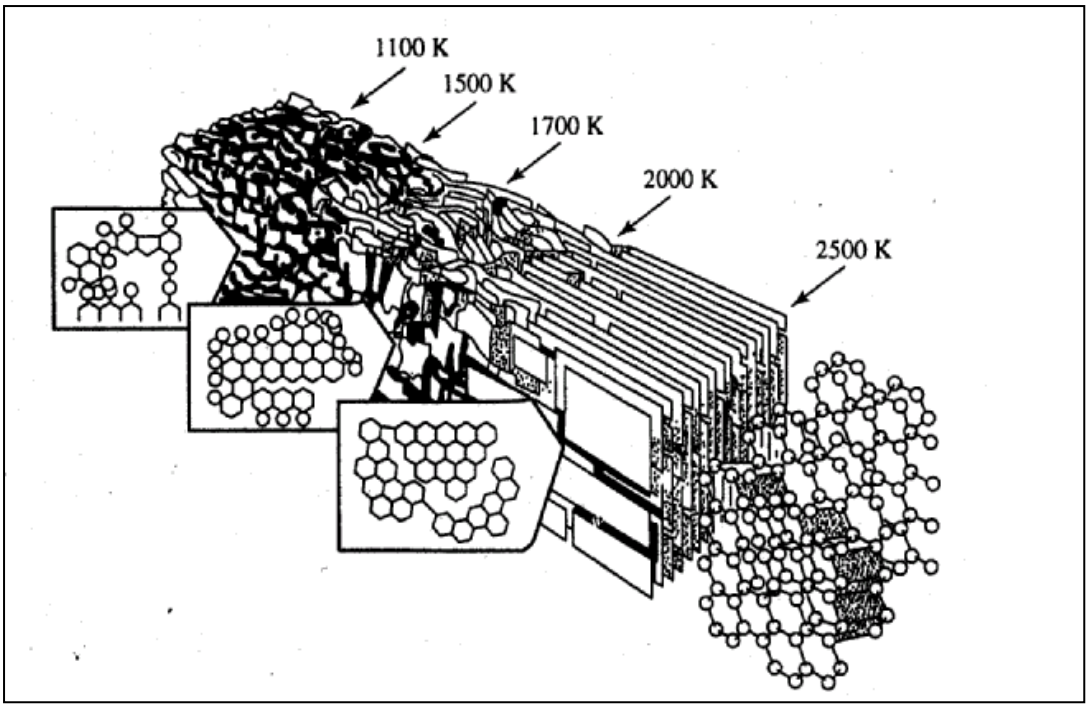


Figure 2-16 Diagram showing molecular re-organisation in anisotropic carbon heat treated from approx 900 - 2220°C (Marsh, 1997)

Sponge coke used in the aluminium industry is usually only treated to 1400 °C. On an atomic scale, as given in Figure 2-17, anisotropic carbon exists of benzene sheets (layers of benzene rings) supported by weak interstitial Van der Waals forces.

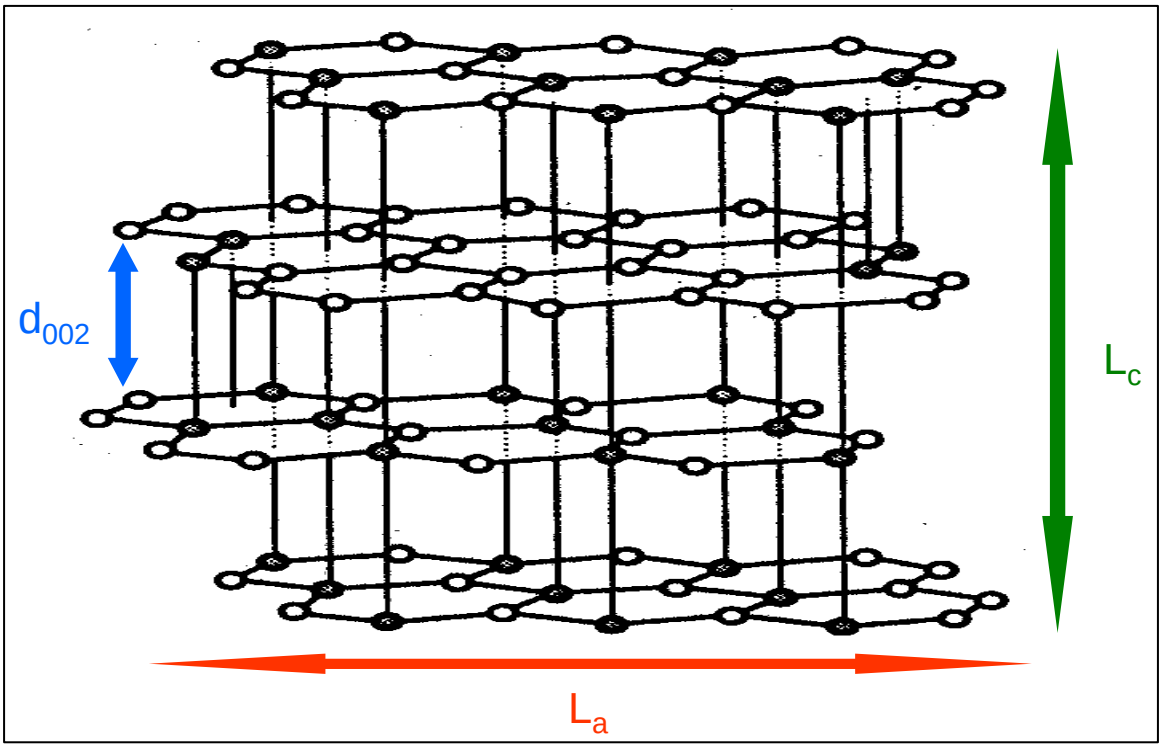


Figure 2-17 Atomic arrangement of benzene sheets within an anisotropic carbon (Marsh, 1997)

The relative degree of anisotropy within a carbon matrix has significant affects on the in-situ performance of the carbon filler within the anode. The weak Van der Waals forces allow for a degree of vibration between the benzene sheets. One of the most important characteristics of a calcined coke for the aluminium industry is the Coefficient of Thermal Expansion (CTE). This measures the effect of sudden thermal shock on a carbon anode. By definition the CTE is the ability to dissipate thermal energy in such a way so as not to cause permanent physical deformation. In more practical terms it means the ability of a carbon body to dissipate thermal energy without cracking.

A classical case of crack formation within a pre-bake anode as a result of thermal shock may be seen in Figure 2-18, which clearly shows the development of "Spade and Corner" cracks. In extreme cases the development of the crack may result in a segment of the anode breaking off (Figure 2-19), which would have disastrous safety, financial and production related implications. It is however important to note that while the crack is seen on a visual level, the cause is more than often rooted on a molecular level. It is for this reason that carbon scientists pay a great deal of attention to the microstructure of candidate cokes for the aluminium industry.

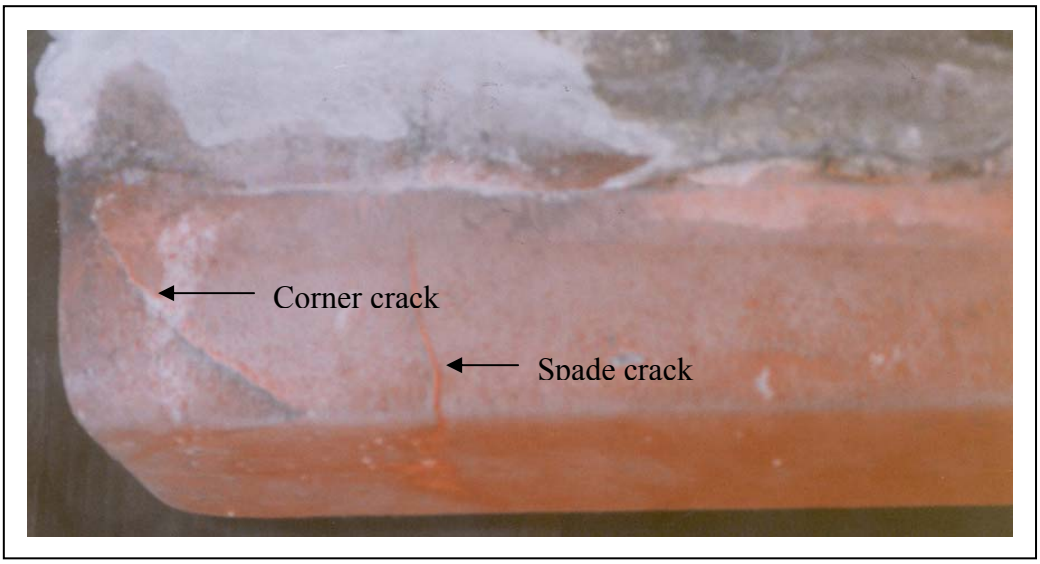


Figure 2-18 Photo of segment of pre-baked anode showing "spade" and "corner" cracks (Clark, 1995)

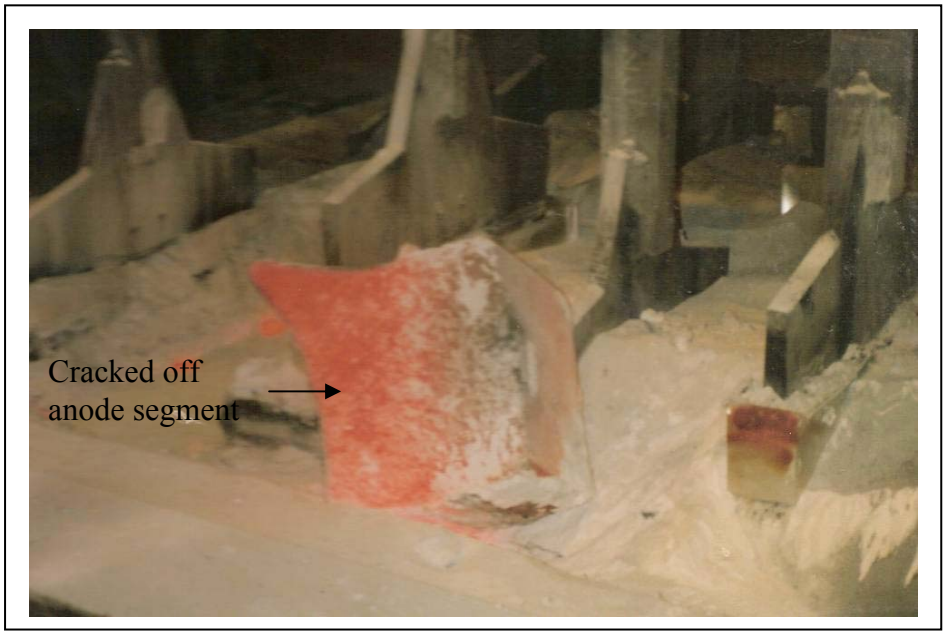


Figure 2-19 Photo of segment of pre-baked anode that cracked off due to thermal shock (Clark, 1995)

When highly ordered anisotropic carbons experience thermal shock the layers vibrate and thus dissipate energy without cracking. These carbons usually have low CTE's.

Within isotropic or less ordered carbons the layers are not stacked parallel to one another and thus when the carbon experiences thermal stress the layers expand against one another at more or less right angles (causing mechanical stress) and thus crack. These carbons have high CTE's.

As with the explanation of CTE, it is possible to explain many of the physical characteristics of calcined coke on a molecular or atomic level.

2.4.4 Graphitisation

Graphitisation involves the heat treatment of either coke particles or artefacts produced by mixing coke and pitch, to temperatures of between 2100 and 2850 ºC.

Coke used in the production of graphitized electrodes for the steel industry and other higher value graphite artefacts utilise calcined needle coke as a filler. The needle coke is mixed with a binder pitch, extruded, baked and graphitized. Electrodes for the steel industry utilise needle cokes and not anode cokes for three main reasons:

- When calcined coke in an electrode is graphitized the sulphur is released at around 1800 ºC. This causes the phenomenon called "puffing" which can cause cracks and increase the micro-porosity
- Any mineral oxide (ash) contamination will reduce at graphitization temperatures to the metal and sublimate. This leaves voids or holes in the electrode which will affect the performance thereof.
- The CTE of anode cokes is 1.6 $x10^{-6}$/ºC, which is far in excess of the CTE (flour rod test) for needle cokes which is typically 0.3 $x10^{-6}$/ºC
- Needle cokes have a lower sulphur and ash content as compared to anode grade cokes

Graphitising coke as **particles** is not common place in industry. Needle cokes used in the production of electrodes would be graphitised in-situ (within the electrode). However heat treating anode grade coke particles to above 2100 ºC will effect the following changes:

- Both the ash and the sulphur content will be reduced
- The coke microstructure will densify and the degree of graphitsation will increase
- The evolution of sulphur oxides will generate micro-porosity
- As the evolution of sulphur and sublimated metals is from the coke particle, the disadvantages of graphitising a carbon artefact (puffing and cracking) are avoided

One of the methods used to describe the degree of graphitisation is X-ray powder diffraction. The degree of graphitisation defines the ordering of the crystal lattice in comparison to that of a pure graphite crystal, e.g. Kish graphite.

As X-ray powder diffraction (XRD) was used to determine the increase in the degree of graphitisation for the anode cokes produced, the theory behind this analysis is described below.

As delayed cokes are polycrystalline they can be characterised in three dimensions (namely h,k,l). X-rays are diffracted from a powdered graphite sample at a series of angles which are given as diffraction peaks according to the intensity of the signal. As given in Figure 2-17, the space between individual graphene sheets is called the d_{002}

value. This peak usually occurs at a scattering angle of 25 or 30 degrees. The more anisotropic a coke, the smaller the d_{002} value will become when heated to graphitisation temperatures. The d_{002} interlayer spacing for a pure graphite crystal is 3.354 Angstrom (Å, 1 $x10^{-10}$ m). An X-ray diffraction pattern for a pure graphite crystal is given in Figure 2-20.

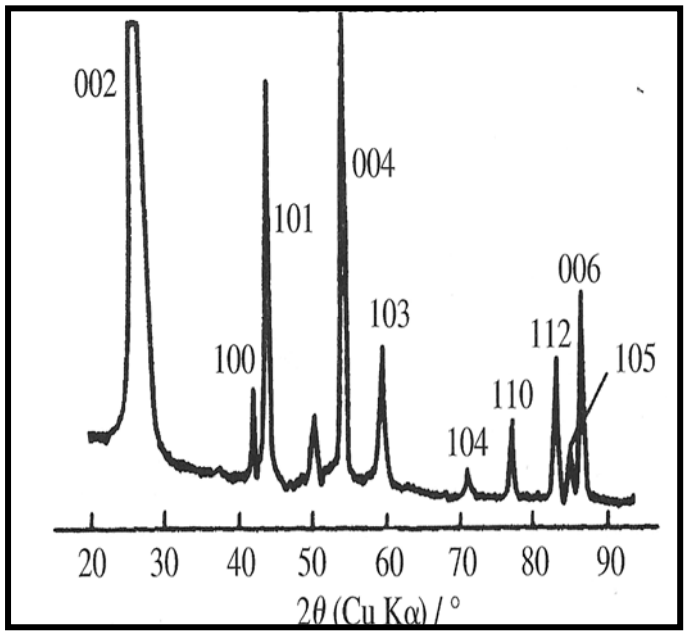


Figure 2-20 X-ray powder diffraction pattern for a pure graphite crystal (Inagaki, 2000)

The height of the crystal lattice is given by the L_c value and the width given by the L_a value (Figure 2-17). In both cases, as anisotropic carbon is heat treated to graphitisation temperatures the (002), (004) and (006) peaks become better defined. X-ray powder diffraction is used in the aluminium industry to examine the crystallite height (L_c value) of candidate filler cokes (Table 2-2).

The development of the crystal lattice as described above is given in Figure 2-21. As the anisotropic carbon is exposed to increasing temperatures both the L_c and the L_a values increase and the d_{002} value decreases showing densification of the carbon crystallite.

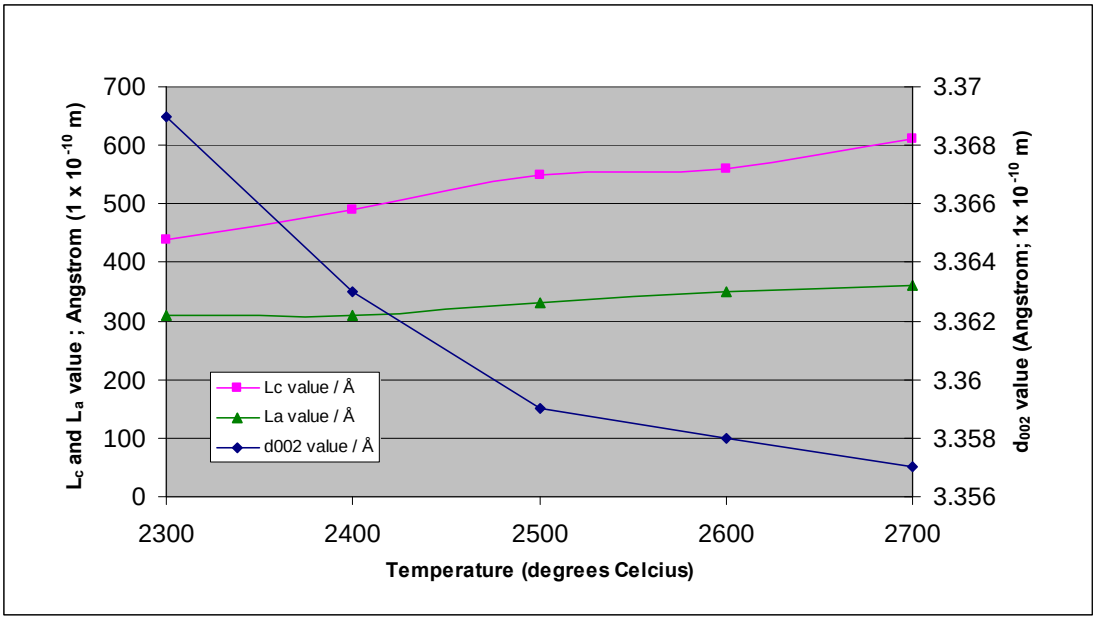


Figure 2-21 Crystalline development as a function of heat treatment temperature for a highly ordered carbon (Burchell, 1999)

Figure 2-22 shows the development of the d_{002} peak with increasing heat treatment temperature. Only graphitisable carbons will show development of these crystallographic peaks. Isotropic delayed cokes do possess short range order and are thus graphitisable although to a far lesser extent.

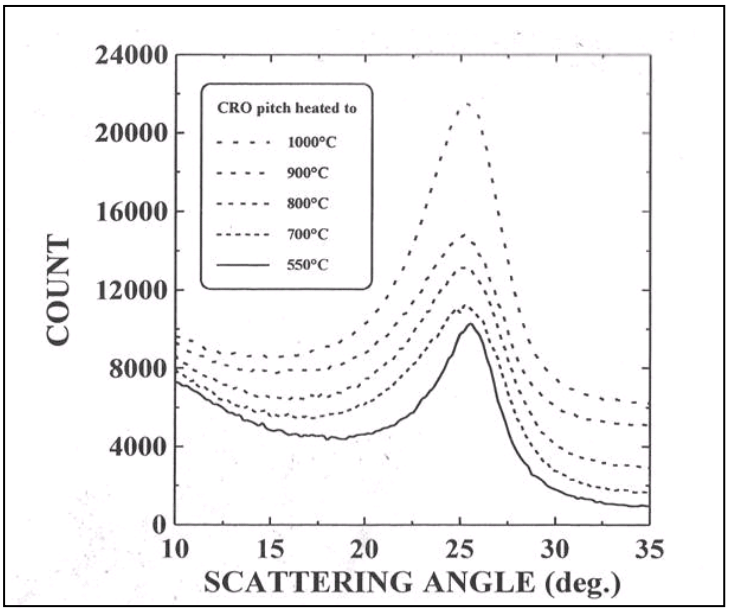


Figure 2-22 X-ray powder diffraction pattern showing the development of the d_{002} peak for an anisotropic pitch treated between 550 and 1000°C (Burchell, 1999)

3 THE DEMAND FOR LIQUID FUELS IN SOUTH AFRICA

3.1 The demand for automotive fuels

The year on year volumetric sale of automotive fuels within South Africa (2000 to 2006) is given in Figure 3-1 and shows that on a national basis, petrol and diesel demand has increased significantly (to 2006) from figures released six years prior (2000).

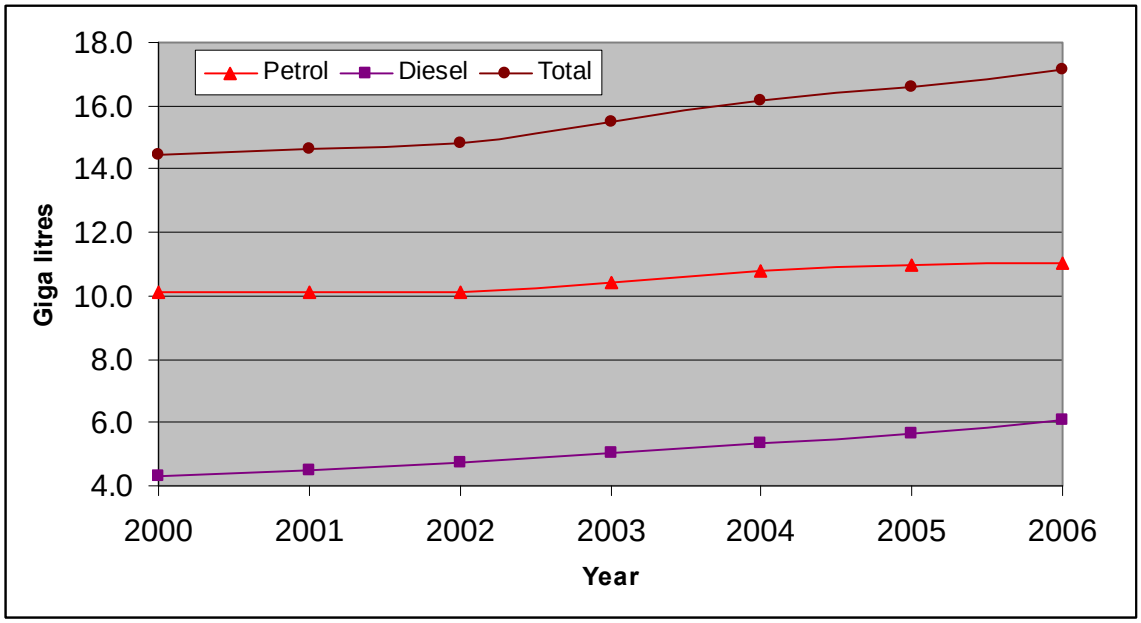


Figure 3-1 Petrol and Diesel sales in South Africa (2000 – 2006) (Botha, 2008)

The South African fuel demand per geographic region is given in Table 3-1. The greatest demand is located in and around the metropolitan cities of Cape Town, Durban and Johannesburg / Pretoria. This stands to reason given the higher density of automobiles in these areas.

Table 3-1 South African fuel demand patterns (DME, 2006)

Geographic region	Fuel demand (Billion litres per annum)	Fuel demand (%)
Cape Town Area	4.60	15.7
Eastern Cape Area	2.40	8.2
Durban Area	5.30	18.0
Inland South Area	2.10	7.1
Inland North Area	12.70	43.2
Namibia	0.95	3.2
Botswana	0.89	3.0
Lesotho	0.19	0.6
Swaziland	0.26	0.9

The fuel demand has also increased the necessity for new roads and highways to handle the increased traffic volumes with specific reference to the density of cars due to townhouse complex developments in metropolitan areas. However, if the fuel supply cannot meet the demand, this capital expenditure may not be viable. As stated in the "Energy Security Master Plan – Liquid fuels" report by the Department of Minerals and Energy (DME).

"Without appropriate energy demand and supply planning, South Africa and the world over could, in less than 50 years, find itself with cars and beautiful highways but on a road to nowhere" (DME, 2007)

3.2 The number of registered motor vehicles in South Africa

The historical dependence of motor vehicles on petrol and diesel derived from fossil fuels has by default yielded a direct correlation between the increase in the number of motor vehicles and the demand growth for automotive fuels. The significance of delayed coking is that it produces both petrol and diesel which would contribute towards the revenue generated from "locally"[1] produced materials as opposed to the contribution to the balance of payments deficit generated by importing crude oil.

Figure 3-2 shows the number of registered motor vehicles on South African roads for the period 1930 to 2006. While a significant increase in the number of motor vehicles on the roads is evident, the trend is divided into 3 major sections:

- 1930 to 1960
- 1961 to 1994
- 1994 to 2007

The most significant of the three distinct sections is the one between 1994 and 2007. Figure 3-2 shows an exponential increase in the amount of registered motorised vehicles on South African roads during this period, catalysed by the change in political dispensation in 1994 which significantly increased the buying power of a larger percentage of South Africans.

[1] While the heavy petroleum residues are produced as a by-product of **imported crude oil,** for the purposes of delayed coking, they would be considered a feed produced within the borders of South Africa. As delayed coking of these residues would diminish the reliance on imported crude oil, they are considered to be **local** feed stocks.

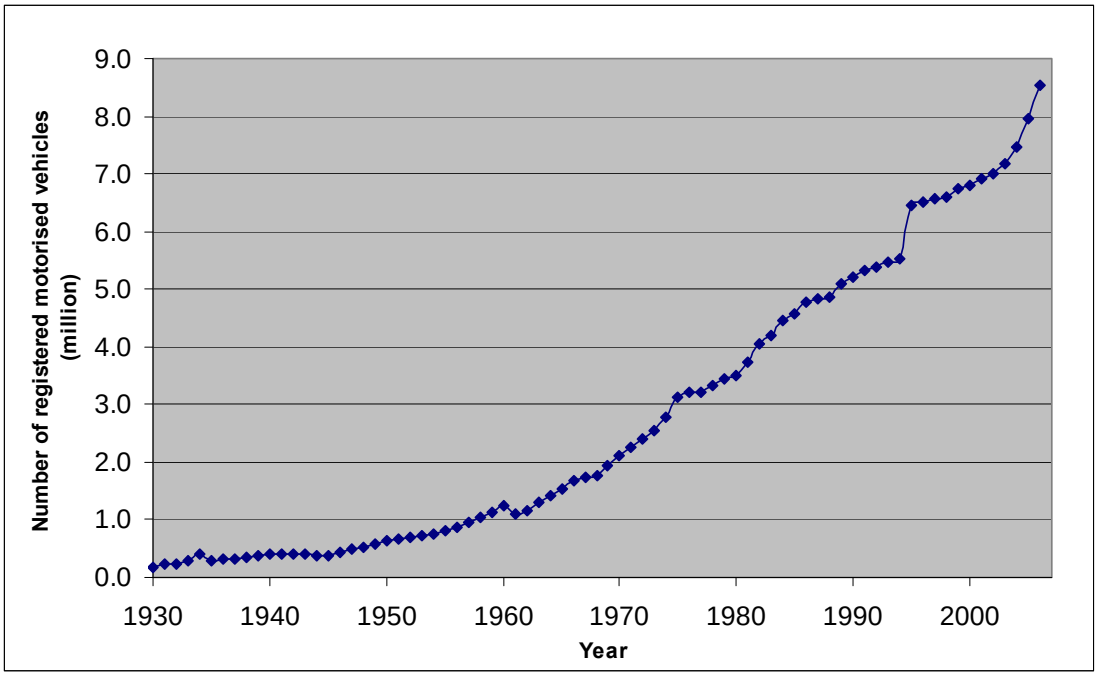


Figure 3-2 Number of registered motorised vehicles in South Africa (1930 – 2006) (Botha, 2008)

3.3 Crude oil supply

3.3.1 Crude oil – A global perspective

Since the first commercial oil well was drilled in Pennsylvania in 1859, the use of crude oil as an energy source has gained increasing prominence. Today crude oil accounts for 35% of the world's primary energy supply (Wakeford, 2007).

Although the world has become increasingly reliant on crude oil to "fuel" economic growth and the socio-economic development of its inhabitants, this trend cannot continue indefinitely as **crude oil is a finite resource and will be depleted in time.**

There is a growing concern as to the time period the world will be able to enjoy and rely on crude oil as its primary energy source. The debate no longer revolves around the question of **if** the crude oil supplies will be sustainable but rather **when** they will be depleted (Wakeford, 2007).

The concern is justified when considering the following trends and statistics in relation to crude oil supply (Wakeford, 2007):

- New oil discoveries peaked in the 1960's and have been declining ever since
- Since 1981 more crude oil has been consumed than has been discovered
- The production of crude oil from conventional sources (excluding heavy crude oil, deep water crude oil, polar oil and natural gas liquids) peaked in 2005
- The production of crude oil (from all resources) is expected to peak within the second decade of the twenty-first century (2010–2020)

- The annual depletion rate thereafter will be in the range of two to eight percent per annum
- While increased consumption of crude oil has been a major contributor to global warming, substitution by coal would produce more CO_2 per unit energy and thus would exacerbate the climatic challenge

It is clear that the world will, in the not too distant future, have to rely on other sources of energy, initially (in all probability) non-renewable sources (coal, natural gas and nuclear power) and then renewable sources (bio-fuels, solar, wind, hydro-electricity, geothermal and hydrogen). The demand for energy either from crude oil or any other resource coupled with the effect on global warming is essentially being driven by the global population increase.

3.3.2 Crude oil – A South African perspective

Only 14% of South Africa's energy needs are met by crude oil. However, crude oil accounts for 65-70% of South Africa's annual liquid petroleum consumption (Wakeford, 2007). The rising crude oil price has exerted pressure on the pump price of petrol and diesel, as well as transport costs of commodities (imported or distributed within South Africa), which in turn has increased the cost of these goods to the end consumer. As crude oil is the single largest import item (by value), this trend will cause inflationary pressure as well as a negative contribution towards the balance of payments current account (Wakeford, 2007).

To understand South Africa's reliance on crude oil it is necessary to examine many contributing factors, which are presented in the following sub chapters.

3.3.3 The capacity to refine crude oil

South Africa imports more than 70% of the country's liquid fuel demand, both in the form of crude oil and refined products (DME, 2006). Of this 70%, South Africa is reliant on both Iran and Saudi Arabia for 80% of this supply of crude oil. The 30% of automotive fuels that are produced from local resources include the Sasol's Coal to Liquids refinery in Secunda and the Petro SA Gas to Liquid facility in Mossel Bay. The production capacity of fuels in South African refineries is given in Table 3-2.

Table 3-2 The production capacity for automotive fuels in South Africa (DME, 2006)

Refinery	Location	Owned by	Feedstock	Local / Imported	Capacity / bbl per day
Sasol	Secunda	Sasol	Coal / Gas	Local	150 000
Petro SA	Mossel Bay	SA Govt.	Gas	Local	45 000
Calref	Cape Town	Caltex	Crude oil	Imported	100 000
Sapref	Durban	Shell / BP	Crude oil	Imported	184 000
Enref	Durban	Petronas	Crude oil	Imported	125 000
Natref	Sasolburg	Sasol / Total	Crude oil	Imported	108 000

Many of the refineries listed in Table 3-2 have expansion plans in various stages of completion. Petro SA announced on the 24th of October 2007 that it would build South Africa's largest crude oil refinery (200 000 bbl per day, capital expenditure estimated at R 39 billion) in Coega, Port Elizabeth (Reuters, 2007). Construction of the oil refinery would commence in 2010 and would generate 20 000 jobs. This is in keeping with the directive from the South African Government to control at least 30% of the liquid energy market or produce it from local resources.

3.3.4 Crude oil imports to South Africa

The data for crude oil imports into South African refineries (from 1990 to 2006) is given in Figure 3-3. Crude oil imports have steadily increased from 1990 (12 mega tonnes or 72 mega barrels, mbbl[2] per annum) to 2006 (29 mega tonnes or 180 mbbl per annum). As many of South Africa's neighbouring states do not have refineries of their own, a percentage of the refined products produced from imported crude oil is exported to countries like Namibia, Botswana and Zimbabwe. The amount of exported refined products has not shown the same steady increase over the past 16 years from 1990 to 2006. This is in part due to the fact that exports of refined products to Zimbabwe have decreased due to credit risks. There has thus been a widening gap between crude oil imports and refined product exports. South African demand for fuel [based on the increase in the number of registered motorised vehicles on the road per annum, (Figure 3-2)] has increased significantly, which accounts for the fact that over the time period in question a greater percentage of imported crude oil has been used to service increased local demand.

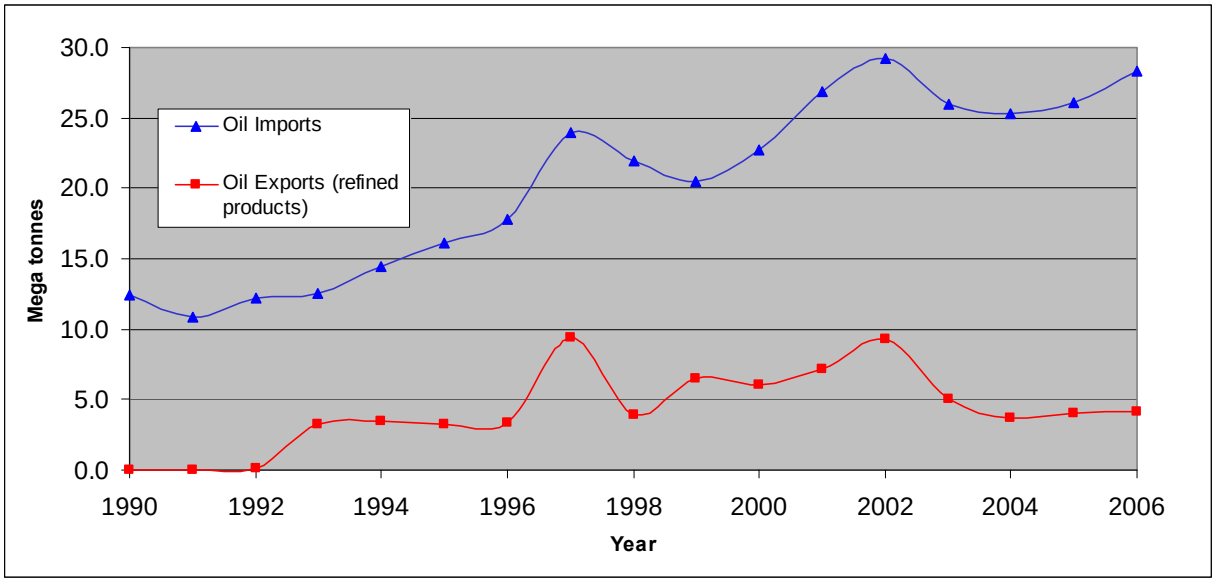


Figure 3-3 Crude oil imports to and refined product exports from South Africa (1990 – 2006) (Enerdata, 2007)

Figure 3-4 shows that while the products from refined oil are used to service other market sectors (inclusive of electricity, households, industry, services and other non-energy uses), by far the greatest demand has been the transportation sector, which

[2] An average density for imported crude oil has been assumed at 0.95 kg/l. There are 159 litres of crude oil in a barrel

over the period from 1990 to 2006 has not only increased in a parallel trend with crude oil imports but has also accounted for two thirds (approximately 66%) of the demand. This again is a direct result of the increased population of registered motor vehicles within South Africa for the same time period. Many of the sectors depicted in Figure 3-4 may be served by other sources of energy (e.g. coal or anthracite), while the automotive transport sector is reliant solely on liquid fuels.

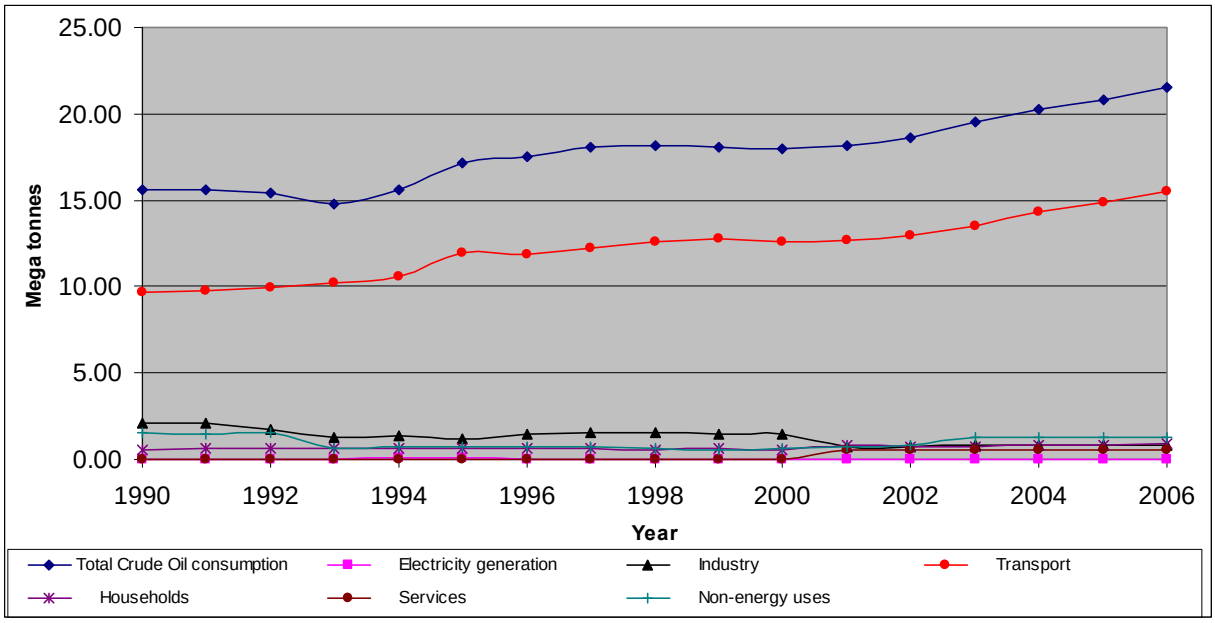


Figure 3-4 Consumption of crude oil (refined products) in South Africa (1990 – 2006) (Enerdata, 2007)

Refining crude oil is cheaper than the production of liquid fuels from either Coal or Gas to Liquid technologies, based solely on the production of the liquid fuel component and not taking into account revenue generated from the production of any other chemicals.

3.3.5 The cost of importing crude oil

The price of crude oil, given in dollars per barrel ($/bbl) is usually reported by the media as the Brent price. As is evident in Figure 3-6, from 1990 to 1998 the price of crude oil was relatively stable (15 to 20 $/bbl). During the corresponding time period, there was a steady increase in oil imports (80 mbbl to a maximum of 155 mbbl).

This period was followed by a relative increase in the oil price until the year 2000, after which there was a slight drop in crude oil imports. However the exponential increase in the oil price (2003 to 2006) has had a stabilising effect on crude oil imports to South Africa. The reason for the significant hike in the cost of oil imports has been linked to:

- Oil cartels controlling the amount of oil on the market in an attempt to stabilise the price

- The insecurity in the Middle East (2002 to present)
- The insecurity in African oil producing countries e.g. Nigeria
- Seasonal fluctuations in the demand for heating oils in the United States of America
- Climatic phenomena in the Gulf Coast e.g. Hurricane Katrina

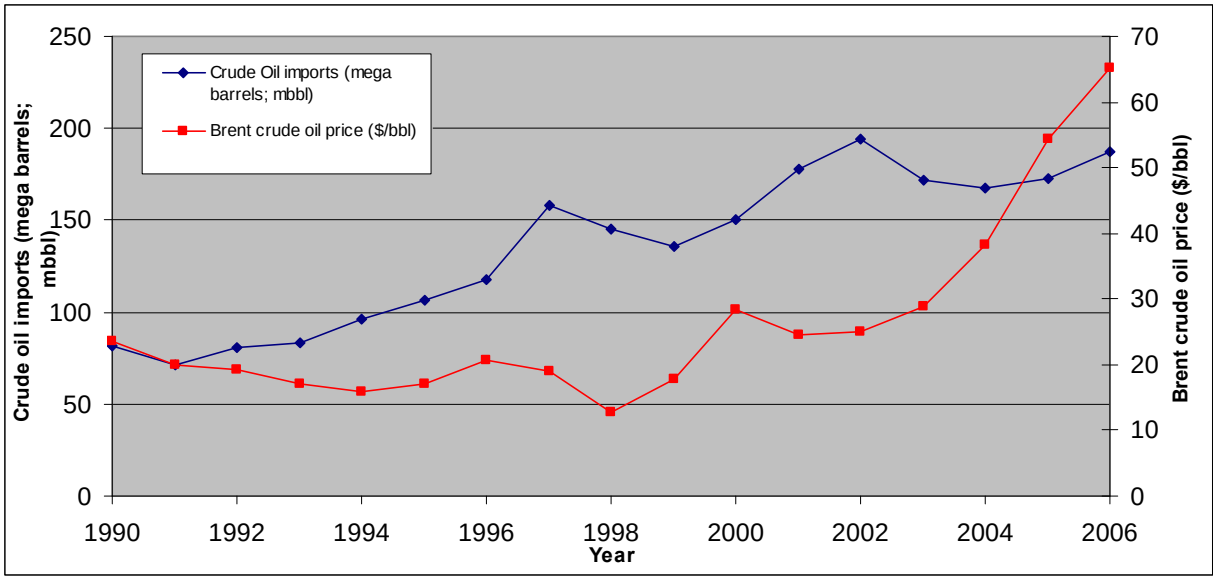


Figure 3-5 Crude oil imports to South Africa vs. the Brent crude oil price (1990 – 2006) (Enerdata, 2007)

Many refineries within South Africa base their forecasts for the price of crude oil imports on a percentage of both the Brent and the Dubai crude oil prices (Figure 3-6). However to evaluate the **real cost** of importing crude oil into South Africa it is necessary to examine the fluctuations in the Rand / Dollar (R/$) exchange rate as well. In 2002, at the peak of the exchange rate hike (R/$ 10), the crude oil price dipped for a short period into a trough. However, as inflationary pressures were relaxed and the exchange rate stabilised to between R/$ 6 and 8, the exponential rise in the crude oil price had an ever increasing effect on the balance of payments (current account) deficit. The projection to 2009 assumes a slight increase in the exchange rate coupled with a slight decrease in the price of imported crude oil.

It should be noted that while the exchange rate has touched the R/$ 13 mark and the crude oil price has increased to above 90 $/bbl, the figures given are yearly averages. Projections concerning the future of the oil price are at best educated guesses; the volatility thereof has followed a fluctuating pattern in reaction to geo-political insecurity over the last four years making accurate predictions difficult.

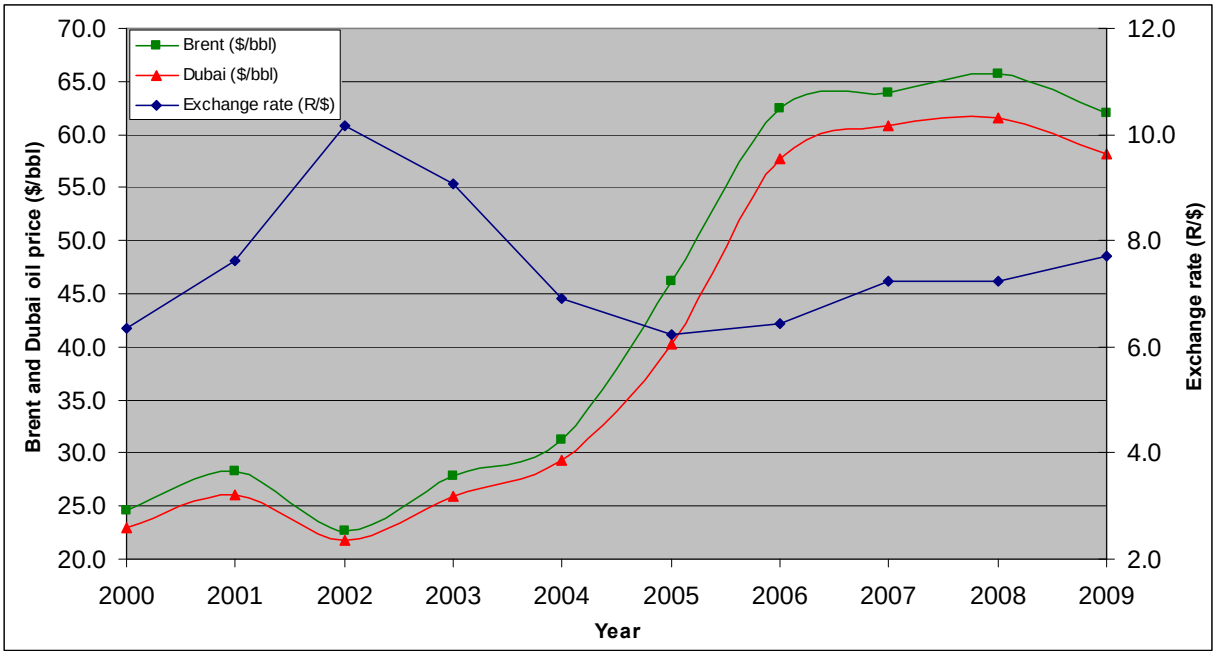


Figure 3-6 Brent and Dubai oil price[3] vs. the Exchange rate (R/$); (2000 - 2006; projection 2007 - 2009) (Enerdata, 2007)

3.3.6 Crude oil imports and the balance of payments

Imports of crude oil to South Africa are the single biggest item contributing to the balance of payments (current account) deficit. Figure 3-7 shows imports of crude oil to South Africa with the corresponding effect this item has had on the balance of payments (1990 to 2006). For the greater duration of the period between 1990 and 2000 the two trends enjoyed a comparable relationship. However, with the sharp increase in the exchange rate (2002), a sharp spike may be seen in the balance of payments deficit. From 2003 to 2006 imports of crude oil have remained relatively stable while the effect on the balance of payments deficit (for imported crude oil) has increased exponentially. As the exchange rate has remained relatively stable for the period 2003 to 2006, the exponential rise is explained by the increase in the crude oil price.

[3] These price indications do not include the cost of transporting the crude oil

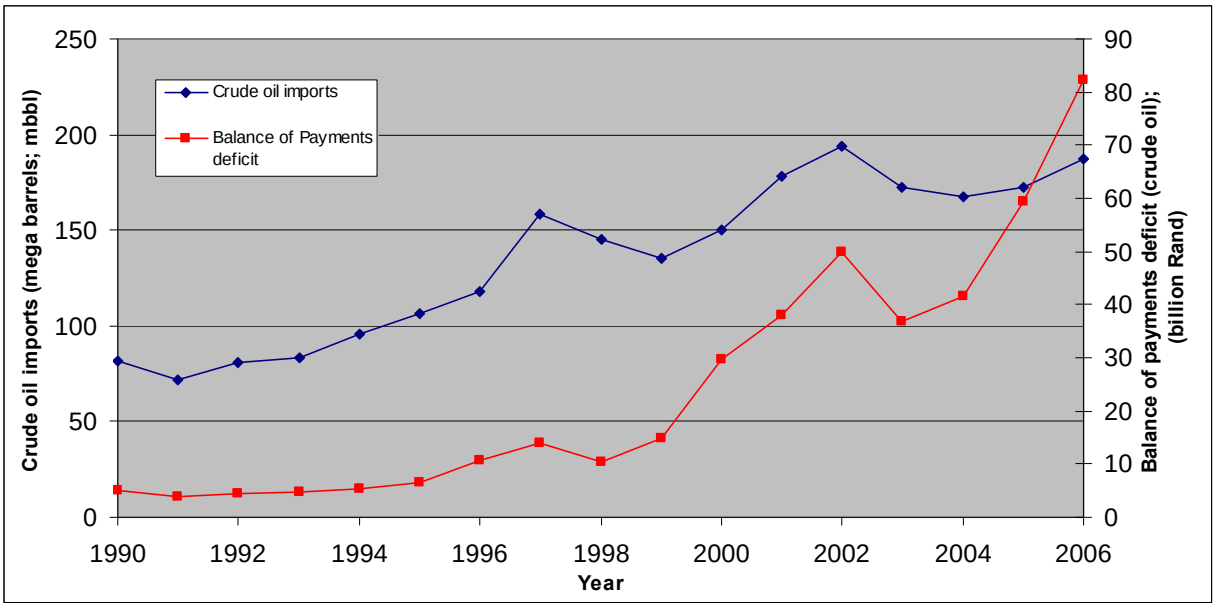


Figure 3-7 Crude oil imports vs. Balance of Payments deficit (crude oil); (1990 - 2006) (Enerdata, 2007)

Figure 3-8 shows cumulative crude oil imports vs. the corresponding cumulative cost to the balance of payments (1990–2006) deficit. Although this figure is more of academic interest as it cannot account for inflationary changes, it is interesting to note that while there was a widening gap between these two cumulative trends (1990-1999), this gap has in the period to 2006 rescinded substantially due to the price of imported crude oil.

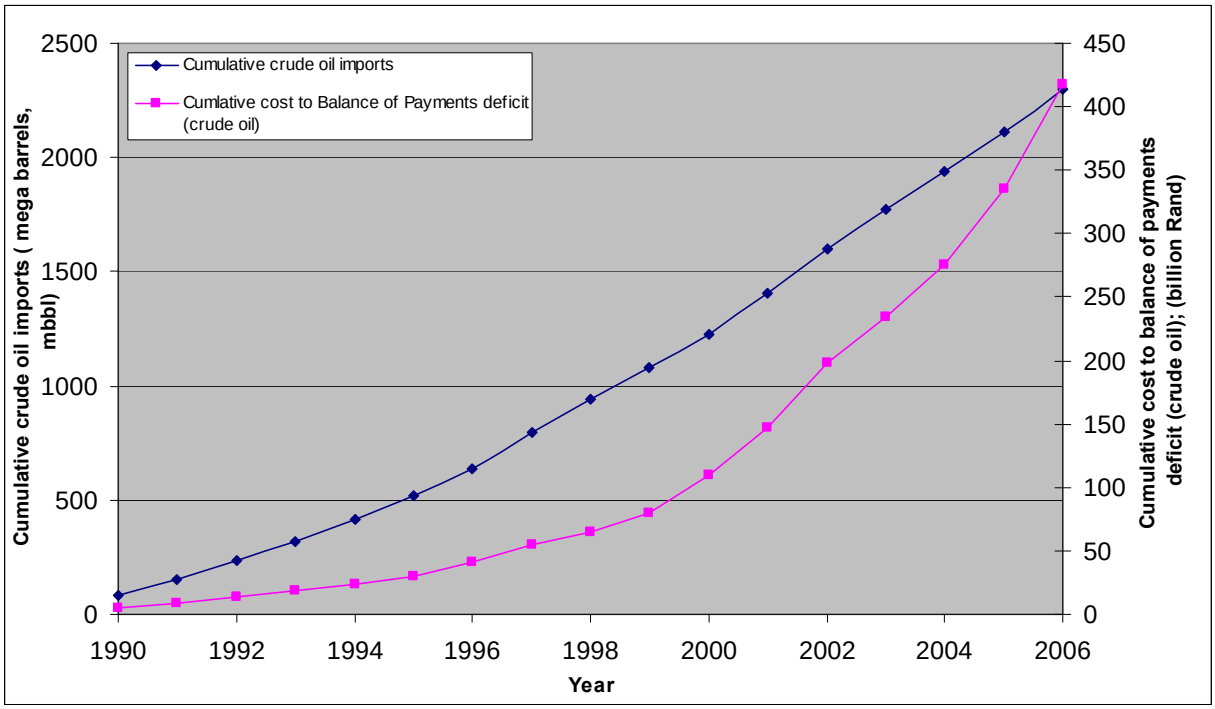


Figure 3-8 Cumulative crude oil imports vs. Cumulative cost to Balance of Payments deficit (crude oil);(1990 - 2006) (Enerdata, 2007)

3.4 The value of delayed coking to South Africa

The rationale behind the somewhat detailed explanation of the growth in the demand for automotive fuels and the effect of ever increasing crude oil imports to service this growth is exactly the same rationale that would be used to explain the need for the production of automotive fuels from local petroleum heavy residues using delayed coking.

The increasing price of crude oil coupled with the effect on the balance of payment deficit would certainly dictate that the maximum value be "squeezed out" of these crude oil imports. Irrespective of the quality of the specific crude oil, it will always have a finite percentage of petrol and diesel which may be extracted, leaving behind a heavy residue whose only use is as a burner or bunker fuel.

Delayed coking of these heavy residues allows for the production of "extra" petrol and diesel components which have a greater energy efficiency and demand than the heavy residues. Furthermore, it stands to reason that the production of more automotive fuels from the same amount of crude oil would in part retard the increasing trend towards higher crude oil imports and lessen the effect on the balance of payments deficit.

This also only accounts for the financial impact of delayed coking. Another impact would be on environmental emissions of SO_x and the energy efficiency (of petrol and diesel components vs. heavy petroleum residues) per tonne of CO_2 emitted into the atmosphere (discussed in Chapter 9).

The growth of the automotive fuel industry is not confined to the South African market. It is common to promote the production of automotive fuels from local resources, thus relaxing the effect of the negative balance of payments incurred through importing crude oil.

In an increasingly competitive petroleum market, the need for the extraction of maximum **value** from imported crude oil heavy residues is by no means limited to South Africa. Many of the same challenges facing South Africa with regards to automotive fuels and anode grade calcined coke are echoed within the global context, none more than within the United States of America (Phillips, 2003). The report highlights:

- A growing demand for transportation fuels (projected deficit for 2010 estimated at 40 million tonnes per annum)
- A reduction in markets for petroleum heavy residues (environmental concerns)
- A reduction in crude oil quality (expected to become heavier and more sour)
- A robust market for anode grade coke

The full report is given as Appendix A. In the 15 years prior to 2003 delayed coking (in the USA) was considered the preferential option to upgrade heavy residues with a capacity growth of 56% versus hydro-cracking (37%) and fluidised catalytic cracking (14%) (Phillips, 2003).

The sustained production of automotive fuels from local resources is encouraged according to the Department of Minerals and Energy (DME, 2006), which recommends that the production of liquid fuels from local resources be maintained at 30% of the total production. However, as the demand for automotive fuels grows yearly, the 30% figure quoted results in an increase of the actual litres of fuel required from local resources. This supports the idea to produce liquid fuels from the delayed coking of heavy residues both to negate the effect of importing crude oil and "squeezing" the maximum value out of South African resources.

By definition, heavy petroleum residues (originating from imported crude oils) would not qualify as "local" resources. However, these heavy residues are produced within the borders of South Africa and it is the author's opinion that these heavy petroleum residues may well be considered to be a "local" resource as their conversion to automotive fuels (using delayed coking) would "squeeze" the maximum value from the crude oil and reduce the amount of future imports.

4 ANODE COKE FOR THE ALUMINIUM INDUSTRY

4.1 The market for anode coke in Southern Africa

The demand for anode grade coke on the East coast of Southern Africa has substantially increased in the 13 years prior to 2008. Specific reference is made to:

- The opening of the BHP Billiton Hillside smelter in 1995-6
- The Hillside expansion project in 2003
- The opening of Mozal in 2000
- The addition of a pot line at the Mozal smelter in 2003
- The recent decision by Alcan to develop a 800 000 tonne per annum aluminium smelter in Port Elizabeth

The production of one tonne of aluminium requires 0.4 tonnes of calcined anode grade coke (Meier, 2006). Any increase in the demand for aluminium will by default result in an increase in the demand for anode coke. A local supply would further alleviate the need to import coke, reducing logistics costs and long lead ordering times of the smelter as well as the reduction in the balance of payments deficit. The current demand market for anode grade coke in Southern Africa is given in Table 4-1.

Table 4-1 Anode grade coke demand in Southern Africa (Milne, 2007)

Smelter	Location	Calcined coke requirement (Kilotonnes per annum)
Mozal	Maputo, Mozambique	170
Hillside Aluminum	Richards Bay, South Africa	250
Bayside Aluminum	Richards Bay, South Africa	70
Total demand		**490**

Apart from the approximately 500 000 tonne per annum demand it is estimated that the planned Alcan smelter in Port Elizabeth would consume a further 300 000–350 000 tonnes of coke annually.

Based on the potential tonnages (discussed in Chapter 8), delayed coking and calcining could yield approximately 216 650 tonnes of calcined coke annually. The coke would have an average sulphur content of 3.3% (Chapter 7).

While demand for calcined coke in South Africa is increasing, both the potential tonnage and the quality thereof have to be examined within the global context to determine the viability of a delayed coker and calciner.

4.2 Anode coke trends

4.2.1 Global supply / demand trends

Anode coke is used as a electrolytic reductant during the production of aluminium from alumina. In establishing demand trends into the future for calcined coke, it is first necessary to determine what the demand for primary aluminium will be. The demand for aluminium is expected to increase from the current level of 38 million tonnes (in 2008), to 48 million tonnes (in 2012) and over the long term to 66 million tonnes per annum (in 2020) (Mannweiler, 2008b). The demand for calcined anode coke will increase accordingly from 14 million tonnes (in 2008), to 18 million tonnes (in 2012) and over the longer term to 26 million tonnes per annum (Mannweiler, 2008b).

In 2007 the total global production of green coke was 91 million tonnes, of which 68 million tonnes (fuel coke) remained uncalcined. The 23 million tonnes of calcinable green coke produced 18 million tonnes of calcined coke. Of the 18 million tonnes, the aluminium industry consumed 14 million tonnes (or 78% of the available tonnage). The other 4 million tonnes was made up by needle coke (1 million tonnes) and carbon raisers for the metallurgical industry (3 million tonnes) (Driscol, 2007).

As given in Figure 4-1, the supply and demand trend for calcined petroleum coke will be in balance to 2009, thereafter the demand growth by the aluminium industry (which accounts for 78% of calcined coke consumption), will drive the demand imbalance. It is speculated that this imbalance will drive the price of calcined coke higher and that merchant calciners and aluminium smelters will need to utilise marginal green cokes (in terms of quality), to service the demand.

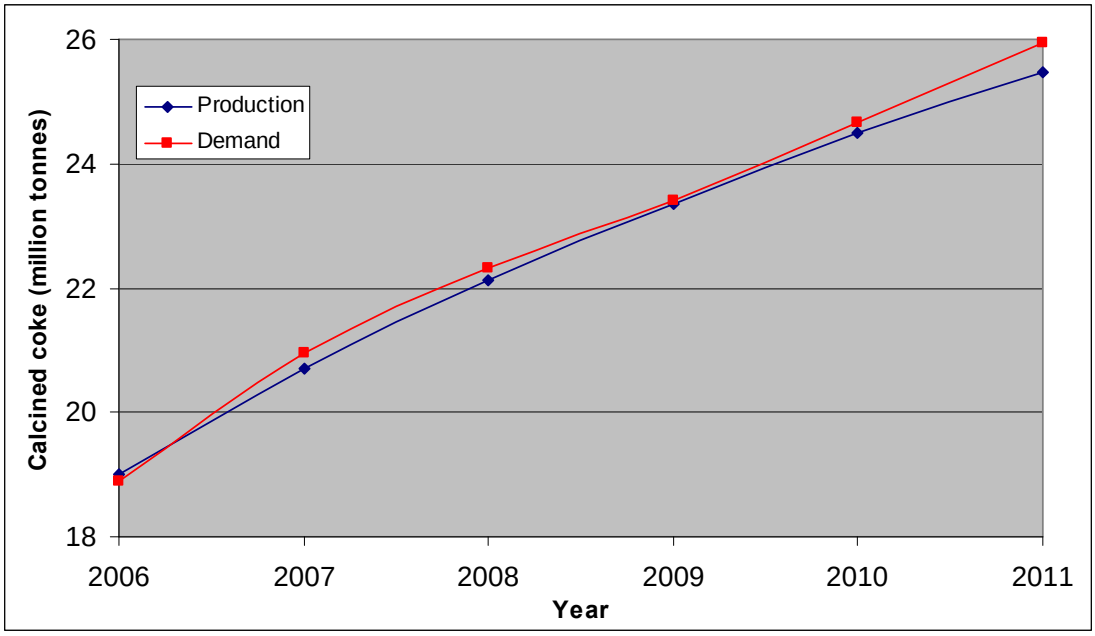


Figure 4-1 Global calcined coke supply / demand balance (2006 – 2007, 2008 – 2011 projected); (Driscol, 2007)

4.2.2 Global green and calcined coke quality

The quality of calcined petroleum coke is mainly determined by the sulphur and metals content. As discussed in Chapter 4.2.1, only a small percentage of the available green coke produced can be calcined. The greater bulk of fuel coke is produced when the delayed coker is operated to maximise petrol and diesel production.

As green coke is the feed for the production of calcined coke, Figure 4-2 shows that there is significant cause for concern given the increase in the sulphur and vanadium contents within the last 24 years.

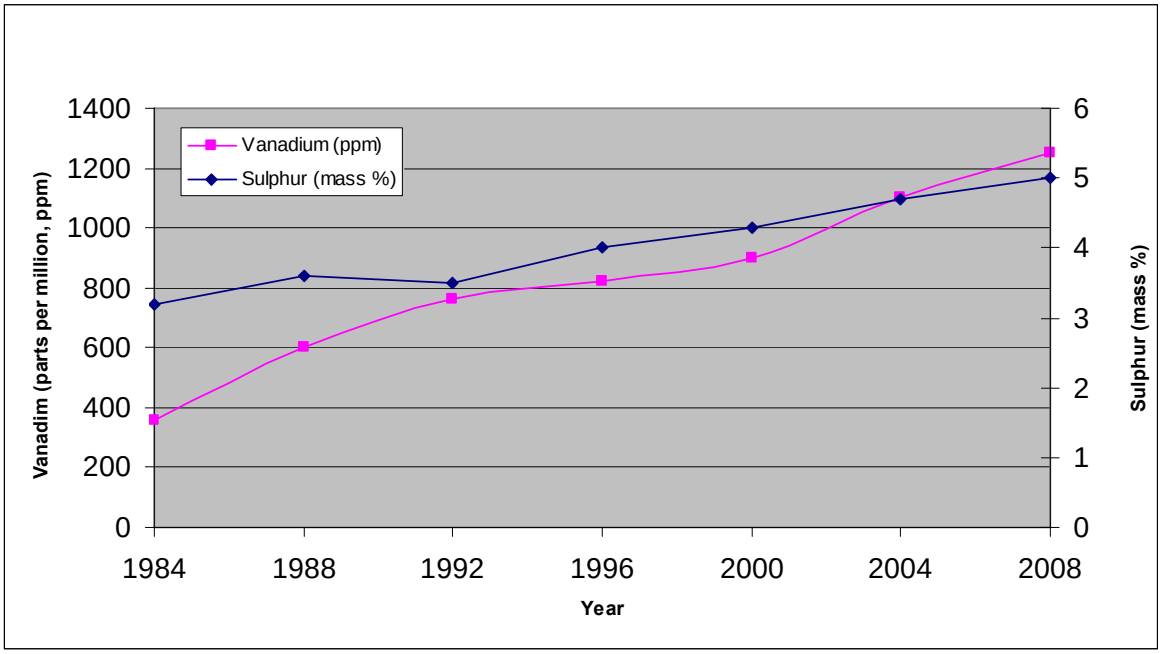


Figure 4-2 Sulphur and Vanadium content of global green coke supply (1994 -2006; 2008 projected) (Meier, 2006)

As the green coke quality deteriorates (Figure 4-2), there is a knock-on affect on the quality of the calcined coke (Figure 4-3). Of the metals listed in green coke (for the years 2000–2008 projected) there has been a significant increase in the vanadium (38%), iron (64%), nickel (60%) and silicon (77%) content of calcined cokes (Driscol, 2007). For the same time period the average sulphur content of calcined coke has increased from 2.5% (in the year 2000) to 3.6% (in the year 2007).

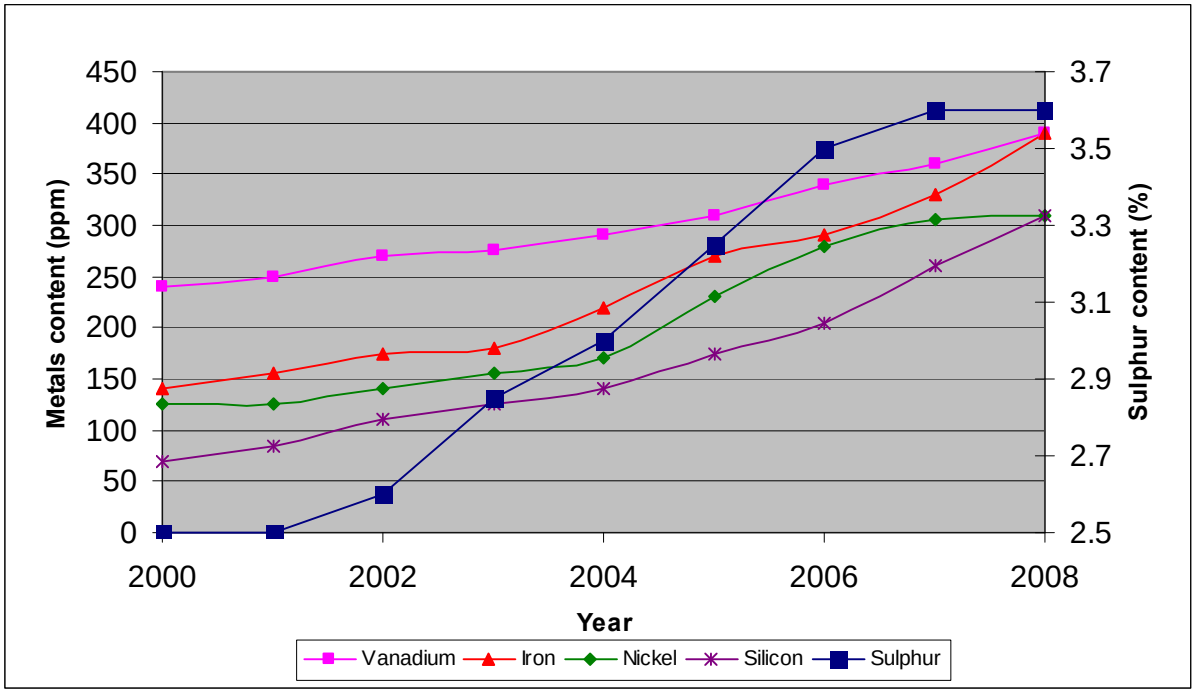


Figure 4-3 Global calcined coke quality trends (2000 – 2007, 2008 projected) (Driscol, 2007)

In order to ensure available volumes of calcinable coke, merchant calciners[1] and aluminium smelters have been forced into utilising lower quality calcined cokes. Merchant calciners have made incremental step changes in the maximum acceptable vanadium content in green coke from 230 ppm (in the year 2000) to 400-450 ppm (in the year 2006) (Meier, 2006). A further consequence is the co-calcining of green and blending of calcined cokes to yield an acceptable anode grade calcined coke. It is the author's considered opinion that the practice of "blending" will stretch further down the value chain in the future, towards the blending of the heavy residues prior to delayed coking. This is currently practised, but to a lesser degree (Clark and Chang, 2001).

Apart from the detrimental quality influences on the production of aluminium, environmental legislation may force smelters to either buy low sulphur calcined coke (at a premium) or invest in SO_x scrubbing abatement systems (discussed in Chapter 9.2.1.3). Quite apart from the process cost thereof, the initial capital outlay can be immense. On the other hand, low to medium sulphur cokes in future will also become more expensive.

4.2.3 Crude oil quality vs. green coke quality

The quality of petroleum derived anode cokes is inherently dependant on the quality of the crude oil (Table 4-2). An oil refinery is dependent both on atmospheric and vacuum distillation units for the production of lighter oils. The bottoms fraction

[1] Merchant calciners purchase green coke from many refineries and co-calcine to yield an appropriate quality calcined anode grade coke

(heavy molecular components) of vacuum distillation may be used to produce sponge or fuel grade coke. Other refinery processes, inclusive of Vis-breaking, Reduced Crude Desulphurisation and Fluidised Catalytic Cracking, may change the composition of the molecular components within a heavy residue. However, for the most part, delayed coking is employed to reduce the sulphur contents of the lighter fuel components produced. Table 4-2 compares a variety of crude oils with respect to their sulphur content, percentage of vacuum oil and Conradson Carbon Residue, which is a predictive test to determine the green coke yield.

Table 4-2 The quality of crude oil vs. the yield and quality of green coke produced (Meier, 2006)

Crude oil	Crude oil Sulphur (%)	Vacuum (% of oil)	Residue CCR (%)	Coke			
				Yield %	(S) %	(V) ppm	(Ni) ppm
Indonesian	0.09	12	13	2	0.3	30	100
Nigerian	0.16	9	12	2	0.7	30	140
Lybian	0.20	15	13	3	0.8	40	140
North Sea	0.28	15	14	4	1.1	100	50
Louisiana	0.32	14	12	3	1.5	70	200
West Texas	0.50	12	10	3	2.2	350	130
Alaskan NS	1.00	22	15	7	3.1	350	140
West Texas	1.40	15	19	6	4.0	165	90
Saudi light	1.80	17	15	6	5.9	160	50
Saudi heavy	3.00	30	23	11	6.8	470	150
Venezuelan Boscan	5.50	61	30	27	7.4	4700	600

Crude oil is generally becoming heavier and sourer. Thus, while the green coke yield is increased, so is the sulphur content of the coke. In developing (e.g. South Africa) or developed (e.g. The United States of America) countries, the sulphur content of calcined cokes used as fillers in anodes for the aluminium industry in future will have a direct impact on the profitability of the smelter (based on compliance with SO_x emission regulations).

5 EXPERIMENTAL PROCEDURES

All experimental procedures were developed at Sasol Technology (Research & Development) Division, Sasolburg. As these procedures were developed for Sasol Medium Temperature Pitch (MTP), they had to be modified to process the petroleum heavy residues (Samples A–E) due to variations in viscosity and thermal reactivity during mesophase formation. The experimental procedures described in this section are for the most part standardised methods.

5.1 Feedstock analysis

The heavy residue samples were drawn from the respective refineries under stable operating conditions. Routine analyses were conducted on the samples at the Sasol Synfuels Laboratory in Secunda. Table 5-1 shows the test methods utilised.

Table 5-1 Feedstock test methods

Analysis	Method	Units
Density @ 20°C	Sasol A121	$g.cm^{-3}$
Sulphur	ASTM D-4239-94	Mass%
Ash Content	ASTM D-4422-89	Mass%

The results for Samples A-E are given in Table 6-1.

5.2 Delayed coking

As described earlier (Chapter 2.4.2) delayed coking involves heating heavy residue feed streams, offsetting two types of reactions:

- **Cracking**: The formation of lighter molecular weight components inclusive of methane rich gas and distillate oils (petrol and diesel precursors)
- **Poly-condensation**: The condensation of large poly-aromatic macro molecules through the mesophase and the formation of carbon (green coke) in the solid phase

All the delayed coking experiments were conducted in the Mini Delayed Coker built by Sasol in the 1980's.

For these experimental trials the feed pot was filled with three litres of petroleum heavy residues (Samples A–E) heated to 100 ºC. Each of the samples was run in duplicate thus a total of ten experiments were conducted. While it is expected that commercial delayed coking would dictate the blending of heavy petroleum residues (to negate variations in consistency of the products), Samples A–E were unknown entities and thus needed to be tested independently in order to ascertain the individual quality of each of the sample's products.

The feed was pumped through stainless steel tubing at 600 ml per hour into a vertical delayed coking vessel (surrounded by three heating coils). As the delayed coking reaction progressed, coke was formed in the bottom of the coking vessel. The three heater coils were controlled at temperatures of 480 ºC, 470 ºC and 460 ºC respectively (from bottom to top). Distillates oil vapours formed from the cracking reaction were condensed in two catch pot condensers and the hydrocarbon gas, remaining uncondensed, was measured by a gas meter and vented to the atmosphere through a chimney.

The feed material was pumped for a total of two and a half to three hours and the coke was left to "heat soak" for a further nine hours at the temperatures given above (as controlled by thermocouples in each of the heater coils and the coker vessel). After the heat soaking period the coker was left to cool overnight. The coke was removed by a vertical pull and tackle and the liquid distillates were drained and weighed. Gas samples were taken online using a gas bomb. The pressure was kept constant (five bar) for the duration of the reaction using nitrogen. The total duration of each run was approximately 24 hours (inclusive of time allowed for cooling) (Schuin, 2004a).

The MDC has over the years been able to mimic expected commercial delayed coker product yields with a fair degree of accuracy. While the microstructure of the coke is almost entirely dependant on the quality of the feed, slight differences are noticeable between the MDC and the commercial delayed coker. Green coke yields on a commercial delayed coker would be slightly increased due to the effect of recycle oil. While it would be possible to mimic this effect on a MDC scale, the number of experiments would be increased by a factor of six (thus sixty runs), and this was not in the scope of this investigation. Another process variant is that on a commercial scale the feed is passed through gas fired heater tubes prior to entering the coking vessel, which is not externally heated.

5.3 Delayed coker products

5.3.1 Off-gas analysis

The off-gas was sampled in a tube bomb online. The GC-MS analysis was conducted on a High speed refinery analyser, Model 7890 in accordance with ASTM D1945/D1946 to determine the hydrocarbon distribution.

5.3.2 Green coke analysis

Routine analyses of the green coke produced during the blended feed delayed coker trial were conducted at Sasol Synfuels Laboratories in Secunda. Table 5-2 shows the test methods utilised.

Table 5-2 Green coke test methods

Analysis	Method	Units
Carbon	Sasol A 268	Mass%
Hydrogen	Sasol A 268	Mass%
Nitrogen	ASTM D-5373-93	Mass%
Sulphur	ASTM D-4239-94	Mass%
Ash Content	ASTM D-4422-89	Mass%

The results for the blended feed green coke analysis are given in Table 7-2.

5.3.3 White products Vacuum Distillation

The condensed distillate was removed from the MDC catch pots 1 & 2, weighed and placed into a 20 litre round bottom flask. The white products were distilled under a vacuum (1 mm Hg) to isolate petrol and diesel fractions.

A simplified diagram of the apparatus used for vacuum distillation is given in Figure 5-1.

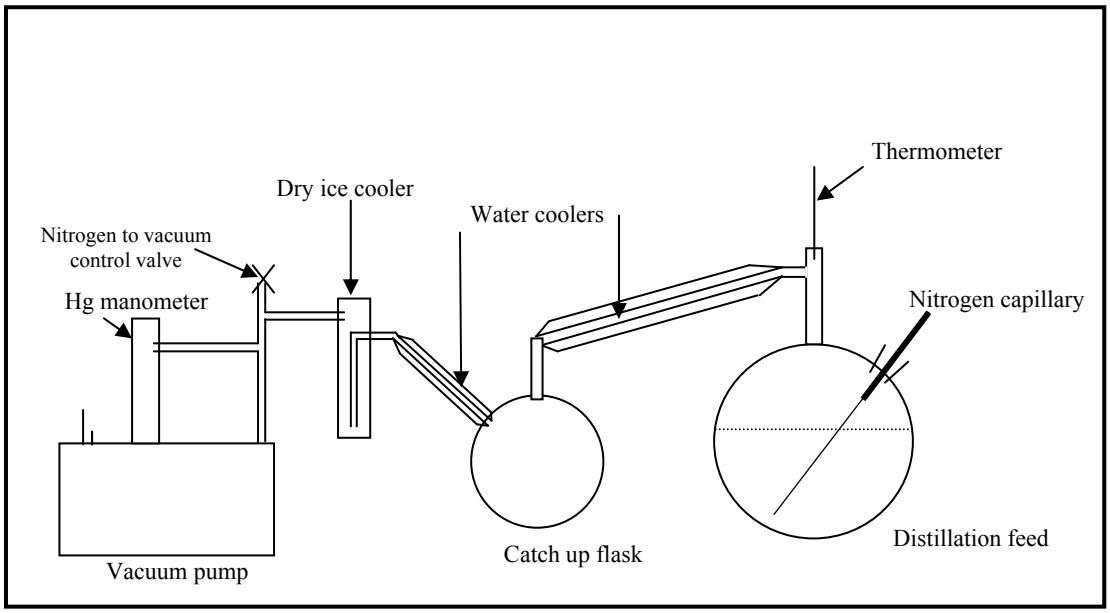


Figure 5-1 Simplified diagram of the vacuum distillation apparatus (Schuin, 2004b)

The apparatus utilised for vacuum distillation consists of a Round Bottom Flask [(RBF); (filled with the condensed distillate from the MDC)] with a capillary (coupled to a Nitrogen stream to prevent oxidation) inserted. The RBF is coupled to a water cooler which drains into a second smaller RBF to collect distillates. The second RBF is coupled in series to a second water cooler and a cooler filled with dry ice (to

condense lighter volatile vapours). This in turn is coupled to a mercury manometer and a vacuum pump.

The condensed distillate in the first RBF was heated to isolate the Naphtha and Coker Gas Oil (CGO) fractions.

5.3.4 Naphtha and coker gas oil analysis

The naphtha and the coker gas oil were analysed by Sasol Technology (Fuels Research) Division. Table 5-3 shows the test methods utilised.

Table 5-3 Naphtha and coker gas oil test methods

Analysis	Method	Units
Olefins	ASTM D1319	Volume%
Paraffins	ASTM D1319	Volume%
Aromatics	ASTM D1319	Volume%
Total aromatics (HPLC)	IP 391	Volume%
Mono	IP 391	Mass%
Poly	IP 391	Mass%
Di	IP 391	Mass%
Tri	IP 391	Mass%
Flash point	ASTM D93	ºC
Energy content	ASTM D240	KJ/kg
Total Nitrogen	ASTM D5453	mg/kg
Total Sulphur	ASTM D5453	Mass%
Bromine number	ASTM D1159	g Br/100g
Viscosity @ 40 C	ASTM D445	CPs
Density @ 20 C	ASTM D4052	CPs
Sodium	ICP	mg/kg
Vanadium	ICP	mg/kg
Nickel	ICP	mg/kg

The results of the naphtha and coker gas oil analyses for Samples A–E are given in Table 6-6; Table 6-10; Table 6-12 and Table 6-14 respectively.

5.4 Green coke calcination

The green coke removed from the coking vessel was weighed (to determine the green coke yield) and then heated to a temperature of 1350 ºC in a muffle furnace under a nitrogen blanket. The coke (approximately one kilogram) was placed in a graphite crucible (with a lid) and heated from ambient temperature to 1350 ºC at 10 ºC per minute. When the temperature reached 1350 ºC, the coke was held at that temperature

for 2 hours and then was allowed to cool, still under a nitrogen blanket. The sample was weighed to determine a calcination mass loss.

The laboratory calcination procedure varies from commercial calcination in that it is static. In commercial operation the coke, while subjected to the same temperature (1350 ºC) and similar heat soaking time, moves down a counter current horizontal calciner and thus is exposed to forces of attrition and erosion, which reduces the Particle Size Distribution (PSD). The laboratory scale furnace is heated electrically (with the coke protected from oxidation by a nitrogen blanket) while the commercial calciner is fired by a blend of air and hydrocarbon rich plant gas, controlled to yield a specific temperature gradient along the length of the calciner.

The calcination loss (on a laboratory scale) in a muffle furnace is usually in the region of 8–10% by mass. However it is recognised that on a commercial scale the oxidative atmosphere will promote combustion, CO_2 and air reactivity, leading to a greater calcination mass loss (approximately 24–26%). The economic evaluation (Chapter 8) would not be realistic, were the expected commercial calcination losses not utilised.

5.4.1 Calcined coke Coefficient of Thermal Expansion (CTE)

Prior to an explanation of the procedure for the determination of the "Fritted Body" CTE, it is necessary to define this characteristic of carbon particulates and artefacts correctly. The CTE of a carbon artefact (for example anodes in the aluminium industry and electrodes in the Steel industry), is a measure of thermal shock that a carbon artefact will experience during rapid heating.

The method for the determination of the CTE is industry specific (e.g. aluminium or steel), and even within the same industry, the method may vary. One of the accepted methods within the aluminium industry was developed by Dr Siegfried Wilkening of Verreenigde Aluminium Werke (VAW) in Germany (Schuin, 2004c). This is the "Fritted Body" method. This method refers specifically to the determination of the CTE on a carbon artefact produced in the laboratory using calcined coke and binder pitch.

The "Fritted Body" was produced by placing 250 grams of calcined coke (0.5 to 1.0 mm) in a tin. Crushed binder pitch (Mettler Softening Point (MSP) of 70 ºC; 350 g) was added to the tin, on top of the calcined coke fraction. The tins were placed in a stainless steel container and packing coke was added around the tins. The tins were heated in a furnace to 950 ºC at a predetermined heating rate and held at temperature for 40 hours. After cooling the "Fritted Body" carbon artefacts were removed from the tin. Cores were drilled from the "Fritted Body". The CTE was measured by a dilatometer on the cores. The cores were machined to form cylinders of 50 mm long with a diameter of 20 mm (Schuin, 2004c).

The cores were placed in a dilatometer and heated from ambient temperature to 300 ºC at a controlled temperature gradient. A silica core was placed on top of the "Fritted Body" core and connected to an electrical sensor, which measured the expansion of the carbon as a function of the temperature increase. The CTE is given in units of 10^{-6}/ºC.

Industrially the measurement of the CTE would be conducted in a similar fashion. The main difference being that a "Fritted Body" would not be prepared, but the core would be drilled from a baked anode. Usually every 50th anode is tested for quality control purposes. The majority of the CTE apparatus (for the aluminium industry) are produced by R&D Carbon located in Sierre, Switzerland.

The electrode industry makes use both of a "with" and "cross" grain CTE measurement. It should be noted that expansion takes place within an anode in all three dimensions. The greatest amount of thermal shock experienced by the anode takes place when it is placed in a pot cell (960 ºC) from ambient temperature. In extreme cases high CTE anodes may crack (as described in Chapter 2.4.3).

5.4.2 Calcined coke analysis

Routine analysis of the calcined coke produced during laboratory calcination was conducted at Sasol Synfuels Laboratories in Secunda. Table 5-4 shows the methods utilised.

Table 5-4 Calcined coke test methods

Analysis	Method	Units
Fixed Carbon	100% – (Ash + Volatiles)	mass %
Sulphur	ASTM D-4239-94	mass %
Carbon	Sasol A 268	g/100g
Hydrogen	Sasol A 268	g/100g
Nitrogen	ASTM D-5373-93	g/100g
Ash Content	ASTM D-4422-89	mass %
Volatile Carbon Matter	BS-1016	mass %
Inherent Moisture	ASTM D-3173-78	mass %
As Received Moisture	ASTM D-3173-78	mass %
Lead	Alusuisse C124/78	mass %
Iron	Alusuisse C124/78	mass %
Nickel	Alusuisse C124/78	mass %
Vanadium	Alusuisse C124/78	mass %
Calcium	Alusuisse C124/78	mass %
Silicon	Alusuisse C124/78	mass %
Aluminium	Alusuisse C124/78	mass %
Sodium	Alusuisse C124/78	mass %
Real (He) Density	ASTM D-4892-89	g/cm^3

The results for Sample A-E calcined cokes are given in Table 6-3; Table 6-5; Table 6-7; Table 6-9; Table 6-11; and Table 6-13 respectively. The blended feed calcined coke results are given in Table 7-2.

5.5 Graphitisation

Green coke produced from the blended feed coking run (Chapter 7) was graphitised at the Nuclear Energy Corporation of South Africa (NECSA). The green coke was weighed (25.7 g) and placed into a graphite crucible. The sample was heated to a maximum temperature of 2081º C in a Radio Frequency Induction furnace. The power was increased over a period of 15 minutes to a maximum of 15 kilowatts. The coke sample was kept at the maximum temperature for 5 minutes after which the power tripped due to the increasing temperature of the cooling water. The experiment was conducted under a nitrogen blanket. The graphite produced was allowed to cool down and weighed.

Due to the small mass of graphite produced, it was only possible to do ultimate and XRD analysis on the sample. The results are given in Chapter 7.2. The XRD analysis was conducted at Sasol Technology (Research and Development) Division.

5.5.1 X-ray diffraction

X-ray diffraction was conducted on samples of green coke and graphite produced. The sample was ground using a pestle and mortar and packed into a stainless steel holder. A Phillips X'Pert Pro multi-purpose diffractometer was used to conduct the XRD analysis. The radiation source utilised was Cobalt at a wavelength of 1.78897 Å. A full description of the experimental conditions is given in Appendix B (Du Plessis, 2007).

The results of the X-ray diffraction are given in Figure 7-1.

5.5.2 Graphite analysis

Routine analysis of the graphite produced during laboratory calcination was conducted at Sasol Synfuels Laboratories in Secunda. Table 5-5 shows the test methods utilised.

Table 5-5 Graphite test methods

Analysis	Method	Units
Carbon	Sasol A 268	Mass%
Hydrogen	Sasol A 268	Mass%
Nitrogen	ASTM D-5373-93	Mass%
Sulphur	ASTM D-4239-94	Mass%
Ash Content	ASTM D-4422-89	Mass%

The results for the graphite are given in Table 7-2.

6 RESULTS OF DELAYED COKING AND CALCINING TESTS

6.1 Analysis of petroleum heavy residues

The analyses of the petroleum heavy residues (Samples A–E) are given in Table 6-1.

Table 6-1 Analysis of heavy petroleum residues (Samples A-E)

Analysis	Units	Sample A	Sample B	Sample C	Sample D	Sample E
Sulphur	Mass%	2.83	3.72	4.60	4.16	4.20
Density (20ºC)	Kg/l	1.069	1.042	1.101	1.140	1.030
Ash	Mass%	0.027	0.047	0.073	0.018	0.027
Calorific value	MJ/kg	41.4	42.0	41.3	42.9	42.5

None of these heavy petroleum residues had previously been subjected to a sulphur removal process, thus the sulphur content (especially in Samples C–E) was comparatively high. While heavy petroleum residues with high sulphur levels often produce high sulphur green and calcined cokes as shown in Table 4-2 (Meier, 2006), a direct comparison of Sample A-E feedstock is not possible, as they have different origins within the refinery. The sulphur content of the green coke is dependant on the manner with which the sulphur is bound to the organic matrix. If the sulphur is predominantly bound as a thiol, the delayed coking reaction would cleave the bond and it should report to either the gas or the white product fraction. If the sulphur is bound within the aromatic structure of the heavy residue as a thiophene, it is likely that it would report to the coke.

The ash content of Sample C is substantially higher than the other samples, which is also evident in the ash content of the calcined coke (Table 6-3). The ash content of the calcined cokes (Table 6-3) is significantly above what would be expected based on the fresh feed (Table 6-1). Accurate sampling of the ash in the fresh feed was problematic due to settling of the ash.

Given the low ash content of the samples, the calorific values shown in Table 6-1 of between 41 and 43 MJ/kg compare well with those given in literature (Vallack, 2007). The determination of the calorific value is of importance as these residues are used to "fuel" the shipping industry. Both the calorific and nett calorific value of any fuel may be used to calculate the energy density per tonne of CO_2 emitted. This is discussed in greater detail in Chapter 9.

6.2 Delayed coker product yields

Table 6-2 Delayed coker product yields

Product	Units	Sample A	Sample B	Sample C	Sample D	Sample E
Green coke	Mass%	38.1	39.1	42.1	37.1	33.5
White products	Mass%	30.4	33.9	36	41.6	42.4
Gas	Mass%	31.5	27.0	22.8	21.3	24.0
Calcination loss	Mass%	7.6	7.6	9.0	7.8	7.2

The green coke yield is shown in Table 6-2. There is a correlation between the density of the heavy residues and the green coke yield, with the exception of Sample D. This correlation is illustrated in Figure 6-1.

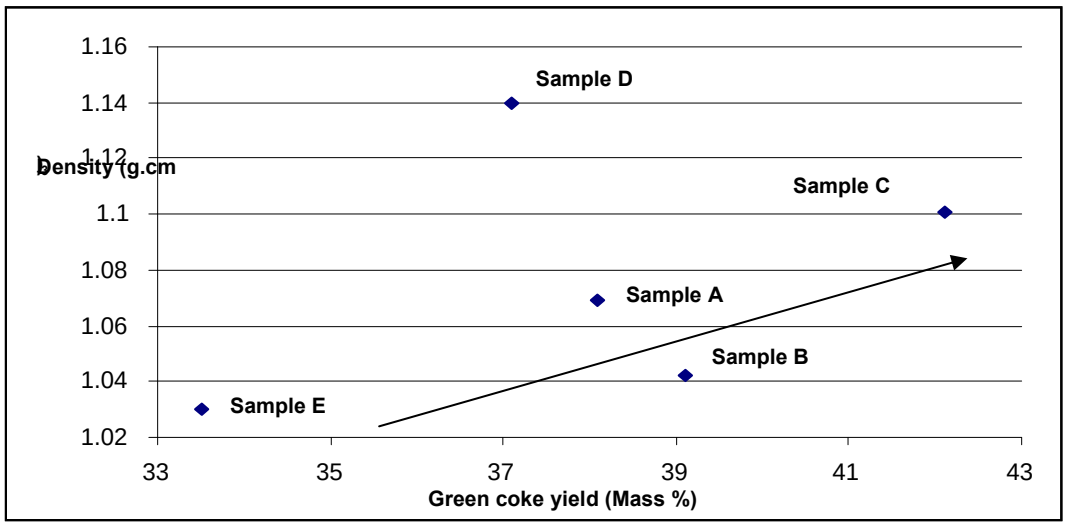


Figure 6-1 The effect of density of the feedstock on the green coke yield

The dependence of the green coke yield on the density of the feedstock, is supported in literature (Marsh, 1997), which indicates a direct relationship between the API gravity of petroleum heavy residues and the green coke yield, under the same coking conditions.

The green coke yield is affected both by the density of the fresh feed and by the amount of volatile organic matter within the coke matrix. It is possible to increase the green coke yield by further cracking the feeds which would deplete the residue of lighter oils and on average increase the percentage of heavier molecular weight components.

The calcination loss of the green coke (Table 6-2), given as 7-9%, is a laboratory based phenomenon; commercially the loss would more likely be in the 23-27% range (based on the author's experience). This is discussed in greater detail in Chapter 5.4.

6.3 Summary of delayed coker product quality

6.3.1 Calcined coke

A summary of the calcined coke quality analysis is given in Table 6-3

Table 6-3 Summary of the calcined coke physical and chemical analysis

Analysis	Units	Sample A	Sample B	Sample C	Sample D	Sample E
Coefficient of Thermal Expansion (CTE)	x 10^{-6}/°C	2.78	3.88	4.37	2.83	3.99
Fixed Carbon	mass %	99.45	99.44	99.02	99.53	99.51
Sulphur	mass %	2.99	3.79	3.85	3.17	1.96
Carbon	g/100g	95.92	94.15	95.10	96.35	96.60
Hydrogen	g/100g	0.02	0.04	0.05	0.06	0.05
Nitrogen	g/100g	0.14	0.15	0.40	0.10	0.67
Ash Content	mass %	0.37	0.33	0.80	0.37	0.38
Volatile Carbon Matter	mass %	0.18	0.24	0.18	0.10	0.11
Inherent Moisture	mass %	0.03	0.03	0.04	0.03	0.02
As Received Moisture	mass %	0.08	0.10	0.16	0.07	0.08
Iron	ppm	540	429	568	413	480
Nickel	ppm	45	54	219	41	282
Vanadium	ppm	2	2	530	1	299
Calcium	ppm	69	48	169	94	74
Silicon	ppm	431	329	905	315	263
Sodium	ppm	5	1	51	1	18
Real (He) Density	g/cm^3	2.127	2.076	2.101	2.101	2.112

Although a detailed description of each of the individual calcined cokes is given in Chapter 6.4, it is prudent to compare the collective results with each other.

6.3.1.1 The influence of feedstock characteristics on the microstructure and CTE of the coke

As mentioned in the introduction, individual delayed coking of each of the feed samples (A-E) would be able to identify feedstock that could be detrimental to a blend of the collective five residues. Assuming that delayed coking conditions were kept constant, mesophase development would be dependant on the molecular make-up of the residue, the QI (made up of semi solid carbonaceous material and ash) and the sulphur content as given in literature discussed below.

The more aromatic a heavy petroleum residue, the greater the extent of mesophase formation resulting in a more anisotropic carbon microstructure, while on the contrary the presence of asphaltenes in the feed may denote the formation of fine mosaic domains (Eser and Jenkins, 1989).

The influence of Quinolene-Insolubles (QI) in the feedstock, on the microstructure is well documented in literature. QI is composed of ash and semi carbons. The removal of QI from the feed may enhance lamellae arrangement and lower the CTE of calcined petroleum coke (Weishauptova, 1985). Research conducted to evaluate the influence of increased QI content in pitch during mesophase development (Tillmans and Pietzka, 1978; Stadelhofer, 1981), denotes the formation of a finer mosaic microstructure leading to an increase of the CTE of the coke. There is a direct correlation between the CTE of the calcined coke and the CTE of the anode (Hulse, 2000). Anodes placed in a pot cell at 960 °C experience thermal shock which can lead to mechanical stress and crack propagation. Thus it is shown that the microstructure and the CTE of candidate cokes may have a substantial influence on the performance of anodes in commercial practice.

The effect of ash content on mesophase development and by default the microstructure of coke has previously been described (Obara and Marsh, 1985). Petroleum pitch was doped with silica gel (< 45 μm particles) and produced a green coke by delayed coking. The silica gel addition was found to reduce the optical texture of the mesophase and increase the CTE of the calcined coke. The reason suggested being that the silica gel restricted molecular motions during mesophase formation.

The addition of fullerene soot (semi carbon) to petroleum pitch studied under hot stage microscopy has shown substantial retardation of mesophase development leading to finer mosaic microstructures (Gentzis, 2001). This is enhanced by the ability of the soot to absorb the developing mesophase.

On the contrary, de-ashing of petroleum feeds has been shown to improve the microstructure of the coke (Junji, 1993). This work refers to a patent application showing that ash can be removed from petroleum heavy oil using a variety of methods inclusive of filtration, centrifugation and electrostatic aggregation. In all the aforementioned cases the ash reduction led to a significant reduction of the calcined coke CTE.

Thus based on the previous work cited, feedstock with higher ash content will form finer mosaic microstructures and calcined coke with a higher CTE.

This is supported by the current research. The ash content of Sample C feedstock (0.073%) was substantially higher than that of Samples A, B, D or E (0.027-0.047%; as shown in Table 6-1). While Samples A, B, D and E produced calcined cokes with granular and laminar flow domains with ash contents of 0.33 to 0.38%, the microstructure of Sample C coke shows finer mosaic domains and has an ash content of 0.80%. Sample C calcined coke has been shown to have the highest CTE value of 4.37 $x10^{-6}$/°C (shown in Table 6-3). The higher ash content of Sample C calcined coke is thus thought to be responsible for the finer mosaic microstructure and higher CTE value.

The calcined cokes of Samples A, B, D and E have a similar ash content (0.33-0.38%), which are lower than that of Sample C calcined coke. Samples A, B, D, and E calcined cokes also display improved microstructures and lower CTE values. These findings which relate to the influence of lower ash content in the feedstock on an improved microstructure and lower CTE, are in agreement with literature (Obara and Marsh, 1985; Junji, 1993; Stadelhofer, 1981).

However, the calcined coke of Samples A and D exhibit CTE values of 2.78 and 2.83 $x10^{-6}$/°C respectively, which are comparatively lower than the CTE values of Sample B and E calcined cokes (3.88 and 3.99 $x10^{-6}$/°C respectively). As mentioned previously the ash content of Samples A, B, D and E are similar, which thus obviates the influence of ash (in this instance) on both the microstructure and CTE of these cokes. However, the ash content is not the only factor determining the microstructure and CTE of a coke. As cited in literature (Eser and Jenkins, 1989), the molecular composition of the feedstock (especially the asphaltene content), the green coke yield and the distribution and morphology of macro-porosity (Hulse, 2000) may also in part determine the quality of the coke. Thus there needs to be an explanation for the variance of CTE values obtained between Samples A and D compared to Samples B and E calcined coke.

Samples B and E green cokes show a significant collection of oval or irregular shaped macro-pores. The lower green coke yield of Sample E (Table 6-1), yielded a significant increase in the white product yield, which is thought to be responsible for the porosity shown in the micrographs (Chapter 6.4.5). Previous research in part fulfilment of a PhD thesis (Hulse, 2000), showed a correlation between the shape of macro-pores examined by optical microscopy and the CTE of the coke. It was proved that highly anisotropic needle cokes have a median pore axial ratio which is less than sponge cokes whose ratio is larger. In effect this means that cokes that have a more rounded or irregular pore shape will tend to have higher CTE values than those cokes showing longer thinner pores which form parallel to the laminar flow microstructure.

Although this evidence is not definitive, it is suggested that the higher CTE of Samples B and E is explained due to the morphology of the macro-pores. However, the current research proves that the contrary is also true. Examination of Sample D optical micrographs reveals a denser carbon microstructure (Chapter 6.4.4.1) with longer thinner pores aligned parallel to the domain flow. This is thus evidence for the lower CTE of Sample D compared to Samples B and E. The laminar flow domains and parallel long thin pores displayed by Sample D are similar compared to those displayed by highly anisotropic needle cokes. This is supported by literature (Mochida, 1987).

With respect to both the microstructure and lower CTE value obtained for Sample A, there is no conclusive evidence as there appears to be a variety of microstructures present (Figure 6-2 to 6-4). Based on the aforementioned evidence and the lower CTE, the denser microstructure would appear to be dominant.

6.3.1.2 The quality of calcined coke with respect to the aluminium industry

Typical calcined anode coke characteristics have previously been shown in Table Table 2-2 (Hulse, 2000).

The CTE of Samples A and D calcined coke are below the industry average of 3.5 $x10^{-6}$/°C (Milne, 2007). Samples B, C and E calcined cokes have CTE values above the industry average. In a blend of the all the feedstocks available (Chapter 7), these variations should cancel each other out, however the resultant CTE will in all probability not correlate directly with the average of the five cokes. The CTE of the coke will depend on the molecular interaction between all the five feedstocks. Similar work has been conducted previously (Clark and Chang, 2001; Clark and Chang, 2002), which describes the effect of concentration variances of gasification coal-tar pitch and petroleum decant oil mixtures on the CTE of the calcined coke.

The major concern with regards to the suitability of the five cokes produced for anode fillers in the aluminium industry pertains to the ash content. While the effect of the higher ash content on the microstructure and CTE have been demonstrated, this may not be the most serious concern. The ash content of all the five calcined cokes is higher than the industry average of 0.10-0.20% (Hulse, 2000).

Of particular concern are the comparatively high levels of iron (413-568 ppm) and silicon (263-905 ppm). This is higher than the typical ranges for calcined cokes used in the aluminium industry (iron: 50-400 ppm and silicon: 50-250 ppm). With the exception of Samples C and E the nickel and vanadium contents are within the typical range. Both nickel and vanadium are known catalysts for air reactivity in anodes (Hulse, 2000) and have been linked (in the presence of sulphur) to the formation of finer mosaic mesophase (Oi and Onishi, 1978). The comparatively low sodium content of all of the calcined coke samples is advantageous. Sodium is known to increase air reactivity at the top of an anode (Fischer, 1995). Both air and CO_2 reactivity of calcined coke in an anode reduce the percentage of carbon used for the electrolytic reduction of alumina and thus have production cost implications.

Various methods have been described in literature to reduce the ash content of the feedstock and thus of the calcined coke as well (Junji, 1993).

The typical sulphur content range for anode coke fillers is 0.50-3.50% (Hulse, 2000). The sulphur content of Samples A-E calcined cokes ranged from 1.96-3.85%. The sulphur content reported for the blended feed coke (Table 7-2) is 3.26% which is not unusually high given that the global projected average sulphur content for calcined cokes has increased from 2.60% in 2000 to a projected value in 2008 of 3.60% [Table 4.3 (Driscol, 2007)]. This is in agreement with the maximum sulphur content for typical calcined cokes of 3.5% (Hulse, 2000).

The real density of the all the calcined cokes were relatively high (2.076-2.127 $g.m^{-3}$), given the wide range which is typical for the anode industry (2.050-2.100 $g.m^{-3}$).

Thus the major challenge would be the removal of the ash from the feed prior to delayed coking for all the feeds to produce coke which would be considered for the aluminium market.

6.3.2 Naphtha and gas oil

A detailed analysis of the white products from each of the samples is shown in Chapter 6.4.1-5.

The yield of the white products (petrol and diesel combined) varied vastly. The naphtha (petrol precursor) fractions could all be considered as petrol blend components after further hydrogenation. The coker gas oil (diesel precursor) fractions were observed to have relatively high sulphur content and contained olefins making hydrogenation essential if viable diesel blend components are to be produced.

Hydrogenation of naphtha and coker gas oil would not usually form part of the commercial evaluation of a delayed coker and are generally regarded as "add on's" to a refinery. Thus the hydrogenation units within the refinery would be utilised to produce petrol and diesel from naphtha and coker gas oil.

The hydrogenation would involve (European Commission, 2003)

- Naphtha hydotreating: used for de-sulphurisation, de-nitrification and stabilisation of the naphtha. The stabilisation of naphtha involves the conversion of unsaturated hydrocarbons to paraffins.
- Coker gas oil hydrotreating: used especially for the stabilisation of cracked components which include saturation of dienes and aromatics.

The availability of hydrogen is another factor which needs to be considered. Unlike Coal to Liquid plants where hydrogen is available as a product of coal gasification, petroleum refineries do not have this source. Hydrogen may be generated from the coker gas or from natural gas in a steam reformer (European Commission, 2003).

6.3.3 Gas

The gas composition of all the delayed coker runs (with the exception of Sample A) were analysed with respect to their individual components. A summary of the component analysis is given in Table 6-4.

Table 6-4 Delayed coker off-gas - GC-MS

Component (mass %)	Sample B	Sample C	Sample D	Sample E	Average
Methane	52.4	23.3	34.1	44.7	**38.6**
Ethane	18.5	20.0	20.9	23	**20.6**
Ethylene	6.1	5.7	4.5	4.4	**5.2**
Propane	8.6	14.9	14.5	12.2	**12.6**
Propylene	8.1	12.0	10.3	8.3	**9.7**
Isobutane	0.8	1.6	2.0	1.6	**1.5**
n-Butane	1.3	3.9	2.7	1.0	**2.2**
t-Butene-2	0.8	1.8	1.5	0.8	**1.2**
1-Butene	1.1	2.4	1.9	1.0	**1.6**
Isobutene	1.1	2.1	2.4	1.5	**1.8**
c-Butene-2	0.6	1.4	1.2	0.6	**1.0**
C5+ HYDROCARBONS	0.2	2.2	2.9	0.7	**1.5**

With respect to the data presented in the normalised hydrocarbon distribution, it is evident that the greater concentration of components lies in the C1 and C2 range, (methane and ethane). The feed is hydrogen rich (comparison of the ethane / ethylene ratio of 4.0 and propane / propylene of 1.3). It is postulated that the parent aromatics of all the feeds contain significant amounts of lower alkyl functions bound to the parent aromatic compounds (--CH_3; --C_2H_5, --C_3H). The hydrogen content is not shown due to an error on the part of the author, who omitted to have it analysed.

6.4 Detailed delayed coker product quality

6.4.1 Sample A



6.4.1.1 Optical microscopy of Sample A green coke

The optical micrographs of Sample A green coke (Figure 6-2; Figure 6-3 and Figure 6-4) indicate variation in the microstructure from coarse mosaic to elongated granular flow. All optical micrographs were prepared under oil immersion with a UV filter.

Figure 6-2 exhibits dense carbon with negligible porosity and (towards the left of the micrograph) areas of elongated granular flow. Figure 6-3 exhibits areas of coarse mosaics (on the right) and elongated granular flow characteristics (towards the left of the micrograph). Figure 6-4 exhibits mostly coarse mosaic activity and is highly porous. Thus the coke is shown to exhibit variability with respect to porosity development. This is probably due to variances in porosity as a function of height zoning in the coker drum. Similar effects were cited in research on a commercial scale (Clark and Chang, 2002).

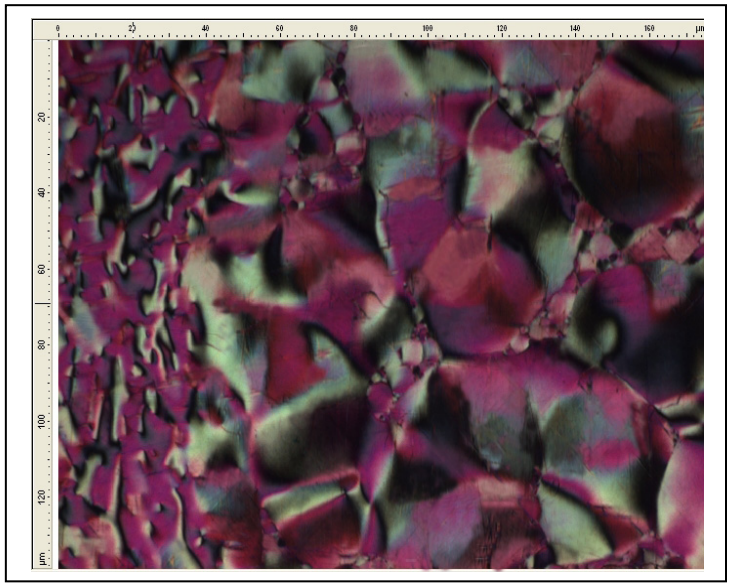


Figure 6-2 Sample A: Polarised Light micrograph 1a (Magnification x 10)

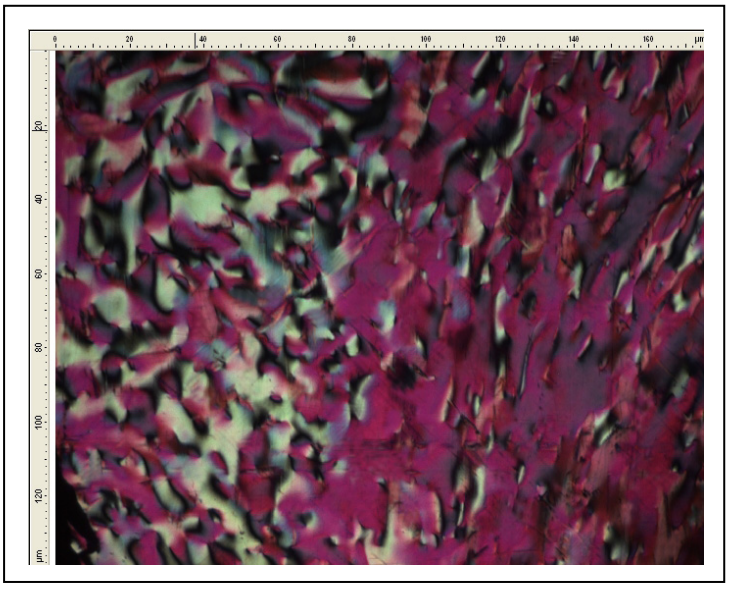


Figure 6-3 Sample A: Polarised Light micrograph 1b (Magnification x 10)

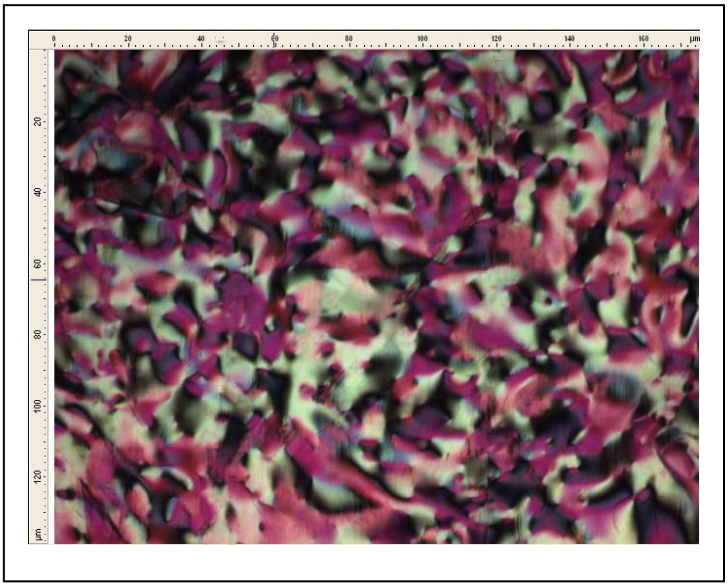


Figure 6-4 Sample A: Polarised Light micrograph 1c (Magnification x 10)

6.4.1.2 Physical and chemical analysis of Sample A calcined coke

With respect to the suitability of Sample A calcined coke for the aluminium industry (Table 6-5), the only challenge would be with respect to the ash content. The CTE (2.78 $x10^{-6}$/°C) is below the typical industry standard of 3.5 $x10^{-6}$/°C (Milne, 2007) for use in pre-bake applications, although the variation in the two runs (3.04 and 2.51 $x10^{-6}$/°C) is a concern. While the duplicate runs were conducted under the same conditions, the variation between the two CTE values is more likely attributed to a variation of the coke structure as a function of coke formation in different parts of the drum.

The sulphur (2.99%) is comparatively low, while ash content (0.37%) is higher than desirable. The VCM (0.18%) seems a little higher than would be desirable (< 0.1 mass%). This is ascribed to the fact that calcination was conducted on a laboratory scale rather than a commercial scale. The major mineral contaminants include iron (540 ppm), silicon (431 ppm) and aluminium (555 ppm). Both the nickel (45 ppm) and vanadium (2 ppm) contents are comparatively low. The real density (2.127 $g.cm^{-3}$) is high given the variation of the microstructure.

Table 6-5 Physical and Chemical analysis of Sample A calcined coke

Analysis	Units	Sample A Run 1	Sample A Run 2	Sample A (Ave)
Coefficient of Thermal Expansion (CTE)	x 10^{-6}/°C	3.04	2.51	**2.78**
Fixed Carbon	mass %	99.30	99.60	**99.45**
Sulphur	mass %	2.99	2.99	**2.99**
Carbon	g/100g	95.83	96.01	**95.92**
Hydrogen	g/100g	0.02	0.02	**0.02**
Nitrogen	g/100g	0.15	0.13	**0.14**
Ash Content	mass %	0.50	0.25	**0.37**
Volatile Carbon Matter (VCM)	mass %	0.20	0.16	**0.18**
Inherent Moisture	mass %	0.03	0.03	**0.03**
As Received Moisture	mass %	0.10	0.06	**0.08**
Lead	mass %	2	1	**2**
Iron	mass %	763	317	**540**
Nickel	mass %	54	36	**45**
Vanadium	mass %	1	2	**2**
Calcium	mass %	95	43	**69**
Silicon	mass %	546	315	**431**
Aluminium	mass %	653	457	**555**
Sodium	mass %	3	7	**5**
Real (He) Density	g/cm^3	2.131	2.123	**2.127**

6.4.1.3 Quality evaluation of Sample A naphtha and coker gas oil

The results of the quality analysis are given in Table 6-6.

The naphtha fraction shows reduced sulphur content compared to Sample B. The density (0.8128 $g.cm^{-3}$) is indicative of the high aromatic content of the naphtha and could be considered as a final petrol blend component after further refining to remove the sulphur and hydrogenate the dienes. Conjugated dienes in petrol may give rise to gum formation during further processing which would be undesirable.

The coker gas oil fraction reports a considerably high aromatic content (78.43%), the greater deal of which are thought to be poly-aromatics. The considerable aromatic content gives rise to the high density of the diesel (1.0199 $g.cm^{-3}$). The sulphur content of this fraction (2.56%) would require further processing before it could be used as a diesel blending component.

The metals content of the coker gas oil fraction is very low and is not considered a challenge for further processing.

Table 6-6 Quality evaluation of Sample A Naphtha and Coker Gas Oil (CGO)

	Units	Naphtha	CGO
Olefins	Volume%	-	-
Paraffins	Volume%	20.2	-
Aromatics	Volume%	62.9	-
Total aromatics HPLC	Volume%	-	78.43
Mono	Mass%	-	8.97
Poly	Mass%	-	69.46
Di	Mass%	-	43.08
Tri	Mass%	-	26.38
Flash point	ºC	-	74
Energy content	KJ/kg	-	41304
Total Nitrogen	mg/kg	123	976
Total Sulphur	Mass%	0.08	2.56
Bromine number	g Br/100g	-	29.51
Viscosity @ 40 C	CPs	-	3.16
Density @ 20 C	CPs	0.8128	1.0199
Sodium	mg/kg	-	< 0.01
Vanadium	mg/kg	-	< 0.01
Nickel	mg/kg	-	0.01

6.4.2 Sample B



6.4.2.1 Optical microscopy of Sample B green coke

The two coke samples examined (Figure 6-5 and Figure 6-6) by optical microscopy exhibit granular and laminar flow domains with intermittent porosity. The tiny thin cracks evident in the micrographs (often at a right angle to the flow domain) are probably caused by shrinkage of the coke on cooling after delayed coking. Figure 6-6 shows tiny carbon particles, appearing as green mosaics. This phenomenon is a pseudo-optical and appears due to suspension of fine carbon particles in the oil.

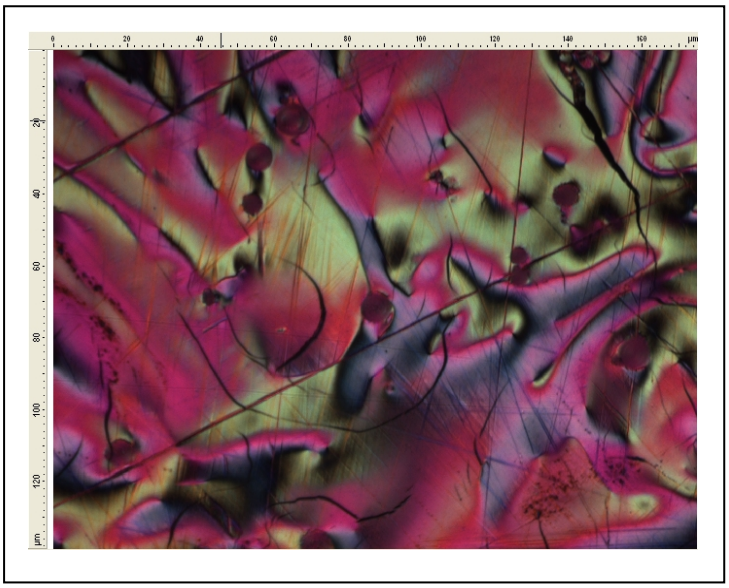


Figure 6-5 Sample B: Polarised Light micrograph 2b (Magnification x 10)

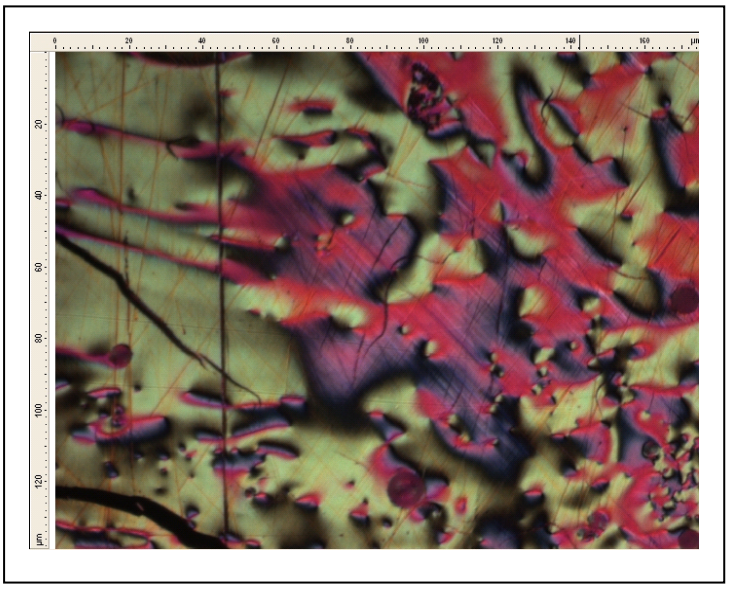


Figure 6-6 Sample B: Polarised Light micrograph 2c (Magnification x 10)

6.4.2.2 Physical and chemical analysis of Sample B calcined coke

With respect to the suitability of Sample B calcined coke for the aluminium industry (Table 6-7), the only significant challenge may be the higher ash content (0.33%) as compared with the typical ash content of calcined anode coke which is 0.10-0.20% (Hulse, 2000). The microstructural evidence suggests that a lower CTE than 3.88 $x10^{-6}$/°C could have been expected. However, the relatively high CTE is supported by the lower average real density (2.076 $g.cm^{-3}$) and the porosity shown in Figure 6-6. The polarised light micrographs are representative of three pieces of carbon, showing variability both in the microstructure and real density. The CTE may be more

representative of the quality of the batch as a whole as this analysis requires a greater portion of the coke sample to be utilised.

The significant variation in the real densities of the two runs may be as a result of sampling from different height zones within the MDC. The slightly higher VCM (0.24%), although higher than would have been desired, is probably just due to the fact that the sample was calcined in a laboratory calciner. The sulphur content (3.79%) is higher than the maximum typical value of 3.50% (Hulse, 2000), however compares well with the global industry average of 3.6% (Driscol, 2007). The iron (429 ppm) and the aluminium (440 ppm) contents are the major mineral contaminants.

The vanadium (2 ppm), sodium (1 ppm) and nickel (54 ppm) contents bode well with respect towards the air reactivity of the coke (Fischer, 1995).

Table 6-7 Physical and Chemical analysis of Sample B calcined coke

Analysis	Units	Sample B Run 1	Sample B Run 2	Sample B (Ave)
Coefficient of Thermal Expansion (CTE)	x 10^{-6}/°C	3.94	3.81	**3.88**
Fixed Carbon	mass %	99.32	99.55	**99.44**
Sulphur	mass %	3.69	3.89	**3.79**
Carbon	g/100g	95.20	93.10	**94.15**
Hydrogen	g/100g	0.02	0.05	**0.04**
Nitrogen	g/100g	0.15	0.16	**0.15**
Ash Content	mass %	0.37	0.29	**0.33**
Volatile Carbon Matter (VCM)	mass %	0.32	0.16	**0.24**
Inherent Moisture	mass %	0.03	0.03	**0.03**
As Received Moisture	mass %	0.08	0.12	**0.10**
Lead	mass %	1	1	**1**
Iron	mass %	464	394	**429**
Nickel	mass %	59	48	**54**
Vanadium	mass %	3	1	**2**
Calcium	mass %	56	40	**48**
Silicon	mass %	391	266	**329**
Aluminium	mass %	512	367	**440**
Sodium	mass %	1	1	**1**
Real (He) Density	g/cm^3	2.091	2.061	**2.076**

6.4.2.3 Quality evaluation of Sample B naphtha and coker gas oil

The results of the quality analysis are given in Table 6-8.

While much of what has been documented relating to Sample A white products holds true for Sample B, it is interesting to note that the higher sulphur content of the Sample B feedstock (3.72%) as opposed to the Sample A is evident with

comparatively higher levels of sulphur in the naphtha (0.14%), coker gas oil (4.13%) and calcined coke (3.79%). The comparative levels for Sample A were feedstock (2.83%), naphtha (0.08%), coker gas oil (4.13%) and calcined coke (2.99%). This shows thus an even distribution of higher sulphur contents throughout the array of delayed coker products of Sample B as compared to Sample A due to the higher levels of sulphur in the Sample B feed.

Table 6-8 Quality evaluation of Sample B Naphtha (Petrol) and Coker Gas Oil (CGO)

	Units	Naphtha	CGO
Paraffins	Volume%	21.8	-
Olefins	Volume%	23.3	-
Aromatics	Volume%	54.9	-
Total aromatics (HPLC)	Volume%	-	83.19
Mono	Mass%	-	4.62
Poly	Mass%	-	78.57
Di	Mass%	-	36.26
Tri	Mass%	-	42.31
Flash point	ºC	-	71
Energy content	KJ/kg	-	41010
Total Nitrogen	mg/kg	22	1390
Total Sulphur	Mass%	0.14	4.13
Bromine number	g Br/100g	-	28.69
Viscosity @ 40 C	CPs	-	4.78
Density @ 20 C	CPs	0.793	1.0524
Sodium	mg/kg	-	< 0.01
Vanadium	mg/kg		< 0.01
Nickel	mg/kg		0.01

6.4.3 Sample C



6.4.3.1 Optical Microscopy of Sample C green coke

Both the optical micrographs (Figure 6-7 and Figure 6-8) exhibit a fine to medium mosaic texture indicative of generally isotropic coke. These microstructural domains are more characteristic of coal-tar gasification coke which are usually hard, brittle cokes and have a higher CTE. This is supported in literature by the work of others (Wolters and van der Walt, 2007; Clark, 2004b) which describes the effect of a fine mosaic coke yielding a hard, brittle pitch coke with a high CTE. Mesophase development is not dependant on a singular feedstock characteristic, and the isotropic microstructure may be as a result of high ash, lower viscosity, comparatively high sulphur content or the effect of molecular composition on the kinetics of mesophase formation (Eser and Jenkins, 1989).

The only obvious reason from the data available may be the influence of the ash content, producing a more isotropic carbon (in comparison to Samples A, B, D and E). Ash particles congregate around the grain boundaries of the developing mesophase and tend to impede coalescence. As viscosity of the mesophase increases it gives rise to a mosaic microstructure.

Unfortunately at such a low magnification (x10) the ash particles cannot be seen. When using Scanning Electron Microscopy (SEM; Magnification 2000x, distance between the white parallel lines equal to 5.04 ům) the ash would appear as white irregular shaped particles gathered around the grain boundaries as shown in Figure 6-9. The considerably high sulphur content of Sample C feed (4.6%) may be a secondary causative factor leading to the higher CTE and isotropic microstructure. The catalytic effect of vanadium and nickel in the presence of sulphur has been shown to form cokes with a finer mosaic domain and higher CTE (Oi and Onishi, 1978). Given that the vanadium (530 ppm) and nickel (299 ppm) contents are comparatively high this may be a secondary causative factor determining the finer mosaic and higher CTE value.

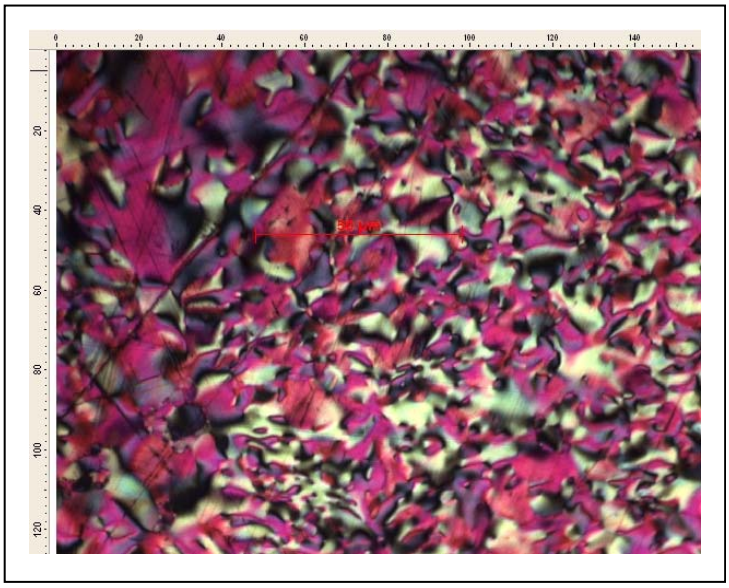


Figure 6-7 Sample C: Polarised Light Micrograph 3a (Magnification x 10)

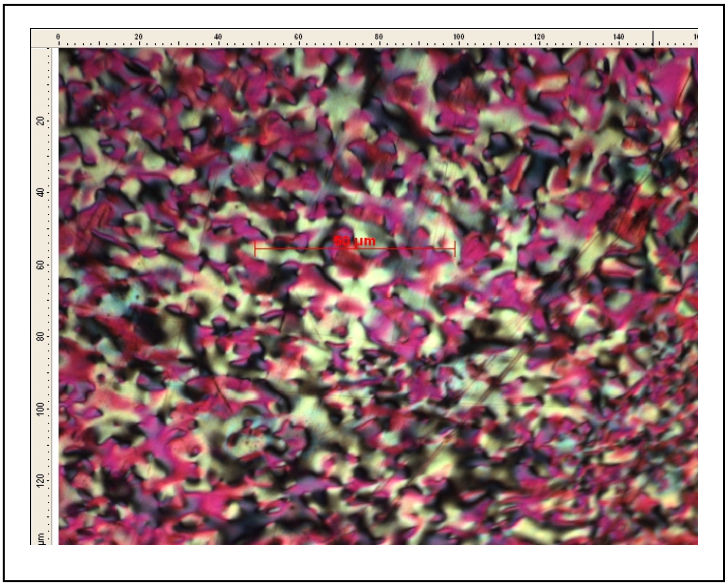


Figure 6-8 Sample C: Polarised Light Micrograph 3b (Magnification x 10)

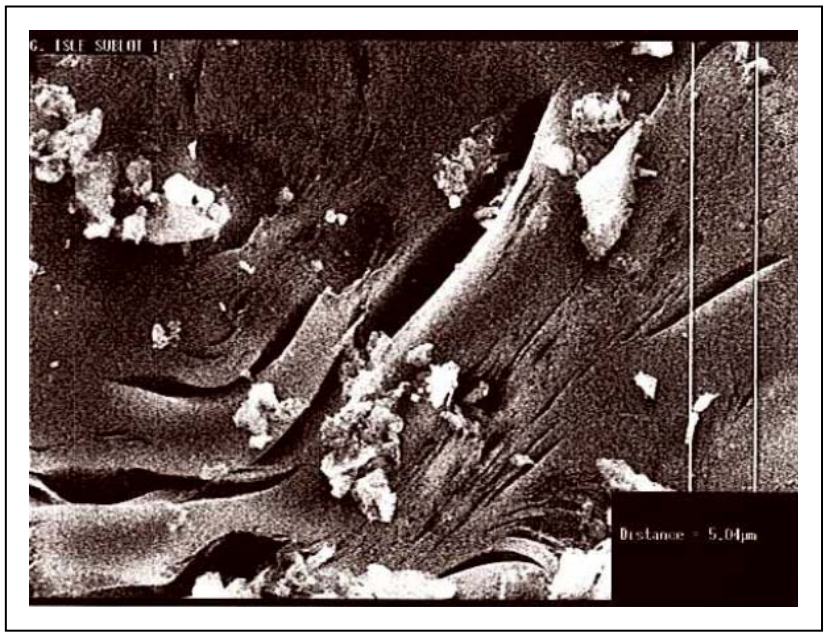


Figure 6-9 Scanning Electron Micrograph (SEM, magnification x 2000) of ash (irregular shaped white particles) disrupting the growth of the crystal lattice (Clark, 1996)

6.4.3.2 Physical and chemical analysis of Sample C calcined coke

With respect to the suitability of Sample C calcined coke for the aluminium industry (Table 6-9), significant challenges would be encountered were this coke to be produced independently on a commercial scale. Even as part of a blend of five feedstreams, Sample C would constitute over half the available feedstock volume and thus would significantly affect the quality of the blended feed coke. There are however methods available to reduce the ash content of the feed (Junji, 1993) which would contribute significantly towards a more organised microstructure, lower CTE and more acceptable minerals content.

Examination of the microstructure analysis yields generally disordered isotropic domains. It is common that isotropic carbons yield significantly higher CTE values, as is the case with Sample C (4.37 $x10^{-6}$/°C). This is supported in literature by previous work (Keshun and Wang, 1985), which determined the relationship between coke microstructure and the CTE of a range of petroleum cokes. Furthermore the ash content (as given by the presence of specific mineral oxides) is cause for concern at such elevated levels. The capital estimation for a commercial plant (Chapter 8.3) has allowed for a feed cleaning facility (a centrifuge) which would remove QI and should reduce the ash content of the Sample C calcined coke significantly.

One of the most significant challenges will be with the elevated vanadium (530 ppm) and the nickel (219 ppm) contents, as both are known catalysts for air reactivity and would not be acceptable at these levels. The silicon content (905 ppm) is higher than

the typical range for silicon in calcined anode coke which is 50-250 ppm (Hulse, 2000). Thus at over three times the maximum allowable concentration, the silicon content known to report to the aluminium metal and cause flowability problems (Milne, 2007), would need to be reduced by de-ashing of the feedstock prior to delayed coking. Industrial centrifugation could however reduce the mineral content of Sample C significantly. It is the author's experience that during trials performed with other decants oils, reduction to levels of 0.1 mass% were achieved in the calcined coke. This is supported by literature (Junji, 1993).

The sulphur content (4.37%) is higher than desirable, given the global average of 3.6% (Driscol, 2007). As the sulphur content of the coke is comparatively high, much of the sulphur in the feed is expected to be bound within the aromatic matrix.

The real density, (2.101 g.cm^{-3}) is higher than expected.

Table 6-9 Physical and chemical analysis of Sample C calcined coke

Analysis	Units	Sample C Run 1	Sample C Run 2	Sample C (Ave)
Coefficient of Thermal Expansion (CTE)	x 10^{-6}/°C	4.25	4.48	**4.37**
Fixed Carbon	mass %	99.11	98.93	**99.02**
Sulphur	mass %	3.88	3.83	**3.85**
Carbon	g/100g	95.30	94.90	**95.10**
Hydrogen	g/100g	0.05	0.05	**0.05**
Nitrogen	g/100g	0.40	0.40	**0.40**
Ash Content	mass %	0.71	0.88	**0.80**
Volatile Carbon Matter (VCM)	mass %	0.18	0.19	**0.18**
Inherent Moisture	mass %	0.03	0.04	**0.04**
As Received Moisture	mass %	0.20	0.11	**0.16**
Lead	mass %	2	1	**2**
Iron	mass %	619	516	**568**
Nickel	mass %	225	212	**219**
Vanadium	mass %	519	541	**530**
Calcium	mass %	148	190	**169**
Silicon	mass %	819	991	**905**
Aluminium	mass %	634	867	**751**
Sodium	mass %	49	52	**51**
Real (He) Density	g/cm^3	2.104	2.098	**2.101**

6.4.3.3 Quality evaluation of Sample C naphtha and coker gas oil

The results of the quality analysis are given in Table 6-10.

The naphtha yield for Sample C was considerably greater than for both Samples A and B. While the sulphur content of the naphtha is high (0.43%) it should be noted that the sulphur content of the feedstock was the highest of the five feedstocks.

Compared to Samples A and B, there is a reduction in the aromatic content coupled with an increase in the olefinic and parrafinic content. Although the Octane number of the final petrol component blend is expected to be low it is still considered to be acceptable.

As with the naphtha, the aromatic content of the coker gas oil is also reduced. Although the sulphur content is considered high, further hydrogenation (which would also lower the density thereof) would yield it acceptable as a diesel blend component.

Table 6-10 Quality evaluation of Sample C Naphtha and Coker Gas Oil (GCO)

	Units	Naphtha	CGO
Olefins	Volume%	27.9	-
Paraffins	Volume%	26.5	-
Aromatics	Volume%	45.6	-
Total aromatics (HPLC)	Volume%	-	39.5
Mono	Mass%	-	23.34
Poly	Mass%	-	16.16
Di	Mass%	-	11.44
Tri	Mass%	-	4.72
Flash point	ºC	-	84
Energy content	KJ/kg	-	40597
Total Nitrogen	mg/kg	268	1814
Total Sulphur	Mass%	0.43	3.89
Bromine number	g Br/100g	-	36.67
Viscosity @ 40 C	CPs	-	3.87
Density @ 20 C	CPs	0.7763	1.021
Sodium	mg/kg	-	< 0.01
Vanadium	mg/kg	-	< 0.01
Nickel	mg/kg	-	0.02

6.4.4 Sample D



6.4.4.1 Optical Microscopy of Sample D green coke

Optical microscopy of Sample D green coke (Figure 6-10; Figure 6-11 and Figure 6-12) shows dense domains of granular and laminar flow. Pores are seen parallel to the flow domains particularly evident in Figure 6-11. The presence of smaller medium mosaic domains in Figure 6-12 is a pseudo-optical effect as described earlier. The effect of the lower sulphur content, lower ash content, longer thinner shape of the pores and flow domain structure (compared to Sample C), are evident in the lower CTE of Sample D calcined coke which is 2.83 $x10^{-6}$/°C.

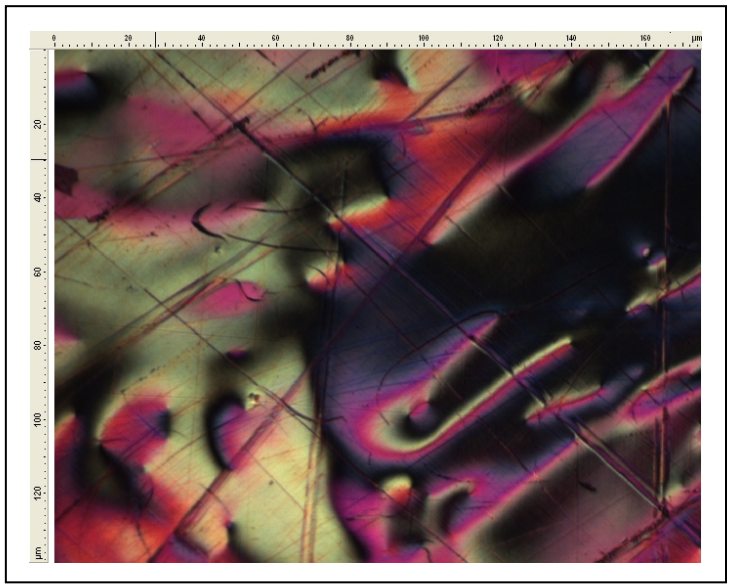


Figure 6-10 Sample D: Polarised Light micrograph 4a (Magnification x 10)

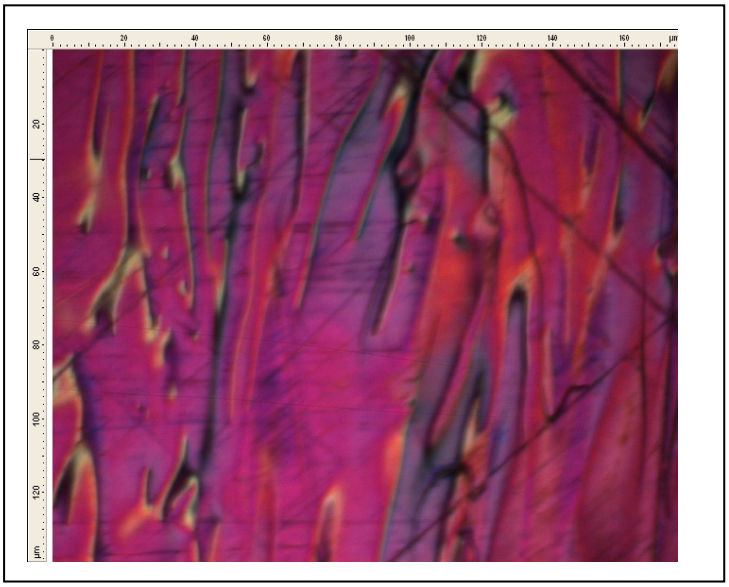


Figure 6-11 Sample D: Polarised Light micrograph 4b (Magnification x 10)

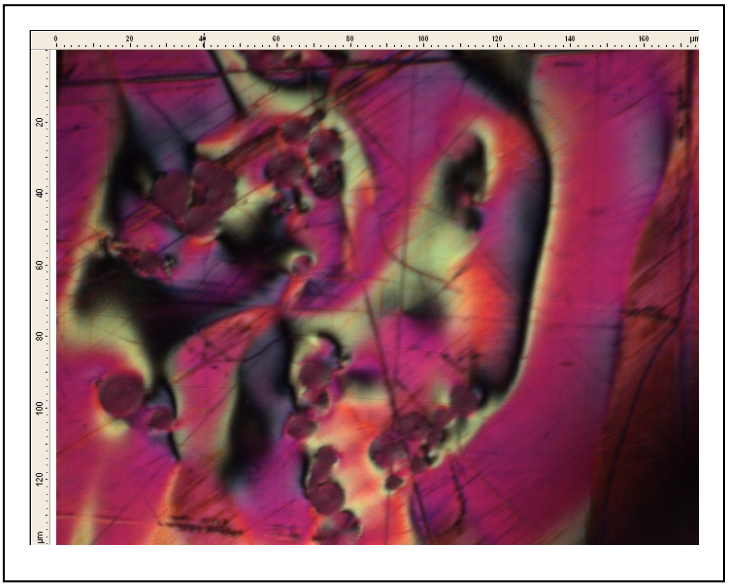


Figure 6-12 Sample D: Polarised Light micrograph 4c (Magnification x 10)

6.4.4.2 Physical and chemical analysis of Sample D calcined coke

With respect to the suitability of Sample D calcined coke for the aluminium industry (Table 6-11), the only concern would be the elevated ash content. The CTE (2.83 x 10^{-6}/°C) is well below the industry average (3.5 x 10^{-6}/°C) and the sulphur content (3.17%) is comparatively low. With respect to the mineral matter, the only concern may be the silicon content (315 ppm); however, the nickel (41 ppm), vanadium (1 ppm) and the sodium (1 ppm) contents are low. The real density (2.101 g.cm^{-3}) is relatively high and coupled with the flow domains exhibited by the optical micrographs should provide for a more than acceptable anode coke.

Table 6-11 Physical and chemical analysis of Sample D calcined coke

Analysis	Units	Sample D Run 1	Sample D Run 2	Sample D (Ave)
Coefficient of Thermal Expansion (CTE)	x 10^{-6}/°C	2.93	2.73	**2.83**
Fixed Carbon	mass %	99.41	99.65	**99.53**
Sulphur	mass %	3.15	3.19	**3.17**
Carbon	g/100g	96.20	96.50	**96.35**
Hydrogen	g/100g	0.06	0.06	**0.06**
Nitrogen	g/100g	0.11	0.10	**0.10**
Ash Content	mass %	0.48	0.26	**0.37**
Volatile Carbon Matter (VCM)	mass %	0.11	0.09	**0.10**
Inherent Moisture	mass %	0.03	0.03	**0.03**
As Received Moisture	mass %	0.07	0.07	**0.07**
Lead	mass %	no signal	no signal	**no signal**
Iron	mass %	440	386	**413**
Nickel	mass %	43	39	**41**
Vanadium	mass %	1	1	**1**
Calcium	mass %	78	109	**94**
Silicon	mass %	240	390	**315**
Aluminium	mass %	no signal	no signal	**no signal**
Sodium	mass %	1	1	**1**
Real (He) Density	g/cm^3	2.101	2.102	**2.101**

6.4.4.3 Quality evaluation of Sample D naphtha and coker gas oil

The results of the quality analysis are given in Table 6-12.

The naphtha fraction is considered highly aromatic (88.9%) which also causes the relatively higher density (0.8581 g.cm^{-3}).

Although there was not enough of the sample to determine the sulphur content of the coker gas oil fraction it is estimated that this fraction (as is the case with all the other samples) would require further hydro-treatment to meet the stringent sulphur specifications.

Table 6-12 Quality evaluation of Sample D Naphtha and Coker gas oil (CGO)

	Units	Naphtha	CGO
Olefins	Volume%	4.3	-
Paraffins	Volume%	6.9	-
Aromatics	Volume%	88.9	-
Total aromatics (HPLC)	Volume%	-	-
Mono	Mass%	-	-
Poly	Mass%	-	-
Di	Mass%	-	-
Tri	Mass%	-	-
Flash point	ºC	-	113
Energy content	KJ/kg	-	43886
Total Nitrogen	mg/kg	64	1368
Total Sulphur	Mass%	1317	-
Bromine number	g Br/100g	14.22	13.91
Viscosity @ 40 C	CPs	-	5.7
Density @ 20 C	CPs	0.8581	1.0713
Sodium	mg/kg	-	<0.01
Vanadium	mg/kg	-	<0.01
Nickel	mg/kg	-	<0.01

6.4.5 Sample E



6.4.5.1 Optical microscopy of Sample E green coke

In general Sample E green coke has a coarse flow and elongated granular microstructure (Figure 6-13, Figure 6-14 and Figure 6-15). All three of the micrographs show significant porosity which is for the most part an oval or irregular shape. As mentioned previously this type of porosity is linked to higher CTE values, compared to long thin pores parallel to the flow domain as shown in Sample D. The extent of porosity development may be attributed to the lower density of the feedstock and lower green coke yield as shown in Tables 6-1 and 6-2. The overhead vapours which pass through the developing mesophase will affect the porosity of the green coke.

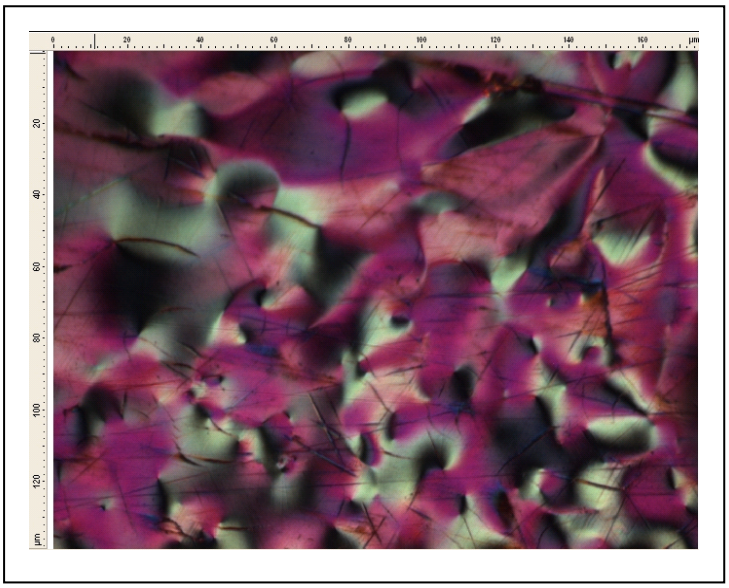


Figure 6-13 Sample E: Polarised Light micrograph 5a (Magnification x 10)

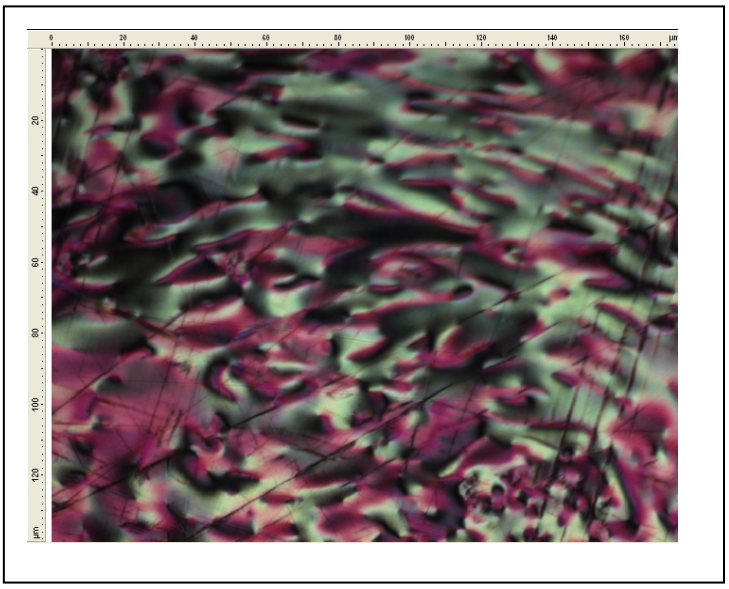


Figure 6-14 Sample E: Polarised Light micrograph 5b (Magnification x 10)

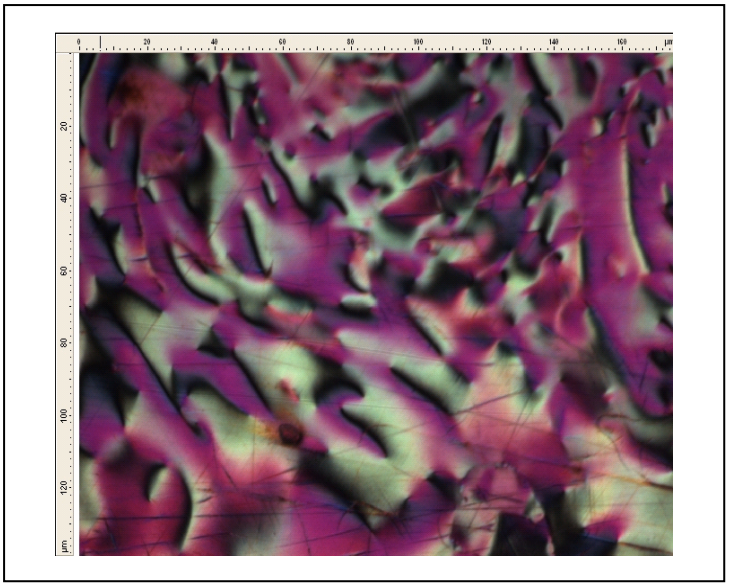


Figure 6-15 Sample E: Polarised Light micrograph 5c (Magnification x 10)

6.4.5.2 Physical and chemical analysis of Sample E calcined coke

With respect to the suitability of Sample E calcined coke for utilisation in the aluminium industry (Table 6-13), only the ash content (0.38%) and the CTE (3.99 x 10^{-6}/°C) are a cause for concern.

The sulphur content (1.96%) is the lowest of all the calcined coke samples produced and in a blend would lower the overall sulphur content, albeit that the green coke yield (33%) is lower than the other feedstocks tested. The nitrogen content does appear unusually high but that is in all probability feed related. Both the vanadium (299 ppm) and the nickel (282 ppm) content are comparatively high although not significantly outside the worldwide range for anode grade cokes (Hulse, 2000).

The development of porosity in Sample E is thought to contribute to the relatively higher CTE. Porosity development in green coke may be caused by hydrocarbon gasses, process pressure, steam or naphtha injection during delayed coking. Steam injection was used to study porosity development along the height of a laboratory delayed coking drum with the aid of computer aided tomography (Karacan and Badger, 2003). This research indicates a greater concentration of longitudinal pores along the height plane of the drum and less pore size variability occurs than without steam injection.

Industrially steam and naphtha injection are also utilised to prevent heater fouling, which describes the laydown of solid carbonaceous material and ash in the tubes of a heater (Van Dyk, 2000). It is the author's experience that high ash feedstock may necessitate either steam or water injection to increase the velocity of the feed through the heater tubes to prevent ash and carbon build-up. This by default requires the heater to be run at a higher temperature, which is energy inefficient. If the heater tubes of a commercial delayed coker with only one furnace should become blocked, due to ash or carbon lay down, the plant would be shutdown to facilitate the removal

of this material. The production loss would have obvious cost implications. This is yet a further and perhaps the most compelling argument for considering the removal of ash from the feed prior to delayed coking.

Table 6-13 Physical and Chemical analysis of Sample E calcined coke

Analysis	Units	Sample E Run 1	Sample E Run 2	Sample E **(Ave)**
Coefficient of Thermal Expansion (CTE)	x 10^{-6}/°C	4.00	3.98	**3.99**
Fixed Carbon	mass %	99.54	99.48	**99.51**
Sulphur	mass %	1.97	1.95	**1.96**
Carbon	g/100g	96.40	96.80	**96.60**
Hydrogen	g/100g	0.05	0.05	**0.05**
Nitrogen	g/100g	0.67	0.66	**0.67**
Ash Content	mass %	0.35	0.41	**0.38**
Volatile Carbon Matter (VCM)	mass %	0.11	0.11	**0.11**
Inherent Moisture	mass %	0.03	0.02	**0.02**
As Received Moisture	mass %	0.08	0.09	**0.08**
Lead	mass %	no signal	no signal	**no signal**
Iron	mass %	385	574	**480**
Nickel	mass %	268	296	**282**
Vanadium	mass %	293	304	**299**
Calcium	mass %	72	76	**74**
Silicon	mass %	247	278	**263**
Aluminium	mass %	no signal	no signal	**no signal**
Sodium	mass %	18	18	**18**
Real (He) Density	g/cm^3	2.115	2.110	**2.112**

6.4.5.3 Quality evaluation of Sample E naphtha and coker gas oil

The results of the quality analysis are given in Table 6-14.

The olefinic content of the naphtha (27.5%) is high as given by the relatively high Bromine number (52.13 gBr/100g). Bromine reacts with the double bonds of the olefins. Although the aromatic content of the naphtha is relatively high, with further hydro-treatment it would be considered acceptable as a final blend component for petrol.

Table 6-14 Quality evaluation of Sample E Naphtha and Coker gas oil (CGO)

	Units	Naphtha	CGO
Olefins	Volume%	27.5	-
Paraffins FIA	Volume%	33.7	-
Aromatics	Volume%	38.8	-
Total aromatics (HPLC)	Volume%	-	43.02
Mono	Mass%	-	25.67
Poly	Mass%	-	17.35
Di	Mass%	-	6.3
Tri	Mass%	-	11.05
Flash point	ºC	-	83
Energy content	KJ/kg	-	42731
Total Nitrogen	mg/kg	293	1850
Total Sulphur	Mass%	1567	-
Bromine number	g Br/100g	52.13	29.57
Viscosity @ 40 C	CPs	-	-
Density @ 20 C	CPs	0.7874	-
Sodium	mg/kg	-	0.02
Vanadium	mg/kg	-	-
Nickel	mg/kg	-	0.01

7 BLENDED FEED DELAYED COKING TEST

The blended feed delayed coker and calciner trials were conducted using the MDC at the same conditions as for the individual runs (Samples A–E). The feedstock samples (A–E) were blended according to their expected annual availability (Sample A – 13%; Sample B 10%; Sample C 53%, Sample D – 16% and Sample E – 8%).

The primary reason for conducting the blended feed delayed coker run was to provide a representative green coke sample for the graphitisation experiment and to determine a sulphur balance over the delayed coking process which is discussed in Chapter 9.2.1.1.

7.1 Delayed coker and calciner yields

The delayed coker yield from the blended feed test is given in Table 7-1.

Table 7-1 Blended feed delayed coker yield

Product	Units	Blended feed
Green coke	Mass %	42.1
White products	Mass %	37.0
Gas	Mass %	20.9

As Sample C constitutes over fifty percent of the available tonnage, the delayed coker yield is similar to that of the individual Sample C run (Table 6-2). The influence of the heavier Sample C feed is to increase the green coke yield and slightly decrease the gas yield.

The effects of heavy residue blending have been widely researched both on a laboratory and commercial scale. This blending research includes:

- Blending of petroleum heavy residues (Santamaria and Blanco, 2003; Granda and Santamaria, 2003)
- Blending of petroleum residues with high temperature coal-tar pitch (Mochida and Korai, 1989)
- Blending of petroleum FCCDO with coal-tar gasification pitch (Clark and Chang, 2001; Clark and Chang, 2002)

In the case of the latter, it has been proved that the delayed coking of different residues (even as varied in origin as petroleum FCCDO and coal-tar gasification pitch) yield a coke whose sulphur and nitrogen content can be correlated with those of the individual feedstocks according to the blending ratio and the delayed coker green coke yield. These blended feed cokes have furthermore been proved to have similar nitrogen and sulphur distribution throughout the height zones in a commercial drum (Clark and Chang, 2002).

However, mesophase formation and the resultant CTE of blended feed cokes is highly dependant on molecular interaction and concentration of the individual feedstreams in the blend and thus direct correlations are not possible.

7.2 Green / calcined / graphitised coke quality

The comparative quality analysis for the green, calcined and graphitised cokes produced from the delayed coking of the blended feed is given in Table 7-2.

Table 7-2 Green / calcined / graphitised coke quality analysis for the delayed coking of the blended feed

Analysis	Units	Green coke	Calcined coke	Graphitised coke
Carbon	Mass %	93.3	97.0	98.8
Hydrogen	Mass %	2.82	0.14	0.07
Nitrogen	Mass %	1.06	0.40	0.36
Sulphur	Mass %	4.84	3.26	0.91
Ash	Mass %	0.24	0.25	0.21

The maximum graphitisation temperature achieved was 2081 ºC. The results indicate that this temperature was not sufficient to remove all the sulphur. Sulphur loss during graphitisation at 2400 ºC and the effect on both meso and micro-porosity generation have been show by various researchers (Legin-Kolar, 1992; Legin-Kolar, 1999; Hardin and Beilharz, 1993). Although there was some sublimation of the ash (given by a reduction from the green coke to graphitised state), at higher temperatures (< 2600 ºC) the reduction of the ash content would have been greater.

The laboratory calcination of green coke yielded a mass loss of 10% while the graphitisation mass loss (directly from the green state) yielded a mass loss of 15%. In commercial application it would make no sense to pre-calcine the green coke before graphitisation, although at higher temperatures (than calcination), mass loss through graphitisation is impeded with the aid of an inert atmosphere (nitrogen).

The value of the XRD analysis is to determine the development of “order” within the crystallographic carbon matrix with increasing temperature. This is supported in literature (Weishauptova, 1986), describing the thermal acceleration of graphitisation by heat treatment temperatures up to 2400 ºC for a range of cokes. The diffractograms for both the green and the graphitised coke are given in Figure 7-1 (Du Plessis, 2007). The full report is given as Appendix B: XRD Analysis of Coke Samples to Determine the Degree of Graphitisation

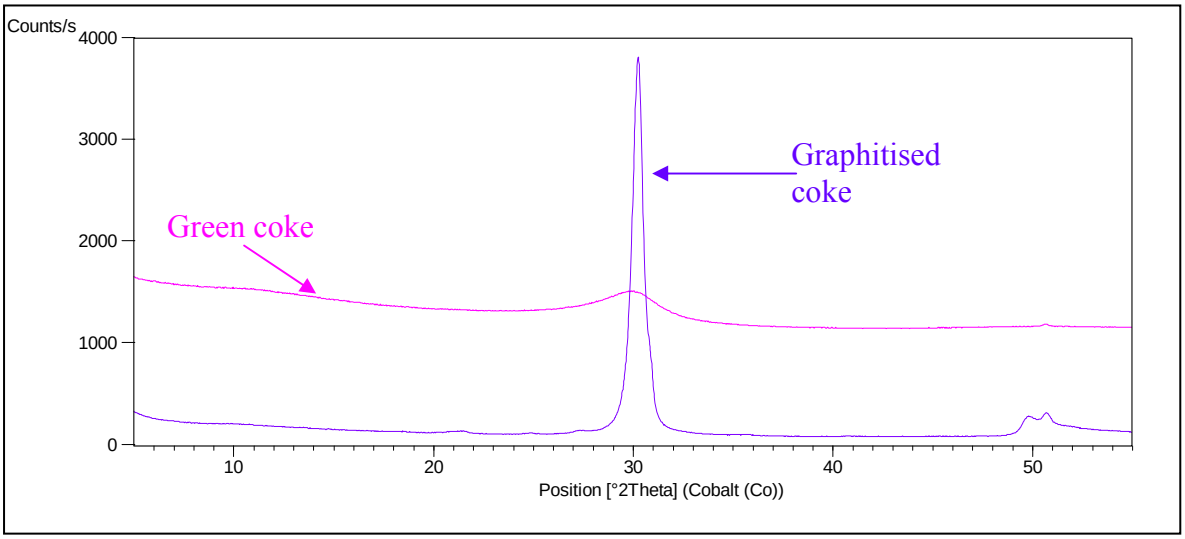


Figure 7-1 XRD diffractograms of blended feed green and graphitised coke

The Bragg angle for the interlayer spacing is given at a º2Theta position of 30[1]. Figure 7-1 indicates that graphitisation of green coke resulted in clarification of the trace from the green coke (which appears as a broad shoulder) to a concise peak for the graphitised coke. In order to calculate the Degree of Graphitisation the following formula was used (Du Plessis, 2007):

Degree of Graphitisation = (3.44 – d_c) / 3.44 – 3.354)

where

- d_c is the interlayer spacing of the sample
- 3.354 nm is the interlayer spacing of pure graphite
- 3.44 nm is the interlayer spacing of turbostatic (unordered) carbon

As the interlayer spacing for the green coke was larger than that of turbostatic carbon the degree of graphitisation cannot be calculated. With increasing heat treatment the crystallite height increases and the degree of graphitisation of the graphitised carbon was 9.1%. It would be possible to promote a more ordered mesophase by removing the ash from the fresh feed, increasing the heat treatment temperature (during graphitisation) to further promote the increase in the crystallite stacking height (L_c value) and conversely a decrease of the interlayer spacing (d_{002} value).

The stacking height of the crystals increases as the carbon becomes more ordered. Calculation of the crystallite stacking height (L_c) value is given by the following equation (Du Plessis, 2007):

Stacking height = [(0.89 x λ) / (β x cos Θ)] x (180 / ∏)

[1] The angle corresponding to the interlayer spacing may vary according to the source of the radiation. Copper radiation will give the angle at 25º while Cobalt yields the angle at 30º. Cobalt was used for this experiment

where

- λ = 1.78897 Angstrom (Å)
- β = FHWM (in degrees)
- Θ = Bragg angle of the (002) reflection (in degrees)
- $\prod$ = 3.14159

The stacking height for the green coke was calculated to be 28 Å while the stacking height of the graphitised coke was 136 Å, which indicates a significantly larger degree of order. The development of the crystal lattice with corresponding increase of the L_c value and decrease of the d_{002} interlayer spacing during graphitisation of a variety of petroleum cokes has previously been show (Hardin and Beilharz, 1993).

The relevance of XRD to the commercial market for carbon relates to the influence of the molecular structure on the physical properties of a carbon artefact (anodes and electrodes). The typical crystallite stacking height for carbon fillers for the anode industry is 25–32 Å (Hulse, 2000).

The CTE and electrical conductivity of the carbon are directly related to the molecular structure. Previous researchers (Ellis and Hardin, 1993) have shown a reduction in the CTE as a function of heat treatment between 850 and 2900 ºC. Both in the aluminium and steel making industries, the more ordered a carbon microstructure, the greater the ease with which electrons will move through the carbon artefact (as determined by unimpeded electron clouds stemming from sp^2 hybridised bonds).

The objective of the graphitisation experiment was to produce chemically pure graphite with a negligible ash and sulphur content. Given the inability to reach a temperature of over 2600 °C this could only partially be achieved. It was not possible to repeat the experiment due to the cost thereof.

8 ECONOMIC EVALUATION

The economics of any delayed coker / calciner are inherently dependant on the fuel alternative value (of the feedstock and the delayed coker products), availability of the feedstock and the demand for the coke. While carbon products command a certain value dependant on their chemical purity, they are also subject to price fluctuations based on the secular metallurgical market within which they are utilised and freight rates.

8.1 Hypothetical commercial volumes

A hypothetical scenario was created to estimate the commercial yields which were based on feedstock availability of the specific streams (Samples A–E) and the results of the experimental delayed coker trials (Chapter 6.2).

The only results that were modified were the expected calcination yields (which are based on commercial experience rather than laboratory trials). The results are presented in Table 8-1.

Table 8-1 Hypothetical commercial delayed coker volumes in the *Carbon* mode

	Units	Carbon mode
Feedstock	**Tonnes per annum**	750 000
Gas	**Tonnes per annum**	165 000
Liquid fuels	**Tonnes per annum**	292 500
Green coke	**Tonnes per annum**	292 500
Calcined coke	**Tonnes per annum**	216 650

The hypothetical tonnages given indicate the average yield of the five streams that were tested individually. It should be noted that when the feedstock is blended there could be slight changes in the yield of the delayed coker and subsequent calciner yields. As opposed to coal based heavy residues it is fairly typical to obtain a lower green coke yield from petroleum based residues (that have not been hydro-cracked). The green coke yield (as a cumulative average of the 5 samples) was 39% which would relate to 292 500 tonnes per annum.

As previously mentioned, the process of calcining drives off any lighter organic matter and coupled by both air and CO_2 reactivity reduces the yield of calcined coke (based on the green coke) to 74% or (based on the fresh feed) to 29%.

The hypothetical production of 216 650 tonnes of calcined coke per annum is significant within the South African context both in relation to supply and demand. Importing calcined coke from the Gulf of Mexico incurs fluctuating freight rates and inconsistency linked to climatic conditions. There would also be a massive cost incentive to produce the calcined coke locally with respect to the ever increasing demand from the aluminium industry along the east coast of Southern Africa.

With respect to the amount of white products produced, the expected figure of 292 500 tonnes per annum (tpa) is significant. It should however be noted that the above quoted figure does not represent final product volumes as both the naphtha and coker gas oil would require hydrogenation in the refinery as delayed coking is a dehydrogenating process. The white products may further be split into approximately 89 550 tonnes of naphtha (petrol component) and 202 950 tonnes of coker gas oil (diesel component) per annum. Allowance has been made in the capital expenditure for this processing step.

Delayed coking will produce a significant amount of off-gas, namely 165 000 tonnes per annum. The relatively high volume of the gas is related to the fact that none of the feed streams has been subjected to a cracker and thus many light ends remain. Two possible outlets may be to fire the calciner with the gas or to sell it for sale (again dependant on quality).

8.2 Assumptions

Assumptions used in the preparation of the economic data include:

- All costs escalated by PPI (5%) on an annual basis
- Feed prices were calculated at 65% of bunker alternative
- The production output does not take into account the production of "smartie"[1] coke
- The economic data considers capital investment at a R/$ exchange rate of 8.0
- The price of crude oil is based on the Dubai budget (not on Brent) and fluctuates between $70 and $120 per bbl
- Capex is expected to vary between 3.25 and 4.35 billion ZAR, dependant on the mode in which the delayed coker is operated.

8.3 Capital expenditure

The expected Capital Expenditure (Capex) and economic indicators are based on data acquired from laboratory scale investigations and are thus a Very Rough Order Of Magnitude (V.R.O.O.M).

Table 8-2 shows the Capex of the delayed coking process on a commercial scale. The major variation in the Capex is dependant on the mode in which the delayed coker is operated. When the delayed coker is operated in the ***Carbon*** mode, allowance needs to be made for a calciner to produce calcined coke, to be used as carbon filler in the aluminium industry. If the delayed coker is operated in the ***White product*** mode (to maximise the production of petrol and diesel precursors), a calciner and feed cleaning unit is not necessary as coke production is minimised and sold at a nominal fuel grade value. This variation has a significant effect on the Capex and accordingly on all the other economic indicators.

[1] "Smartie" coke is produced when refineries change the feed to the coker. The changeover drum contains coke stemming from both the feeds and is heterogeneous in nature. This coke is usually downgraded to a lower value market.

The Capex is based on Foster Wheeler & ABB Lumus estimations, who are vendors for delayed coking technology. The Capex has been escalated according to inflation.

Table 8-2 Capital Expenditure (V.R.O.O.M) for the delayed coking of petroleum heavy residue streams

Capital item	Currency	*Carbon* mode	*White product* mode
Feed cleaning	Million ZAR	100	0
Coker	Million ZAR	1000	1000
Calciner	Million ZAR	1000	0
Pipe line	Million ZAR	200	200
White products (Refinery)	Million ZAR	200	200
Sulphur recovery from off-gas	Million ZAR	350	350
Hydrogenation	Million ZAR	1500	1500
Total	Million ZAR	**4350**	**3250**

8.4 Delayed coking in the *Carbon* vs. the *White Product* mode

The economic model used for the economic analysis is a variant of a model developed for commercial delayed coking and calcining. Economic indicators used are defined in Business Accounting and Finance for Managers (Hartley and Ford, 2004).

A detailed sensitivity analysis was developed to examine the influence of the crude oil price variance on the economic data. Due to the confidentiality agreement the author is not permitted to divulge this information in detail.

However, it is possible to show the sensitivity of delayed coking in both the ***White Product*** and ***Carbon*** modes on the cumulative IRR differential (the compound effect over a number of years) as shown in Figure 8-1.

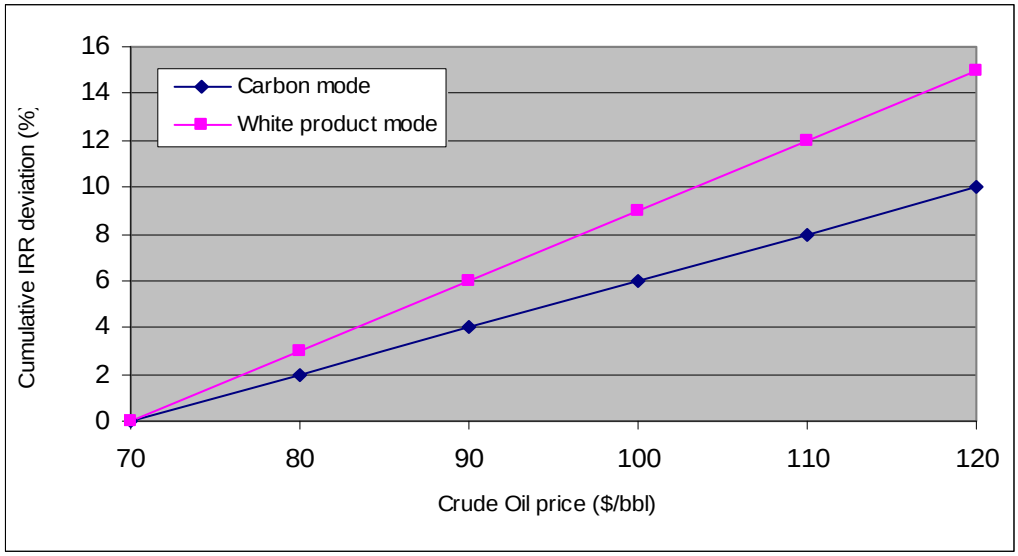


Figure 8-1 Influence of the crude oil price ($70-120 /bbl) on the cumulative IRR deviation for delayed coking in the *Carbon* and *White product* modes

In this figure a crude oil price of $ 70/ bbl was chosen as a base reference point. Every time the crude oil price increased by $ 10/bbl, the cumulative deviation from the IRR at $70 /bbl was calculated in both delayed coking modes.

Figure 8-1 shows that delayed coking in the ***White Product*** mode is more sensitive to an increase in the price of crude oil, compared to the ***Carbon*** mode. This stands to reason as the price of petrol and diesel are higher than that of anode grade carbon.

Delayed coking to maximise the production of white products benefits in relation to the ***Carbon*** mode in two main arenas:

- The capital cost of the commercial unit is significantly lower (25% or 1.10 billion ZAR less) due to the fact that capital is not required for a calciner. Further it is unlikely (except in cases of high ash content), that the feed would be cleaned as the microstructure of the coke is of little significance when the coke is sold for its calorific value.
- The sensitivity of the economic indicators towards a movement in the oil price is significant. This stands to reason as the process is designed to maximise the white product yield. For the same feed tonnage, delayed coking in the ***White Product*** mode would produce approximately 137 250 tonnes of naptha (petrol component) and 312 750 tonnes of coker gas oil (diesel component) per annum. The yields are based on estimations received from literature (ConocoPhillips, 2007). The IRR is seen to increase 3% for every $10 /bbl hike in the price of crude oil.
- The price petrol and diesel is linked to the price of crude oil

Delayed coking in the ***Carbon*** mode is less sensitive to crude oil price fluctuations as less of the delayed coker products are liquid fuels. As previously mentioned the price of calcined coke for the aluminium industry does not have a direct link to the crude oil price and is rather affected by the international price of aluminium. While the quality of the calcined coke will affect the price aluminium smelters are willing to pay, the substantial increase in the freight rates over the last two years (as a function of the crude oil price increase) would be the greatest contributing incentive favouring local production.

8.4.1 Graphitisation of carbon

The graphitisation of particulate anode grade cokes is not common place in industry. It is however the aim of this dissertation to challenge commonly held paradigms surrounding the use and value addition to sponge cokes. Thus this section is highly experimental in nature and while the process is subjected to the same stringent conditions surrounding the more conventional delayed coker modes, an economic comparison to commercially available processes is not possible as they are extremely scarce.

As given in Chapter 7, the graphitisation of green coke failed to produce chemically pure graphite. While significant reductions in both sulphur and to a lesser degree the ash were evident, the temperature (2081 ºC) was not high enough. Future work would

have to graphitise the green coke at temperatures above 2600 ºC. However, as previously mentioned, commercial graphitisation of particulate carbon is not common place, which makes the value of a sensitivity analysis negligible, given the amount of variables, which would include:

- The commercial yield of the graphitised product
- The temperature and soaking time the carbon would require to fit the required specification on a commercial scale

It is known that the economics would be less sensitive to a movement in the crude oil price as they would be predominantly determined by the value of the carbon and not the petrol or diesel.

The Capex may not be significantly affected. Instead of investment in a calciner, the green coke would be heat treated in either an induction or plasma furnace. Thus the capital investment could be very much the same. The major difference would include the control of the atmosphere, to reduce burn-off at higher temperatures.

In order to obviate the price differential coke and liquid fuel products the value of the graphite produced would have to be larger than that of the average price of the liquid fuel products. At an oil price of $100 per bbl, the associated graphite price would need to increase to $850 per tonne.

The market drivers for the oil price and value added graphites cokes are different, but in the short to medium term it is estimated that the increase in the oil price would dominate, thereby making the production of white products more attractive. It would however not be realistic to assume that all the available feed would be of such a quality to produce high value graphites based on the ash and the microstructure of the coke. Flooding the high value graphite market with an excess of product would serve to depress market prices.

It would be possible for the delayed coker to be run in either the ***Carbon*** or ***White product*** modes dependant on varying quality of the feed and market demand for the products. If one of the feeds is of a quality which would support the production of high value graphite it may be worthwhile to switch to the ***Carbon*** mode and then back to the ***White product*** mode when the feed was more suitable for the production of petrol and diesel, in order to maximise profit and diversify market risk.

8.5 Economic value add to the balance of payments

In order to estimate the imported crude oil saving, average crude oil imports to South Africa were regarded as producing 15% vacuum oil (Table 4-2). If only 85% of the crude oil was utilised to produce automotive fuels, the 292 500 tonnes produced annually (Table 8-1) would be equivalent to 344 118 tonnes or 2.28 mbbl of crude oil. Assuming a crude oil price of $100 /bbl and an R/$ exchange rate of 8, the saving to the balance of payments deficit would be 1.82 billion ZAR annually. These calculations have not taken into account the freight cost savings. The calculations are based on delayed coking in the ***Carbon*** mode and would vary dependant on the available heavy petroleum volumes.

Assuming an operating capacity of approximately 90% (330 out of 365 days in the year to allow for planned shutdowns), South African refineries would process 170 mbbl of crude oil annually. Using the results of the current research, delayed coking would only save 1.33% of South Africa's annual crude oil requirement.

While 1.82 billion ZAR (2.28 mbbl) would not be significant given the annual cost of crude oil to South Africa, it constitutes a direct foreign savings benefit. Within the South African context, 1.82 billion ZAR could finance the building of 49 824 low cost houses [assuming that a low cost house was 36 528 ZAR as given in literature (The Times, 2007)].

Similarly, the direct foreign saving of producing 216 650 tonnes of local calcined coke would be approximately 580 million ZAR.

9 ENVIRONMENTAL IMPACT

9.1 Introduction

The use of fossil fuels as a "vehicle" of liquid energy has contributed to much of the effects of global warming and sulphur emissions, but it is unrealistic to dismiss our reliance on them, until alternative sources of clean energy become commercially viable. This chapter evaluates the potential environmental impact of delayed coker products and abatement processes with specific emphasis on SO_x and CO_2.

The potential of a new delayed coker in South Africa will not only depend on the financial viability or the market demand, but ever increasingly on the environmental impact. It is clear from the statement below (Address by the Minister of the Environment and Tourism, Mr Marthinus Van Schalkwyk) that the Government of the Republic of South Africa will not allow new energy projects which have the potential to harm the environment or by default the citizens of the country. The full address is given in Appendix C and states that:

"Given that the energy sector is the single largest source of emissions in South Africa, mitigation and technological interventions are aimed at energy efficiency, diversifying energy sources away from coal, promoting energy security and also the research and development of new technologies that will lead to a cleaner, more sustainable, low carbon energy future" (Van Schalkwyk, 2007a)

9.2 Environmental impact of delayed coker and calciner products

9.2.1 Sulphur emissions from a hypothetical delayed coker

9.2.1.1 Sulphur balance

The sulphur balance is based on the results of a delayed coker trial (Chapter 7) that was conducted using a blend of all five heavy residue streams. The Sulphur

While laboratory scale experimentation of this research cannot exactly mimic commercial practice it is the aim to present the sulphur content as it is distributed between the hypothetical basket of delayed coker products. These results are given in Table 9-1.

Table 9-1 Sulphur balance for the delayed coking of blended feeds (Samples A – E)

Sample	Sulphur (%)	Delayed coker yield (%)	Product (tpa)	Sulphur (tpa)
Blended feed (A - E)	3.7	na	750 000	27 750
Gas	4.7	20.9	156 750	7 322
Coker gas oil	1.9	37.0	277 500	5 272
Green coke	4.8	42.1	315 750	15 156
Calcined coke	3.3	na	216 650	7 149

As all the heavy petroleum streams tested are currently utilised as burner or bunker fuels, it would be fair to assume that the greater proportion of the 27 750 tonnes of available sulphur in the residues per annum would be emitted to the atmosphere as SO_x.

While the sulphur content of the white products and green coke (given in Table 9-1) were analysed, the sulphur content of the gas was calculated by difference.[2]

If the coke were to be used in one of the aluminium smelters on the East coast of Southern Africa, the impact on SO_x emissions within the specific area in would be reduced by over 25%, given that a large proportion of the sulphur would report to the calcined coke. However, "relocating" the sulphur problem is not a comprehensive solution. The requirement to remove SO_x (using available abatement systems) in a smelter would be dependant on emission control levels in the area and the comparable sulphur content of imported coke.

Sulphur removed as Hydrogen Sulphide (H_2S) from both the petrol and diesel precursors as well as the off gas could be reduced to elemental sulphur and sold into the market for the production of Sulphuric acid (H_2SO_4). With respect to the white products, sulphur would be removed in accordance with legislation governing the sulphur content of petrol and diesel sold to the public.

It may be argued that, as much of the sulphur from bunker fuels will be emitted as SO_x within international waters, delayed coking would not be a beneficial option wrt localised SO_x release. However the bunker fuel market is under pressure to reduce the sulphur content due to pressure from the International Maritime Organisation (IMO, 2005a). This is discussed in greater detail in Chapter 9.4.3.

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9.2.1.2 Hydrogen Sulphide (H_2S) emissions from a delayed coker

Sulphur is present in heavy petroleum residues in a variety of compounds. The stability of the sulphur in the aromatic matrix will determine the concentration thereof in the coker gas. Sulphur bound within the aromatic matrix (e.g. in thiophenic type molecules) would be less likely to release sulphur into the coker gas, than sulphur bound in less stable forms (e.g. thiols). Delayed coking is a dehydrogenative process and therefore with the abundance of hydrogen, sulphur is emitted as H_2S in the coker gas.

It is common practice for H_2S in coker gas to be extracted using an amine solvent followed by conversion to elemental solid (which includes a partial combustion of H_2S to produce SO_2, and reaction over an alumina catalyst to form elemental sulphur) (European Commission, 2003).

[2] The Mini Delayed coker uses nitrogen to attain system pressure and thus the off gas is by default contaminated. As this contamination is up to 96%, normalisation to determine the sulphur content would not be accurate.

A variety of amine based solvents (mono ethanol amine, di glycol amine, di isopropanol amine and methyl di ethanol amine) may be used for H_2S capture. The amine solvent is recovered and reused.

The most widely used sulphur recovery process is called the Claus process as described above. The Oxy-Claus process is used when air is replaced with oxygen to aid in combustion (European Commission, 2003).

9.2.1.3 Sulphur Oxide (SO_x) emissions from a calciner

The main source of SO_x would originate from low sulphur delayed coker gasses utilised in part to fuel a gas fired calciner and during calcination of the green coke. It is assumed that the greater concentration of H_2S would have been removed from the raw delayed coker gas using prescribed abatement techniques. SO_x would be present in the flue gasses from the incinerator attached to the calciner.

The removal of SO_x from waste gasses involves an alkaline absorbent which converts the gas into elemental sulphur or gypsum (both solid). While there are a host of available abatement processes, one of the most widely used is the Additive injection / Spray Dry absorber. The waste gas is passed over wet limestone followed by spray dry scrubbers. While the process is 92% efficient (for low SO_x waste gasses) the product may contain unreacted lime which would require conditioning before disposal (European Commission, 2003).

Other processes include the SNOX process, the Walther process (SO_x absorbed by Ammonia) and the Wellman Lord process (based on sodium sulphite / bi-sulphite process) (European Commission, 2003).

9.2.2 Other environmental considerations

9.2.2.1 Water used for cooling and cutting of green coke

Water is utilised in two main parts of the delayed coking process (European Commission, 2003)

- Water is used (in the form of steam and process water) to quench the coke drum after the drum cycle has been completed. The purpose of the water is to cool the coke (approximately 450 ºC) to temperatures which will allow it to be cut with a water jet. The water may be contaminated with organic compounds and particulate matter. This contaminated water is not exposed to the atmosphere but is treated in a “slop” drum which removes both the particulate and organic contaminants.
- A high pressure water jet is used to cut the green coke from the reactor drum. The water and the coke are collected in the “pit”. The process water and fine particulate coke are separated in a “maze” (an inclined plate separator). As the process water may be contaminated with dissolved salts, a portion thereof

needs to be bled off to the waste water treatment facility (this includes treatment in a sour water stripper).

9.2.2.2 Handling and storage of coke

Green coke cut from the reactor drum is usually crushed and stored on a concrete pad prior to calcining to dewater. Particulate emissions are not usually problematic as the green coke fines are relatively wet.

During calcination there is an unavoidable reduction of the Particle Size Distribution (PSD), which causes a dust fraction to be formed. Upon exiting the calciner, "de-dusting oil" may be added to retard fine particulate emissions. The conveyer belts used to move the calcined coke from the cooler to the silos should be hooded to prevent particulate emissions (during high winds). Rail cars used to transport the calcined coke should receive the material directly under the silos and this area should be contained. Negative pressure may be considered an option within this area. A particulate emission of 25 mg/Nm^3 (European Commission, 2003) is considered acceptable.

9.2.2.3 Soil contamination

Green coke must be stored on a concrete pad. However the possible contamination of soil is a more a matter of good housekeeping. After the pad has been cleared of green coke (to be calcined) the area should be either swept or cleared of dust using a vacuum hose. Enclosed areas (e.g. hooded conveyer belts or silo discharge areas), require regular cleaning to prevent dust escaping. The primary concern relates to the contamination of the soil with heavy metals present in the coke (European Commission, 2003).

It is the author's considered opinion that particulate air pollution from a delayed coker can further be suppressed by either building open storage pads below ground level or increasing the size and number of storage silo's. One of the major problems with respect to good housekeeping in a delayed coker plant is the design of the de-watering and storage pads.

9.3 Introduction to the Clean Development Mechanism (CDM)

The CDM is an arrangement under the Kyoto protocol which allows industrialised countries with a Green House Gas (GHG) reduction commitment, to invest in projects that would reduce GHG in developing countries, as these projects would not be economical on their own. These reductions are bought in the form of carbon credits.

In an attempt to reduce giving credits to projects that would have happened anyway [i.e "free riders" (Wikipedia, 2008)], projects have to ensure additionality to the project, which in layman's terms means that any given project would reduce emissions more than would have occurred in the absence of tradable CDM credits. The two main additionality criteria currently being debated include:

- **Environmental additionality** – which dictates that the emissions from a project should be lower than the baseline
- **Project additionality** – which dictates that the project would not have occurred were it not for tradable CDM credits

While many of the new projects focus on utilising renewable energy to replace energy from fossil fuels, the bulk of the 2100 global projects applying for CDM accreditation concern the destruction of Hydro Flouro Carbons (HFC's). It is estimated the cumulative GHG reduction (to 2012) will be in the order of 2.2 billion tonnes of CO_2 (Wikipedia, 2008).

The drive for the implementation of the CDM in South Africa was reinforced in a speech by the Minister of Environmental Affairs and Tourism, Minister Marthinus van Schalkwyk, given as Appendix D, which states that:

", carbon markets will remain an important element in the climate architecture after 2012. In this regard, three issues deserve some attention, namely:
1. broadening the scope of the Clean Development Mechanism (CDM),
2. de-fragmenting the status quo
3. ensuring a more equitable geographic spread of CDM projects."

(Van Schalkwyk, 2007b)

South Africa ratified the United Nations Framework Convention on Climate Change (UNFCCC) in August 1997 and acceded to the Kyoto Protocol (as an Annex 1 country) in March 2002 (WWB, 2007). Within the South African context there are (as of the 31st of August 2007) 54 CDM project applications [34 Project Idea Notes (PIN) and 20 Project Design Documents (PDD)] which have been submitted to the Designated National Authority (DNA). This project range includes energy efficiency, fuel switching, hydro-electricity, co-generation, nitrogen oxide reduction, methane recovery, bio-fuel production and renewable energy (DME, 2007).

Of particular interest to the research for this dissertation would be fuel switching and energy efficiency projects. Fuel switching projects include switching from heavier to lighter fossil fuels and increasing the nett thermal energy per tonne of CO_2 emitted. As delayed coking would produce diesel (which could be used as a marine diesel) to

either replace the bunker fuel or partially substitute it, it would aim to register under the fuel switch project type (Chapter 9.4.3.3) in the future.

9.4 Delayed coking as a potential CDM project

To the best of the author's knowledge there have been no applications made to date for **new delayed cokers** to be registered as CDM projects. The potential for delayed coking to be registered as a CDM project is based on the fact that all the products (excluding the coke) will have a greater Nett Calorific Value (NCV) than the HFO which is used as the feed, due to higher energy efficiencies.

9.4.1 Calculating the CDM potential over the delayed coking process

The environmental factors relating to GHG emissions from delayed coking would include:

- The electricity used to run the delayed coker which would need to be calculated in terms of the CO_2 emissions from a coal fired power station
- The CO_2 emission saving from transporting 2.8 mega barrels less imported crude oil
- The CO_2 emission saving from transporting 216 650 tonnes less imported calcined anode coke
- The potential for CDM credits by using the delayed coker gas as a combustion fuel for the calciner, thereby reducing the amount of natural gas supplied from external sources
- The increase in the energy density per unit of CO_2 emitted of petrol and diesel compared to Heavy Fuel Oils (HFO) which has a lower energy density per unit of CO_2 emitted
- If the coke were not used as a fuel but rather in the production of aluminium for the fabrication of cars, the fuel consumption savings due to the lighter weight thereof

As the amount of unknowns relating to an evaluation over the whole delayed coker process are immense it would be more realistic to consider the potential of a fuel switch project type in the shipping industry. These results are presented in Chapter 9.4.3.3.

9.4.2 Green House Gas (GHG) and SO_x emissions from aluminium smelters

SO_x is also formed during the electrolytic reduction of aluminium. The calcined coke used for the production of pre-bake or Söderberg anodes is consumed during the electrolytic reduction of alumina to aluminium. As the positively charged anode contains varying amounts of sulphur and is attacked by divalent oxygen cations (O^{2-}), one of the gasses that are emitted includes SO_2. The obvious way to reduce SO_x emissions in an aluminium smelter would be to use a low sulphur calcined coke as

filler for the anode. This is not always a realistic option due to price, availability and logistic (sea freight) considerations.

As many of the Southern African aluminium smelters are situated along the east coast (to allow easy access for the delivery of bauxite from Australia) the seawater scrubbing process may also present a cost effective option for SO_x reduction (Hammingh, 2007). The SO_x reacts with natural alkaline bi-carbonates. The process may achieve up to 92% sulphur recovery and produces sulphates which are disposed of in the sea. The same type of process is utilised in the shipping industry (Hammingh, 2007).

The dominant consideration with respect to the emission of GHG stems from the electricity demand per tonne of aluminium produced. Due to improved smelting efficiency, the amount of electricity utilised worldwide for the production of aluminium will reduce by 10% (based on electricity consumption figures between 1990 and projected to 2010) according to the World Aluminium Institute (World AluminiumInstitute,2008a).

Other factors which effect the emission of GHG include:

- CO_2 from the oxidation reaction at the anode
- Emissions of Per Flouro Carbons (PFC's)

However, the quality of calcined coke used as filler for an anode may have a significant effect on the CO_2 intensity per tonne of aluminium produced. The presence of metals like sodium, vanadium, nickel and calcium catalyse side reactions (CO_2 and air reactivity), which increase the amount of carbon used to produce a tonne of aluminium. The combined effect of these side reactions can effectively increase the CO_2 emissions per tonne of aluminium produced by 20%.

However, the aluminium industry has had an indirect effect on lowering GHG emissions. As aluminium is lighter than steel, motorised vehicles produced are lighter and thus fuel consumption per kilometre is lower. Over the lifetime of a motorised vehicle it is claimed that the CO_2 emission reduction may be as much as 79 tonnes (World Aluminium Institute, 2008b). While this figure would seem to have minimal impact, if it were multiplied by the number of motorised vehicles in the world it would become significant. In South Africa alone, if it were assumed that each of the eight and a half million vehicles currently on our roads (Botha, 2008) had a lifetime saving of 50 tonnes of CO_2, the total saving in GHG emitted would be 425 million tonnes of CO_2.

Recycling of aluminium products costs only five percent of the cost to reduce the metal from alumina (World Aluminium Institute, 2008c). The reduction in green house gasses is, by default, significant, given the reduction in energy consumption.

9.4.3 Delayed coking and the shipping industry

9.4.3.1 Introduction

The production of delayed coker diesel for automotives is not the only potential market for this product. The hypothetical case study used in this chapter examines the use of Heavy Fuel Oil (HFO), from which the heavy residues used in this research are commonly prepared, to fuel the shipping industry. The study evaluates the potential for marine diesel (produced by delayed coking) to partially replace HFO as a fuel for shipping, describing the potentially beneficial effects of reducing SO_x and CO_2 emissions. The amount of delayed coker diesel used for the replacement of HFO is based on the figures generated by the current research both in the ***Carbon*** and ***White Product*** modes as described in the economic evaluation (Chapter 8).

9.4.3.2 SO_x and CO_2 emissions from the shipping industry

Ships that run on bunker fuels emit SO_x into the air, the amount of these emissions being dictated by the organically bound sulphur content of the bunker fuel. While specifications for bunker fuels limit the sulphur content, emission controls in open water are currently not stringent (4.5%) (Rauta, 2007). Emissions in control areas (within a certain perimeter of the harbour) (Krystallon, 2008a), are far stricter forcing many ships to run on marine diesel oil (sulphur content of 0.05 to 0.5%).

However, with crude oil becoming heavier and the sulphur content increasing, coupled with the fact that there will be (in the future) a significant legislated decrease in the sulphur content of the bunker fuels, it is the author's opinion that these ships could become increasingly reliant on larger percentages of marine diesel. Apart from the environmental benefits, this would decrease the demand for bunker fuels and make the delayed coking option more attractive. Another option would include on board abatement systems like seawater scrubbing.

According to a presentation by Intertanko (Rauta, 2007), the current maximum sulphur content for bunker oil (4.5%), will be reduced to 0.5% (as recommended by the European Parliament [EU]) for all ships traversing EU waters by 2015. The typical sulphur content of global bunker oil is currently 2.9% (Rauta, 2007). The presentation suggests the blending of Marine Diesel Oil (MDO) (sulphur content of 0.1%) with the bunker fuel. The presentation further mentions the positive affect on CO_2 emissions not only from the increased thermal energy efficiency of diesel but a reduction in the amount of heavy sludge generated by using the bunker fuel, which remains unburnt. The Norwegian Ministry of the Environment is pushing for the IMO to adopt a 0.5% maximum sulphur content by 2015, contending that it will reduce SO_x emissions from the shipping industry by 50-60% (Einemo, 2007).

Onboard shipping abatement systems for the removal of SO_x from the flue gas are available based on seawater scrubbing (Krystallon, 2008b), which use natural bicarbonates in the seawater to form soluble sulphates, which are pumped back into the ocean. The seawater scrubbing system is marketed to "future-proof" ships from future legislation to reduce the sulphur content of the bunker fuel.

The Intertanko presentation further mentions that replacement costs of bunker fuel by marine diesel cannot only be seen in the context of their current price differential.

Concern relating to pollution from ships has until recently been limited to oil spills while atmospheric pollution has enjoyed only marginal significance. However although shipping is the most environmentally sound mode of transport (Krause and Michaelowa, 2002), it provides a significant source of air pollution, as shown in Table 9-2.

Table 9-2 Annual air pollution from the global shipping industry (Gunner, 2007; IMO, 2005a)

Emission	Abbreviation	Annual emission (million tonnes)	Percentage of global emissions
Sulphur Oxides	SO_x	4.5 - 6.5	4
Nitrous Oxides	NO_x	5	7
Chloro Flouro Carbons	CFC	0.003	3
Carbon Dioxide	CO_2	1'245	1

While significant efforts continue to reduce the sulphur content of the bunker fuels, the three year rolling average (2002–2004) was 2.67% (IMO, 2005b).

According to Intertanko and the International Maritime Organisation (IMO) (Gunner, 2007), there are 59 859 Annex VI class ships traversing global waters. These ships consume a cumulative total of 352 474 giga tonnes of Heavy Fuel Oil (HFO) per annum and emit 1.25 billion tonnes of CO_2 into the atmosphere. This figure accounts for one percent of total global CO_2 emissions per annum.

The global CO_2 emissions attributed to the shipping industry, given in literature (IMO, 2005a) of 1.245 billion tonnes per annum are similar to that reported in a recent article (Petropoulos, 2008). The article refers to the emission of 1.120 billion tonnes of CO_2 per annum. This article supports the negative environmental sentiment emanating from the utilisation of HFO in the shipping industry, which is becoming evermore prevalent in the press. This article quotes *"It is so thick that it has to be heated to become mobile and is ranked as the dirtiest type of fuel"* (Petropoulos, 2008). This article has been included as Appendix E.

According to a Greenpeace International report (Hare, 2007), GHG emissions from air and shipping modes of transport are currently **excluded** from the Kyoto Protocol. Concern over the GHG emitted from the combustion of bunker fuels is a relatively new development and the integration of the shipping industry into the global climate change policy regime will present a new challenge. However it is likely that they will be included into the climate regime of the Kyoto protocol in years to come (Krause and Michaelowa, 2002).

Proposals have however been made to include aviation within the EU trading scheme, effective from 2011 to 90% of the 2004–2006 levels (Point Carbon, 2007). It is

widely believed that emission limits of GHG from the shipping industry will be targeted by the EU Parliament in the not too distant future (Point Carbon, 2007).

Difficulties with the inclusion of shipping emissions are based on how to allocate them. Options being investigated include allocation according to nation, country where the bunker fuel is sold, nationality of the transporting company and the country of departure or destination.

The shipping industry is concentrating on voluntary agreements for the adoption of emission or energy efficiency standards. There are many factors that may affect CO_2 reduction in the shipping industry including design of the hull and choice of propeller. However, a switch from HFO to marine diesel has been quoted as increasing fuel efficiency by four to five percent (Krause and Michaelowa, 2002). With respect to the figures presented in this research (given in Table 9.3 and 9.4), the increase in the fuel efficiency may be close to 20%.

The partial or complete substitution of HFO (which is equivalent to the heavy residues tested in the research for this dissertation) by diesel would have economic consequences on freight charges and would require an economic incentive (in the form of either taxes or carbon trading credits) to be viable.

Concerns relating to the detrimental atmospheric effect of the shipping industry are very much in the public eye. An article in the Sunday Times (Jordan, 2008), entitled *"WHO NEEDS PETROL",* refers to a conceptual project to power ships using massive kites in order to reduce environmental emissions. A German company "BELUGA PROJECTS" have invented the "SKY SAIL", which is expected to reduce carbon emissions by between 10 and 35%. An extract from the article states:

"But things will begin to look different on the byways and skyways, and particularly in the world's shipping lanes, where large vessels - among the worst emitters of climate changing exhaust gasses – are again harnessing sail power"

"WHO NEEDS PETROL", Bobby Jordan, Sunday Times, 13 January 2008

9.4.3.3 Calculating the CDM potential for delayed coking in a "Fuel Switch" for the shipping industry

As indicated above the shipping industry is under pressure to reduce the sulphur content of bunker fuel. Furthermore as the sulphur content of crude oil is increasing and as the capital cost of onboard SO_x abatement systems may not be viable for smaller vessels (Hammingh, 2007), the only available solution is to dilute the bunker fuel with marine diesel.

Apart from reducing SO_x emissions, the energy efficiency of the fuel would be considerably better. For the purposes of this hypothetical scenario, it is assumed that a ship would replace the amount of HFO consumed with the annual production of diesel from a hypothetical delayed coker (based on the results of this research in Chapter 8). This scenario is depicted in Figure 9-1.

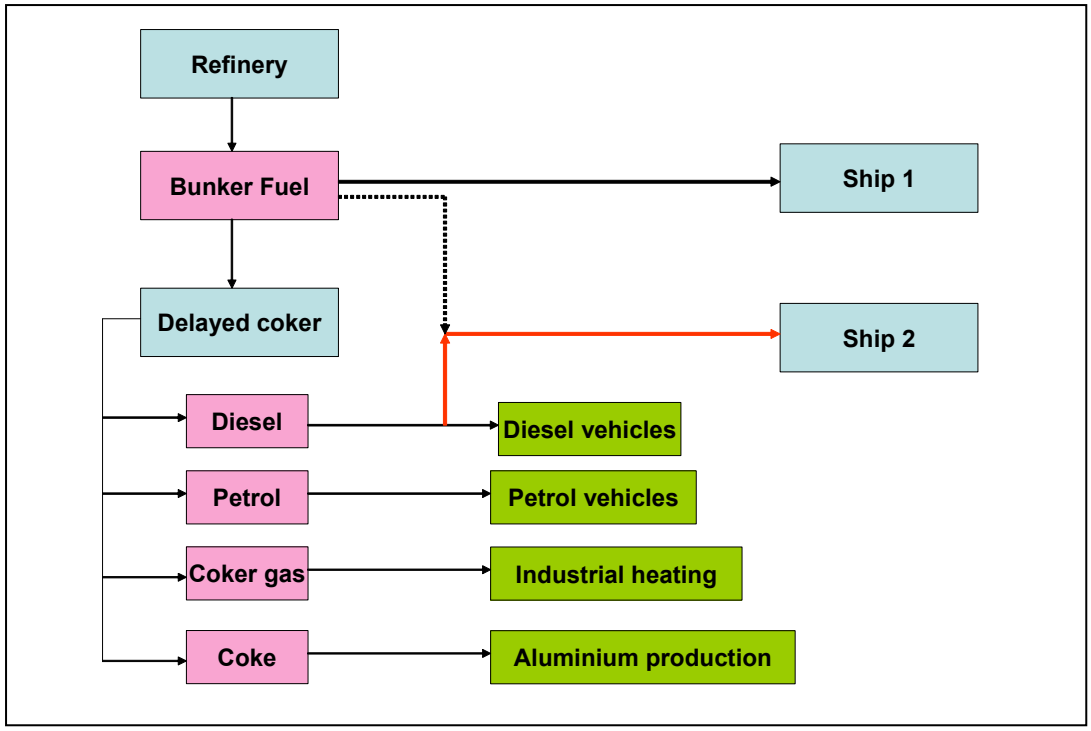


Figure 9-1 Schematic of a CDM fuel switch in the shipping industry

The amount of diesel produced by delayed coking is taken from the available data used in the current research. The annual production of diesel from delayed coking (based on the experimental results) may vary according to the mode of operation:

- Delayed coking in the ***Carbon*** mode would produce 202 950 tonnes of diesel per annum (Table 9-3)
- Delayed coking in the ***White product*** mode to maximise the petrol and diesel precursors would produce 312 750 tonnes of diesel per annum (Table 9-4)

Table 9-3 CDM fuel switch of diesel (delayed coking in the carbon mode) for HFO [3]

Analysis	Units	HFO	Marine Diesel
Calorific Value (Vallack, 2007)	(MJ/kg)	40.2	43.3
Energy efficiency (Wahlström, 2006)	(%)	42	50
Nett Calorific Value	(MJ/kg)	16.9	21.7
Carbon	(%)	87	86
Delayed coker products	(tpa)	750 000	202 950
Energy produced	(TJ)	12 663	4 394
Energy replacement value of diesel	(TJ)	4 394	4 394
Fuel required	t	260 239	202 950
Tonnes CO_2 emitted per tonne of Fuel (IMO, 2005b)		3.11	3.21
CO_2 emitted	t	810 487	650 658
CO_2 saved	t	na	159 829

[3] Mega Joule (MJ); tonnes per annum (tpa); Terra Joules (TJ); tonnes (t)

The annual energy production from delayed coker diesel (202 950 tonnes) is 4 394 TJ (Terra Joules) producing 650 658 tonnes of CO_2. If the equivalent amount of energy (4 394 TJ) was produced from HFO, the amount of fuel required would be 260 239 tonnes. This amount of HFO would emit 810 487 tonnes of CO_2. Thus the annual CO_2 emission saving is estimated to be 159 829 tonnes (Table 9-3).

A similar calculation may be made for diesel produced by delayed coking in the ***White product*** mode (Table 9-4).

Table 9-4 CDM fuel switch of diesel (delayed coking in the white product mode) for bunker oil[4]

Analysis	Units	Bunker fuel	Marine diesel
Calorific Value (Vallack, 2007)	(MJ/kg)	40.2	43.3
Energy efficiency (Wahlström, 2006)	(%)	42	50
Nett Calorific Value	(MJ/kg)	16.9	21.7
Carbon	(%)	87	86
Delayed coker products	(tpa)	750 000	312 750
Energy produced	(TJ)	12 663	6 771
Energy replacement value of diesel	(TJ)	6 771	6 771
Fuel required	t	401 033	312 750
Tonnes CO_2 emitted per tonne of Fuel (IMO, 2005b)		3.11	3.21
CO_2 emitted	t	1 248 976	1 002 677
CO_2 saved	t	na	246 300

As delayed coking to maximise petrol and diesel production would increase the amount of diesel (312 750 tpa), it is estimated that CO_2 emissions would decrease by 246 300 tonnes per annum.

9.4.3.4 The "cost" of reducing CO_2 emissions in the shipping industry

The potential to reduce CO_2 emissions by substituting marine diesel for HFO has been demonstrated in Tables 9-3 and 9-4. However, the cost of marine diesel is significantly higher than that of HFO. Based on the economic data received on the 20th of March 2008 the spot price of HFO was $ 502 or € 326.3 per tonne and that of marine diesel $ 986 or € 640.9 per tonne (van der Walt, 2008), based on a $/€ exchange rate of 0.65 (Fin24, 2008b).

Based on the energy equivalents of HFO and diesel (used in Tables 9-3 and 9-4), one tonne of HFO would have the same nett energy equivalent of 0.78 tonnes of marine diesel. As the cost of marine diesel is almost twice as expensive as HFO, the financial viability thereof could prove to be a disincentive to the shipping industry. However, as shown in Figure 9-2, the increased replacement of HFO by diesel increases the CO_2

[4] Mega Joule (MJ); tonnes per annum (tpa); Terra Joules (TJ); tonnes (t)

savings. However, as the CO_2 savings increase so does the differential cost of the fuel replacement.

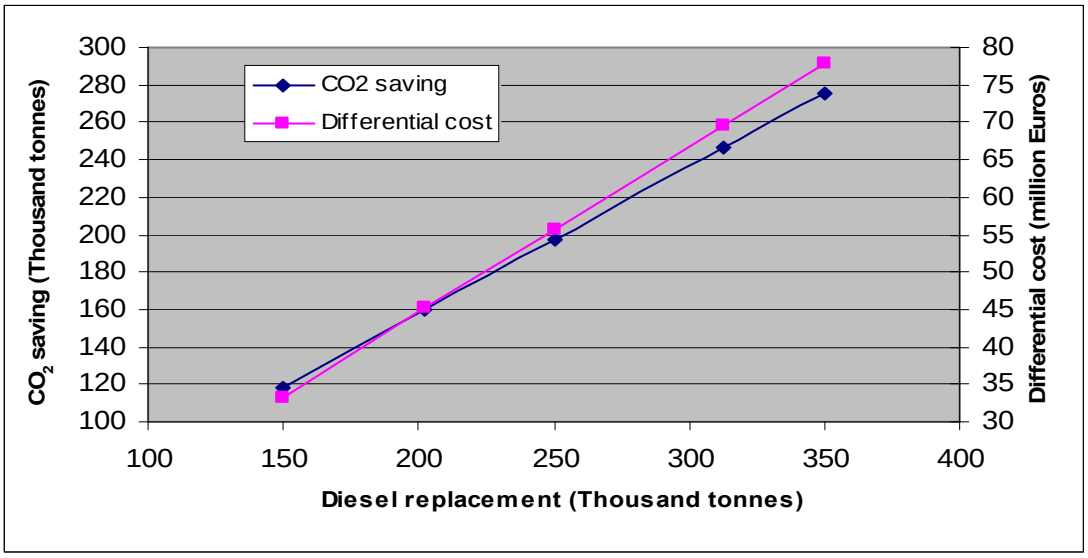


Figure 9-2 The effect of marine diesel replacement of HFO on CO_2 saving and differential cost

As there is a direct relationship between the three variables it is possible to calculate the cost per tonne of replacing HFO with diesel. The cost of emitting 1 tonne less of CO_2 is € 281.

While the CDM has been specifically developed for CO_2 reduction projects in under developed or developing countries, the effect on the shipping industry would be global and would depend on how these credits were allocated. Thus in order to attribute a value to these CO_2 reductions, the European Allowance Trading unit, which is based on the European Climate Exchange value of € 22 per tonne of CO_2, is used (New Carbon Finance, 2008). Thus it may be concluded that the cost of replacing HFO with marine diesel, based solely on the reduction of CO_2 (€ 281 per tonne of CO_2), is at least an order of magnitude higher than the value that would be paid (€ 22) per tonne of CO_2. Thus the CO_2 saving by the replacement of HFO with marine diesel would only account for approximately 8% of the additional costs.

The value of SO_x emissions reduction by replacing HFO with marine diesel is not published as it is considered an issue for the future. The only way to estimate what this future value may be, is to look at the cost of onboard desulphurisation of flue gasses from ships. The cost of seawater scrubbing, as previously described (Krystallon, 2008a) in open water is € 450-550 per tonne of SO_x (Hammingh, 2007).

In order to quantify the possible financial incentive / disincentive for the replacement of HFO with diesel a hypothetical balance sheet is shown in Table 9-5. This hypothetical scenario considers the cost of onboard seawater scrubbing of HFO with the cost and value of CO_2 emission reduction attributed to the marine diesel.

Table 9-5 The effect of SO_x and CO_2 reduction on the overall cost of marine diesel compared with HFO seawater scrubbing

	Units	HFO	Marine diesel
		Seawater scrubbing	
Energy	TJ	1.689	1.689
Amount of fuel	Tonnes	100	78
Sulphur content of fuel	%	4.5	0.5
Cost of fuel	€ per tonne	326.3	640.9
CO_2 reduction	Tonnes	0	79
Value of CO_2 saving	€ per tonne	0	22
SO_2 produced from fuel	Tonnes	9	0.4
Value of SO_2 cost	€ per tonne	550	0
Total fuel cost	€	32630	49990.2
Total value of CO_2 saving	**€**	**0**	**-1738**
Total value of SO_2 cost	**€**	**3960**	**0**
Total cost	**€**	**36590**	**48252**
Cost per tonne of fuel	**€**	**366**	**483**

In the example shown in Table 9-5, 100 tonnes of HFO is compared against 78 tonnes of marine diesel, as both amounts have an equivalent energy density (1.689 TJ). The cost of seawater scrubbing the HFO (maximum sulphur content of 4.5%) is given at the maximum cost of € 550 per tonne and an efficiency of 80 % (Hammingh, 2007).

As shown in Table 9-5, seawater scrubbing of HFO is financially more attractive than replacement with marine diesel. Seawater scrubbing of the HFO increases the price from € 326.3 (van der Walt, 2008) to € 366 per tonne. The price of marine diesel decreases significantly by over € 157 from € 640.9 (van der Walt, 2008) to € 483. The cost of marine diesel per tonne is given for the equivalent energy density compared to HFO. The cost reduction of the marine diesel is attributed a lower tonnage for the same energy density (88.5%) and the value of CO_2 emission reduction (11.5%).

Based on example given in Table 9-5, it would still be more financially viable for the shipping industry to consider onboard flue gas desulphurisation than replacement with marine diesel. However, seawater scrubbing only abates the sulphur emissions while using comparative more fuel tonnage and negating a potential CO_2 reduction. As previously mentioned, the breakeven value for HFO replacement with marine diesel with specific reference to the value of a CO_2 emission reduction, would have to be € 281 per tonne of CO_2 emitted. Considering the increased cost of HFO desulphurisation this cost would reduce to € 169 per tonne of CO_2 emitted. While this is very much a move "in the right direction", it is still substantially higher than the current value of € 22 per tonne of CO_2.

Were the USA to ratify the Kyoto Protocol it is probable that the demand for carbon credits would increase which by default increase the value thereof. The future of HFO replacement with marine diesel will depend on the future value of carbon credits on the global market.

These calculations have not taken into consideration the potential costs of reducing the Nitrous Oxides (NO_x), particulate emissions and the clearing the sludge that HFO produces.

The aim of the Kyoto Protocol was to reduce GHG emissions by 5% of the 1990 levels over the time period from 2008 to 2012 (WWB, 2007). In summary in terms of the shipping industry the relative economics need to be seen within the context of future SO_x and CO_2 caps when these controls will be enforced.

9.5 Environmental epilogue

The delayed coking of heavy residues can be an extremely profitable endeavour. It is also a fact that the costs of investing capital to reduce the "environmental footprint" thereof are significant, at least in the short term. However, protecting the environment is the only long term sustainable solution for industrial growth. If marketed correctly, delayed coking put through an "environmental laundry" will be both more sustainable and profitable in the long run. As a conclusion to Chapter 9, the research has shown how delayed coking can embrace many of the environmental challenges.

The "environmental footprint" left by delayed coking is significant. However the opportunity they bring to change industrial paradigms may be considered in light of the following quotations:

"*We are altering the most basic forces of the planet's surface – the content of the sunlight, the temperature and aridity – and that brings out one of the most powerful questions about who is in charge. If you wanted to give a name to this phenomenon, I think you could call it de-creation"*

Bill McKibben, Christianity Today, December 1996

and

"*The supreme reality of our time is ……...the vulnerability of our planet"*

John F Kennedy (1917 – 1963) 35th President, Speech No 28, 28 June 1963

10 CONCLUSIONS AND RECOMMENDATIONS

10.1 Conclusions

Commercial delayed coking of heavy petroleum residues has been practiced for over a century. Furthermore, delayed coking and calcining technology is considered "off the shelf" technology items. Therefore the question to be asked is; has the current research contributed towards unlocking the value of previously untested heavy residues, within the South African context and provided evidence to challenge paradigms currently held within the aluminium (anode coke), value added graphites and shipping (from an environmental viewpoint) industries?

10.1.1 Contribution towards South Africa's sustainable growth

As a developing economy, South Africa needs to promote self-sustaining strategies and extract the maximum value from her available resources. The change of political dispensation in 1994 has included a greater percentage of citizens in the economicall middle and upper classes.

It may be concluded that the number of registered motor vehicles in South Africa has increased exponentially in the period from 1994 to the present day and will continue to grow (Botha, 2008). The demand for automotive fuels will by necessity also increase. This demand could in part be served by a new crude oil refinery in Port Elizabeth to process 200 000 bbl/day planned for operation in the year 2010 (Reuters, 2007). It has been shown that while the R/$ exchange rate is currently relatively stable (between 7 and 8), the price of Brent crude oil has almost quadrupled from 2004 to 2008 [in the year 2004 the average crude oil price was $ 28/bbl (Botha, 2008) while on the 14th of March 2008 the crude oil price increased to a record $ 111/bbl (Fin24, 2008a)]. This will continue to exacerbate the exponential increase in the balance of payments deficit attributed to the purchase of crude oil, and increase inflationary pressure within South Africa.

The hypothetical commercial scenario (based on the experimental results) has shown that delayed coking of approximately 750 000 tonnes per annum of the heavy petroleum residues, would produce in excess of 290 000 tonnes of liquid automotive fuels. It may further be concluded that while the 1.33% crude oil saving generated by delayed coking may not seem significant, it would save South Africa 1.82 billion ZAR in direct foreign savings, which, by way of example, could finance approximately 50 000 low cost houses (The Times, 2007).

The same rationale may be used to evaluate the direct foreign savings from the local production of 216 650 tonnes of calcined anode coke. Assuming a landed cost of $ 250-350 per tonne (Mannweiler, 2008a) the direct foreign savings could be approximately 580 million ZAR, which, by way of example could finance almost 16 000 low cost houses (The Times, 2007). The nett saving on freight costs alone (assuming $ 70/tonne freight cost from the Gulf of Mexico) would be approximately 121 million ZAR.

The foreign savings calculations have been based on the experimental results used in the hypothetical scenario. While these figures are only approximations based on the available feed indicated and are a very rough order of magnitude, it may none the less be concluded that delayed coking would contribute significantly to South Africa's economy.

It has been shown that in respect of the sulphur content of crude oil and subsequently of calcined coke, there are significant quality challenges, while the sharp rise in the crude oil price (which is not being driven by normal market forces) will continue to have an ever increasing effect on the disposable finances of the majority of South Africans.

The research has shown that delayed coking of these five available heavy residues could supply both petrol and diesel into the market as opposed to their use merely as a burner or bunker fuel. Given the potential to produce delayed coker products from the available feedstock tonnages, the project cannot totally alleviate the automotive fuel crisis. However given the data provided, any opportunity that will "squeeze" the maximum value from available resources and thereby support South Africa's drive towards sustainable growth warrants further investigation.

10.1.2 The influence of feedstock quality on the microstructure and CTE of the coke

The five heavy residues tested varied with respect to origin, green and calcined coke quality.

It may be concluded that the high ash content of Sample C had a substantial influence on mesophase development, producing green coke microstructures with fine to medium mosaics. The isotropic nature of the high ash coke (Sample C) also yielded the highest CTE. These results are supported by literature (Obara and Marsh, 1985). Furthermore both samples C and E contained elevated levels of nickel and vanadium. Thus it is suggested that the catalytic effect of nickel and vanadium in the presence of sulphur may be a secondary causative effect leading to the formation of finer mosaic microstructures leading to higher CTE values, as evident from both samples. This is in accordance with literature (Oi and Onishi, 1978).

On the contrary it may further be concluded that feedstock samples (A, B, D, and E) which had lower ash content produced green cokes with a more anisotropic flow domain microstructures and a lower CTE. This is supported by literature (Tillmans and Pietzka, 1978).

Apart from the effect of ash on mesophase development, it may be concluded that the lower density of Sample E resulted in the lowest green coke yield and highest white product yield, was responsible for the development of significant porosity in the green coke microstructure. The effect of pore morphology also contributes towards the determination of the CTE of calcined cokes. It was demonstrated that while Samples D and E had similar ash contents, the longer thinner pores parallel to the laminar flow domains in Sample D produced coke with a lower CTE than the excessive ovular and

irregular shaped pores of Sample E. These findings are in agreement with literature (Hulse, 2000; Mochida, 1987).

10.1.3 The potential for the cokes produced to be utilised as anode coke

The influence of feedstock quality on the microstructure of the green coke and the CTE of the calcined coke has been discussed in the previous section. One of the aims was to compare how these results as they pertain to typical anode cokes used in the aluminium industry (Hulse, 2000) and where necessary suggest possible remedies.

It may be concluded that the greatest concern stems from the high ash content of all the feedstocks and by default the calcined coke. High ash feed would be detrimental in several respects:

- High ash feedstock increases the CTE of the coke
- High ash feedstock may lead to fouling in the heater tubes
- Vanadium, nickel and sodium promote air reactivity of the anode
- Silicon may cause flowability problems in the aluminium metal produced
- The ash content of calcined coke could decrease the market price thereof

Methods to remove the ash content from the feedstock have been suggested in literature (Junji, 1993).

It may also be concluded that although the sulphur content in the cokes varied significantly, the blended feed calcined coke had a sulphur content of 3.26%, which is below the global average 3.6% (Driscol, 2007) and the maximum typical value for anode cokes, 3.5% (Hulse, 2000), and thus should be acceptable. It may further be concluded from literature (Driscol, 2007) that the sulphur content of available calcined coke (on a global scale) has been increasing and will continue to increase, given the quality of crude oil reserves. An increase in the sulphur content reduces the percentage of elemental carbon per tonne of calcined coke available for the reduction of alumina. The current research has proved that it is possible to significantly reduce the sulphur content of these cokes using heat treatment at graphitisation temperatures.

The CTE of the cokes produced also varied vastly, although when in a blend such products should be acceptable to the anode industry. Given the variety of the CTE results it is also concluded that the typical anode coke characteristics cited in literature (Hulse, 2000) should include a typical range of values for the CTE, which is currently omitted. The research has proved that not all heavy petroleum feed will necessarily yield a calcined coke which would be acceptable (in terms of the CTE) to the aluminium industry.

The real density of all the calcined cokes produced would be acceptable to the aluminium industry based on typical values (Hulse, 2000).

10.1.4 The opportunity for value added graphites

The research was not able to yield graphite that would be acceptable in higher value markets due to temperature limitation on the laboratory equipment. However, what has been shown is that heat treatment (2081 ºC) of the green coke would reduce the ash content, reduce the sulphur content and increase the yield.

The removal of sulphur from cokes may have benefits to both the aluminium and graphite markets.

However, it may be argued that, as sulphur is not released during anode baking, the effect thereof is merely related to environmental issues. Thus the removal of sulphur before anode manufacture may not be any more beneficial than processing high sulphur cokes and scrubbing the SO_x formed in the electrolytic reduction of alumina. However this argument negates the fact that an anode formed with lower sulphur coke (e.g. using heat treatment) would contain a greater percentage of carbon. Thus the greater the amount of carbon in an anode, the longer it would remain in the pot cell reducing production costs.

A further argument for high temperature treatment of cokes has been highlighted by the current research. The green coke which was graphitised in an inert atmosphere showed a yield of 85% compared to what would be commercially expected in a commercial calciner (in an oxidative atmosphere) of 75%. Analysis of the calcined coke further showed an increased ash content whose composition was inclusive of minerals which have been cited in literature as (Hulse, 2000; Fischer, 1995) promoting side reactions within an aluminium pot cell. Apart from de-ashing the feed, the current research has shown that graphitisation in an inert atmosphere could reduce the mineral matter content and increase the carbon content of a coke to be used in the production of aluminium. Thus given all the evidence provided, it is concluded from the current research that graphitisation of green cokes for the aluminium industry could be highly beneficial and warrants further research.

It has further been proved using XRD crystallography that heat treatment results in a significant “ordering” of the crystal lattice from a turbostatic green coke to a graphitic carbon. Evidence of graphitisation is given by a reduction in the interlayer spacing (d_{002}), increase in the stacking height (L_c value) and is in accordance with the work of previous researchers (Ellis and Hardin, 1993; Hardin and Beilharz, 1993).

Based on the abovementioned trends the author is confident that by “tweaking” the feed (removal of the ash content) and graphitising at temperatures of greater than 2600 ºC, a product could be produced that would have potential in high value graphite coke markets.

The value added graphite coke market may benefit from a graphitised coke due to:

- Increased availability of coke (Driscol, 2007)
- Less puffing due to sulphur release during graphitisation (Ellis and Hardin, 1993)
- Less sublimation of ash leaving voids in the graphite artefact

- An improved development of the crystal lattice reducing electrical resistance (Ellis and Hardin, 1993)
- A reduction of the CTE (Ellis and Hardin, 1993)

These potential benefits do not negate the possible negative effect of reduced macro-porosity and increased micro-porosity as cited in literature (Legin-Kolar, 1999; Legin-Kolar 1992; Hardin and Beilharz, 1993). The research does not serve to obviate the potential detrimental effect of a reduction in the bulk density.

10.1.5 Delayed coking as an environmental solution

The results of the blended feed trial have shown that over 50% of the sulphur in the feedstock will report to the green coke which acts as a sulphur "sink". It may be concluded that the capture of sulphur in the green coke reduces the sulphur content of the liquid fuels and off-gas and thus would reduce hydrogenation costs. The sulphur content of the petrol, diesel and off-gas will need to be removed as H_2S and reduced to elemental sulphur for sale into the sulphuric acid production market. The capital costs of the de-sulphurisation will need to be included in the capital estimate of the greater project.

The possible sale of coke to the aluminium industry at one of the sites on the East coast of Southern Africa does not solve the sulphur problem but merely "relocates" it. However, it may be concluded that as all the aluminium smelters are situated on the east coast of Southern Africa, and as seawater scrubbing is the lowest cost process to desulpurise flue gas (Hammingh, 2007), this will be a cost effective abatement method to reduce SO_x emissions. While it alleviates the immediate concern of SO_x emissions within the immediate vicinity in which the delayed coker is situated, the responsibility for sulphur capture would be shifted to the concerned smelter.

It has been shown that the sale of HFO (352 474 giga tonnes) into the global shipping industry emits 4.5-6.5 million tonnes of SO_x into the atmosphere, which is substantial (Gunner, 2007; IMO, 2005a). It has further been shown that future legislation governing the maximum sulphur content of bunker fuels which is currently 4.5% (Rauta, 2007) will require onboard cost effective seawater scrubbing (€ 450–550 per tonne of SO_x) or significant dilution with marine diesel to comply with the suggested specification in 2015 of 0.5% (Rauta, 2007).

Delayed coking of heavy petroleum residues would by default significantly reduce the available tonnage of HFO currently used as fuel for the South African shipping industry. The relationship between delayed coking and the shipping industry may not necessarily be, as it would appear, to be a "parasitic" one. The potential production of delayed coker diesel could provide the shipping industry with a source of lighter fuel with substantial benefits.

It may be concluded that this potential synergy (between the delayed coking and shipping industry) could also serve to address the challenges of Green House Gas (GHG) emissions from the shipping industry which are significant contributors towards global warming (IMO, 2005a).

It has been shown that replacement (in part) of HFO by marine diesel will serve to increase the energy density of the bunker fuel per tonne of CO_2 emitted and substantially reduce the sulphur content (Vallack, 2007; Wahlström, 2006). It may be concluded that given the hypothetical scenario (based on the current experimental results) by which delayed coking was utilised to supply marine diesel to the shipping industry, the CO_2 savings per annum (between 159 and 246 kilo tonnes dependant on the mode of delayed coker operation) would be significant using a fuel switch mechanism. A literature search has further shown that there are currently no listed GHG reduction projects linked to delayed coking. This reduction in CO_2 emissions would qualify for CDM accreditation, when and if the shipping industry is listed under the Kyoto protocol.

However, it has also been shown that onboard sulphur removal (using seawater scrubbing) would currently still be a more cost effective option compared to marine diesel replacement even though this practice would not serve to address CO_2 reduction targets.

It may be concluded that the relative cost discrepancy between HFO ($ 502 or € 326 per tonne) compared with marine diesel ($ 986 or € 641 per tonne) may force the shipping industry to only address SO_x reduction in the short to medium term. The current research has proved that based on an economic breakeven for the replacement of HFO with marine diesel, the value of carbon credits alone would have to be in the order of € 281 per tonne of CO_2 emitted. If the cost of flue gas desulphurisation were to be included this value would decrease to € 169 per tonne of CO_2 emitted. These values are far in excess of the current market value of € 22 per tonne of CO_2 emitted. Based on these findings, the only manner in which to realistically consider marine diesel replacement would be for the demand market for carbon credits to increase and thus their value.

Many of the press and literature articles cited have only presented a subjective over view of the environmental challenges facing the shipping industry (Jordan, 2008; Point Carbon, 2007; Hare, 2007; Petropoulos, 2008) or only based the relative economics of marine diesel replacement on the relative cost of SO_x reduction alone. The current research has proved how it is possible to address both the SO_x and CO_2 challenges in the shipping industry by supplying economic targets (for CDM credits) which would guide the shipping industry **based on a futuristic scenario where GHG emissions from ships were included under the Kyoto Protocol**, rather than only addressing SOx reduction (as given by the process of seawater scrubbing of the HFO).

This research has been presented in a way to put numbers to the marine diesel in light of its higher energy density, lower sulphur content, and ability to reduce CO_2 emissions in order to compare it with the seawater scrubbing of HFO.

10.1.6 Validation of the hypothesis

In the introduction to this dissertation a hypothesis was made:

“The author proposes a hypothesis that South Africa is not making the most potential of the heavy petroleum residues available and that delayed coking will in part serve to

unlock the value of these resources to service local demand for anode coke and automotive fuels."

The primary aim of this dissertation was to examine the delayed coking of five heavy residues in the carbon mode and evaluate the calcined cokes as potential anode coke fillers. However, this dissertation has also examined many facets associated with delayed coking in South Africa, inclusive of:

- A simple introduction to this science for South African students, where it is relatively unknown
- South Africa's fuel requirements and the contribution of delayed coking to the economy
- The potential synergy of delayed coker diesel with the future SO_x and CO_2 emission targets in the shipping industry

It is the author's opinion that examination of these facets does not dilute the primary focus but rather serves to enhance the potential for delayed coking in South Africa.

In conclusion the author believes that the research has provided enough evidence to warrant further investigation of the opportunities presented. The research has served in part to unlock the potential for deriving additional value from the heavy petroleum residues.

10.2 Recommendations

Opportunities for further work are recommended in terms of feedstock modification, delayed coking, calcining, graphitisation and environmental impact.

10.2.1 Feedstock

- Harvesting and determining the PSD of the ash content of the feed to establish the best method to utilise for de-ashing
- De-ashing of the feedstock prior to delayed coking should be conducted to evaluate the effect on both the coke microstructure and the CTE
- Determining the effect of ash reduction with respect to specifications of anode cokes
- As the feeds were tested independently of one another, mixability and settling tests would need to be conducted
- Analysis of the asphaltene content of the individual feeds
- Blending trials to determine the CTE of the blended coke using variations of the feed concentrations

10.2.2 Delayed coking

- Trials to determine the optimum delayed coking (in the carbon mode) conditions for the production of anode coke would need to be conducted; this would include optimisation of the temperature, pressure and feed rate.
- Trials to evaluate the effect of the recycle oil will need to be conducted
- The delayed coker white products would need to be hydro-treated to determine approximate variable costs
- Trials to determine the effect of fouling (coke laydown) in the heater tubes as a result of the ash content of the feedstock will need to be conducted

10.2.3 Calcining

- Trials to determine optimum calcining conditions with respect to the yield, air and CO_2 reactivity's must be considered
- The calcined coke would need to be tested by an independent facility for qualification as an anode filler material in the aluminium industry

10.2.4 Graphitisation

The graphitisation of the green cokes has opened up a scope of opportunity. The following trials could be considered:

- Graphitisation of larger samples to determine the CTE (flour rod), puffing rate, grain stability and electrical conductivity of the graphites

- Production of samples to be tested as needle coke, low sulphur recarburisers and speciality graphites according to industry standards
- Detailed investigation of the effect of heat treatment temperature on the graphitisation behaviour (X-ray powder diffraction) of the cokes produced to investigate the effect of green coke anisotropy on the degree of graphitisation
- The maximum graphitisation temperature reached during this research was 2081 ºC. Future graphitisation experiments should be conducted at temperatures of over 2600 ºC
- Particulate graphitisation of cokes is not widely practised in industry. While this may not be financially viable for the aluminium industry, for the higher value graphite markets may be justified due to the lower availability of acceptable quality coke.
- While the industrial focus of heat treating low ash petroleum cokes may exclusively be for desulphurisation purposes, establishing a link between the XRD analysis and the physical attributes (e.g. CTE and electrical conductivity) of a range of sponge cokes could prove extremely beneficial.
- While specification sheets have been the historical mainstay for the qualification of cokes for both the aluminium and steel industries, in-situ performance and advanced technological techniques are gaining momentum. This creates scope for a greater deal of academic work on the subject of commodity petroleum sponge cokes for advanced graphite applications.

10.2.5 Environmental aspects

- Determining the cost of de-sulphurisation of delayed coke products and a further study of the environmental impact would be beneficial
- Evaluating the impact that future sulphur restrictions in the bunker oil market will have on the value of the heavy petroleum residues and the opportunity this may open up for delayed coking
- A techno-economic study of the of the benefits of marine diesel replacement of HFO in terms of SO_x, NO_x, particulate and CO_2 emissions to refute or confirm the findings of the current research for a fuel switch project
- Further research to position delayed coking as a (CDM) project

11 REFERENCES AND BIBLIOGRAPHY

11.1 References

Botha, G. (2008). Year-End Vehicle Population. Excel spreadsheet. Road Traffic Management Council (RTMC) of South Africa, Research and Development. SOUTH AFRICA

Burchell, T. (1999). **Carbon Materials For Advanced Technologies**, 1st Edition, Pergamon, Amsterdam, HOLLAND, pp 20, 356, 364, 365

Clark, JG and Chang, CF. (2001). *Improvement of the quality of delayed coke produced from coal gasification pitch by addition of FCCDO to the feedstock*. ACS Fuel Chemistry Division, Preprints, 2001, 42 (2), pg 569

Clark, JG and Chang, CF. (2002*). Properties of delayed coke along the coke drum height*. AIChE Spring National Meeting, 2002, USA

Clark, JG. (1995). Aluminium photo file, Sasol Technology (R&D) Division, Sasolburg, SOUTH AFRICA

Clark, JG. (1996). Coking fundamentals, Internal report, Sasol Technology (R&D) Division, Sasolburg, SOUTH AFRICA

Clark, JG. (2004b). *Coal-Tar Gasification Pitch Coke*. PowerPoint presentation, State of the Industry Address, Consortium for Premium Carbon Products from Coal (CPCPC) Spring Meeting, 2004. Hershey, PA, USA

Clark, JG. (2005). Industrial Coking and Calcining, PowerPoint presentation, Sasol Synfuels Marketing, Johannesburg, SOUTH AFRICA

ConocoPhillips. (2007). Technology solutions: ThruPlus technical specifications. INTERNET. http://coptechnologysolutions.comthruplus_delayed_coking/thruplus/tech_spec_pg 1. Cited 30 March 2008

Crelling, JC. (1990). **The Petrographic Atlas**. INTERNET. http//:www.mccoy.lib.siu.edu/projects/crelling2/atlas . Illinois, USA, Frame ID: Q09, Q10, Q12, G26. Cited 22 February 2008

DME, (2007). *South Africa's CDM Project Portfolio*. INTERNET. http://www.dme.gov.za/dna/dna_project_portfolio. Cited 11 January 2008

DME. (2006). *Energy Security Master Plan – Liquid Fuels*. Department of Minerals and Energy. South African Government, SOUTH AFRICA, pp 18, 21, 54

Driscol, K. (2007). *CRU analysis*, Powerpoint Presentation, Commodities Research University (CRU) International Limited, London, UNITED KINGDOM, slides 1-12

Du Plessis, E (2007*). XRD analysis of coke samples to determine the degree of graphitisation*. Internal report. Sasol Technology (Research and Development) Division

Einemo, U, (2007). *Norway still pushing for distillates*. INTERNET. http://www.sustainableshipping.com/news/2007/06/68160. Petromedia Ltd publishers. Cited 23 February 2008

Ellis, PJ and Hardin, EE. (1993). *How petroleum coke forms in a drum*. Light Metals 1993, pp. 509-515

Ellis, PJ. (1998). *Delayed Coking Tutorial*. INTERNET.http://www.jechura.com/ChEN409/DECOKTUT.pdf. Cited 23 January 2008

Enerdata. (2007*). Key Energy Statistics – South Africa***.** INTERNET. http://www.enerdata.fr. Exel Spreadsheet. Cited 25 January 2008)

Eser, S and Jenkins, RG. (1989). *Carbonisation of petroleum feedstocks: Relationships between chemical constitution of the feedstock and mesophase development*. Carbon, vol. 27, no 6, pp. 877-887

EUROPEAN COMMISSION. (2003). *Reference document on the best available techniques for mineral oil and gas refineries*, Reference Document, Integrated Pollution Prevention and Control (IPPC), pp 124, 258, 193-198, 207-209

Fin24. (2008a). *Oil slips from $ 111*. INTERNET. http://www.fin24.com/articles/default/display_article.aspx?ArticleId=1518-1793_2288058 . Published 14 March 2008. OPA publishers. Cited 16 March 2008

Fin24. (2008b). US dollar / Euro exchange rate. INTERNET. http://www.fin24.com/currencies. Published 20 March 2008. OPA publishers. Cited 20 March 2008

Fischer, WK. (1995), **Anodes for the Aluminium Industry,** 1st Edition, R&D Carbon, Calligraphy, Sierre, SWITZERLAND, pp 50-52

Gentzis, T. (2001**).** *The effect of carbon additives on the mesophase induction period of athabasca bitumen*. Fuel Processing Technology, vol 69, no 3, pp. 191-203

Granda, M and Santamaria, R. (2003). *Preventing mesophase growth in petroleum pitches by the addition of coal-tar pitch*. Carbon, vol 41, no 9, pp. 1854-1857

Gunner, TJ. (2007). *Shipping, CO_2 and other Air Emissions*. INTERNET. http://www.ipieca.org/activities/fuels/downloads/workshops/oct_07/gunner.pdf. Cited 13 February 2008

Hammingh, JMM. (2007). *Effectiveness of international control measures for North Sea shipping on Dutch air quality. Netherlands Environmental Assessment Agency.* INTERNET. http://wwwmnp.nl/bibliotheek/rapporten/500092004.pdf , pg 22. Cited 21 March 2008

Hardin, EE and Beilharz, CL. (1993). *A comprehensive review of the effect of coke structure and properties when calcined at various temperatures*. Light Metals 1993, pp 501-508

Hare, B. (2007). *Undermining the Kyoto Protocol: Environmental effectiveness versus political expediency*, Report, Greenpeace International, DENMARK

Hartly, WCF and Ford, JC. (2004). **Business Accounting and Finance for Managers: An Introduction, 4th Ed**, Witwatersrand University Press, Johannesburg, SOUTH AFRICA, pp 173-184

Hulse, KL. (2000). **Anode Manufacture**. 1st Edition, PhD thesis, R&D Carbon, Calligraphy, Sierre, SWITZERLAND, pp 8-9,80,90,94-95

IMO. (2005a). *Prevention of air pollution from ships*. INTERNET. http://www.imo.org/Environment/mainframe.asptopic_id=233. Cited 27 February 2008

IMO. (2005b). *Interim guidelines for voluntary ship CO_2 emission indexing for use in trials*. INTERNET. http://www.imo.org/includes/blastDataonly.asp/data_id%3d12740/471/pdf. Cited 15 February 2008

Inagaki. (2000). **New Carbons: Control of Structure And Functions**, Elsevier, Kawasaki Steel Co. LTD, JAPAN, pg 15

Jordan, B. (2008). *Who needs petrol*, Sunday Times News paper, 13 January 2008, Avusa Media Ltd, pg 7

Junji, E. (1993). *Process for producing petroleum needle coke*. INTERNET. Patent 08/071637. http://www.freepatentsonline.com/5695631. Cited 24 February 2008

Karacan, CO and Badger, M. (2003). *Effect of steam injection on pore structure and distribution in coke samples produced by delayed coking*. Fuel, vol 82, no 8, pp. 909-917

Keshun, S and Wang, C. (1985). *Influence of microstructure on thermal expansion and graphitisation of oil cokes*. Fuel, vol 64, no 2, pp. 174-177

Krause, K and Michaelowa, A. (2002). *Climate policy: Analysis of ecological, technical and economic implications for international maritime transport*. International Journal of Maritime Economics, vol 4, no 2, pp164-194

Krystallon. (2008a). *Sulphur Regulations*. INTERNET. http://www.krystallon.com/regulations. UNITED KINGDOM, pp 1–2. Cited 21 January 2008

Krystallon. (2008b). *Seawater Scrubbing*. INTERNET. http://www.krystallon.com/sea-water-scrubbing. UNITED KINGDOM, pg 1. Cited 21January 2008

Legin-Kolar, M. (1992). *Optical and crystallographic structure of pitch cokes*. Carbon, vol 30, no 4, pp. 613-618

Legin-Kolar, M. (1999). *Changes in structural parameters of different cokes during heat treatment to 2400 ºC*. Fuel, vol 78, no 13, pp. 1599-1605

Mannweiler, U. (2008a). *Carbon products: a major concern to aluminium industries*. PowerPoint presentation. Mannweiler Consulting. Metal Events, 2nd Middle East Aluminium Conference, Dubai, 4-6 February 2008, slide 6

Mannweiler, U. (2008b). *Anodes – Today, Tomorrow, and Beyond*. PowerPoint presentation. Mannweiler Consulting. Jacobs Consultancy Petcoke Conference, New Orleans, USA, 7-8 March 2008. Slide 5

Marsh, H. (1997**). Introduction to Carbon Science, 4th Edition**, Secretariado de Publicaciones, SPAIN pp 360, 478, 491, 495, 496, 521

Meier, M (2006). **Anodes – From Raw Materials to the behaviour in Hall-Heroult cells**. Proceedings, Sierre, SWITZERLAND, ch 1 pp 2, 5, 9, 17, ch 6 pg 3, ch 10 pg 2

Milne, J. (2007). BHP Billiton, personal communication

Mochida, I and Korai, Y. (1989). *Carbonisations in a tube bomb: co-carbonisation of petroleum vacuum residue and a FCC decant oil into a better needle coke*. Carbon, vol 27, no 3, pp. 359-365

Mochida, I. (1987). *Optimisation of carbonisation conditions for needle coke production from a low sulphur petroleum vacuum residue*. Journal of Material Science, vol 23, no 1, pp. 298-304

New Carbon Finance. (2008). ECX CFI Futures controls: Prices and volumes. INTERNET. http://wwwnewcarbonfinance.com/?gclid , pg 6. Cited 21 March 2008

Obara, T and Marsh, H. (1985). *Carbonization behaviour of pitch in the presence of inert material*. Fuel, vol 64, no7, pp. 995-998

Oi, O and Onishi, N. (1978**).** *Influence of organic sulphur compounds and metals on mesophase formation*. Carbon, vol 16, no 6, pp. 445-452

Onder, H. (1997). **Everything you always wanted to know about petroleum coke, 4th Edition**, Svedala Industries, pp 11–14

Petropoulos, T (2008). *Changes ahead for ship fuel.* INTERNET. http://www.energypublisher.com/article?id=14569 . Published 21 February 2008. EnerPub. Cited 18 March 2008

Phillips, G. (2003). *Drivers for additional delayed coking capacity in the refining industry*. INTERNET. http://www.petroleum-economist.com/default.asp?page=14&SID=326466. Cited 23 February 2008

Point Carbon. (2007). *Parliamentary aviation proposal to boost EU demand*. INTERNET. http://www.pointcarbon.com/article25450-868. Cited 19 January 2008

Rauta, D. (2007). *Use of MDO by ships, the rationale behind the proposal.* PowerPoint presentation, Future Marine Fuels – Challenges to the Marine Industry, Cimac Circle, NORWAY 2007

Reuters. (2007). *Petro SA To Build R 39 Bn refinery*. INTERNET. http://www.africa.reuters.com. Reuters report, 24 December 2007. Cited 30 February 2008

Santamaria, R and Blanco, C. (2003). *Mesophase development in petroleum and coal-tar pitches and their blends*. Journal of Analytical and Applied Pyrolysis, Vols 68-69, pp. 409-424

Schuin, E. (2004a). Work procedure for Mini Delayed Coker (MDC). Internal report, Number sct004, Sasol Technology (R&D) Division, Sasolburg, SOUTH AFRICA

Schuin, E. (2004b). Work procedure vacuum and atmospheric distillation. Internal report, Number sct006, Sasol Technology (R&D) Division, Sasolburg, SOUTH AFRICA

Schuin, E. (2004c). Work procedure for Coefficient of Thermal Expansion (CTE). Internal report, Number sct018, Sasol Technology (R&D) Division, Sasolburg, SOUTH AFRICA

Stadelhofer, JW. (1981). *The manufacture of high value carbon from coal-tar pitch*. Fuel, vol 60, no 9, pp. 877-882

The Times. (2007). *Housing options for lower income people*. INTERNET. http://thetimes.co.za/Property/Article.aspx?id=314362 . Published 03 April 2007. Cited 15 March 2008

Tillmans, H and Pietska, G. (1978). *Influence of the quinoline-insoluble matter in pitch on carbonisation behaviour and structure of pitch coke*. Fuel, vol 56, no 3, pp. 171-173

Vallack, H. (2007). *The global atmospheric pollution forum air pollutant emissions forum inventory manual*. INTERNET. http://www.sei.se/editable/pages/sections/atmospheric/Forum_emissions_manual_v1.3doc. Cited 18 February 2008

Van der Walt (2008). Sasol Synfuels Marketing – Shipping Logistics, personal communication

Van Dyk, HJ. (2000). Sasol Synfuels, personal communication

Van Schalkwyk, M. (2007a). *Address by the Minister of Environmental Affairs and Tourism, Energy Security and Climate Change meeting*. INTERNET. http://www.polity.org.za, Washington DC, USA. Cited 13 February 2008

Van Schalkwyk, M. (2007b*). Address by the Minister of Environmental Affairs and Tourism, International Emissions Trading Association Forum*. INTERNET. http://www.polity.org.za, Washington DC, USA. Cited 23 February 2008

Wahlström. (2006). *Ship emissions and technical emission reduction potential in the northern Baltic sea***.** INTERNET. http://www.environment.fi/publications. Cited 27 January 2008

Wakeford, J. (2007*). Introduction to Peak Oil and South Africa*. INTERNET. http://www.aspo.org.za. Cited 15 January 2008

Weishauptova, Z. (1985). *Pitch coke structure and its transition into graphite, influence of the separation process of quinoline-insoluble matter*. Fuel, vol 64, no 7, pp. 999-1006

Weishauptova, Z. (1986). *Properties of graphitised pitch cokes: Influence of pre-carbonisation treatment of pitch on the formation of graphitic structure*. Fuel, vol 65, no 5, pp. 732-736

Wikipedia. (2008). *Clean Development Mechanism*. INTERNET**.** http://www.en.wikipedia.org/wiki/Clean_Development_Mechanism, pp 2-6. Cited 16 February 2008

Wolters, F and van der Walt, TJ. (2007). *Upgrading Coal Tar Pitch by Delayed Coking at Sasol.* 24th Annual International Pittsburgh Coal Conference 2007, CD Rom proceedings, Session 5, Paper 5-1, Johannesburg. SOUTH AFRICA

World Aluminium Institute. (2008a). *Greenhouse Gasses*. INTERNET. http://www.world–aluminum.org/environment/climate/index, pg 3. Cited 27 February 2008

World Aluminium Institute. (2008b). *Greenhouse Gasses*. INTERNET. http://www.world–aluminum.org/environment/climate/index, pg1. Cited 24 February 2008

World Aluminium Institute. (2008c). *Recycling Aluminium*. INTERNET. http://www.world-aluminum.org/Sustainability/Recycling, pg 2. Cited 23 February 2008

WWB. (2007). *The Kyoto Protocol and Emissions Trading*. INTERNET. http://www.wwb/view/wwb/en/page8890. Cited 14 February 2008

11.2 Bibliography

Ang-Olsen, J and Ostria, S. (2005*). Assessing the effects of freight movement on air quality at the national and regional level*. INTERNET. http://www.fhwa.dot.gov/environmental/freightaq .

ASTM. (2008). ASTM Standards Worldwide. INTERNET. http://www.astm.org
British Standards. (2008). British Standards On-Line. INTERNET. http://www.bsiglobal.com

EPPO. (2007). Oil industry conversions. INTERNET. http://eppo.go.th/ref/UNIT-OIL

Greefkes, *J. (1993).* Process for the removal of sulphur oxide constituents from a waste gas. INTERNET. http://www.freepatentsonline.com/5225176 .

Hallowes, D and Munnik, V. (2006). *Poisoned Spaces, Manufacturing Wealth Producing Poverty*. INTERNET. http://wwwgroundwork.org.za/publications/groundWorkReport2006pdf .

HEALTH24. (2005). Sulphur Dioxide and Trioxide poisoning. INTERNET. http://www.health24.com/medical/condition_centres.

ISO. (2008). International Organisation for Standardisation. INTERNET. http://www.iso.org

Lohmann, L. (2007). *Carbon Trading*. INTERNET. http://www.dhf.uu.se.seminars/12_march_2007.

NPL. (2007). *Calorific values of solid, liquid and gaseous fuels*. INTERNET. http://www.kayelaby.npl.co.uk/chemistry.

Onder, H. (1997). **Everything you always wanted to know about Petroleum coke, 4th Edition**, Svedala Industries

Petroleum World. (2007). Opinion Forum. INTERNET. http://www.petroleumworld.com.

Port of Durban. (2003). The Shipping World. INTERNET. http://www.ports.co.za/shippingworld/index.

SAPIA. (2006). *2006 Annual Report*. INTERNET. http://www.sapia.co.za/pubs/2006_ARep/index. Cited 12 February 2008

SARB. (1991). *South Africa's Balance of Payments: Sources, Methods And Reliability*. INTERNET. http://www.reservebank.co.za.internet/Publication.nsf/LADV/Occpaper3.pdf.

SARS. (2007). *South African Trade Statistics for April 2007*. INTERNET. http://www.sars.co.za.

SSA. (2002). *Natural resource accounts for South Africa*. INTERNET. http://www.statssa.gov.za/publications.

Van der Merve, E. (2007). *The Fallacy of Fuel Imports***.** INTERNET. http://www.moneyweb.co.za/mw/veiw/mw/en.

Zeismer, BC. (1991). *Outlook for high sulphur petroleum coke*. INTERNET. http://petcokes.com/HighSulphurstudy.pdf .

APPENDICES

Appendix A: "Drivers for additional delayed coking capacity in the refining industry", Graham Phillips, Foster Wheeler, 2003

DRIVERS FOR ADDITIONAL DELAYED COKING CAPACITY IN THE REFINING INDUSTRY

The refining industry has for some time been facing weak and volatile refining margins and asset expansion is likely to remain limited. Refiners have historically had access to very limited capital expenditure budgets with investment limited to 'stay in business' expenditure, generally driven by the need to meet increasingly stringent product quality legislation. Certainly, where more strategic investment has proceeded, companies have been under pressure to achieve shorter payback periods.

Bottom-of-the-barrel processing is increasingly likely to be considered, certainly in USA and Europe, for a number of reasons:

- Growing demand for transportation fuels)
- Potential reduction in markets for residues) The combination of these leading to an unbalanced production slate at refineries
- Crude oil quality, availability and light/heavy price differentials
- Refineries' competitive position
- Demand for anode grade coke
- A reluctance to meet demand changes by investment in additional grassroots crude processing

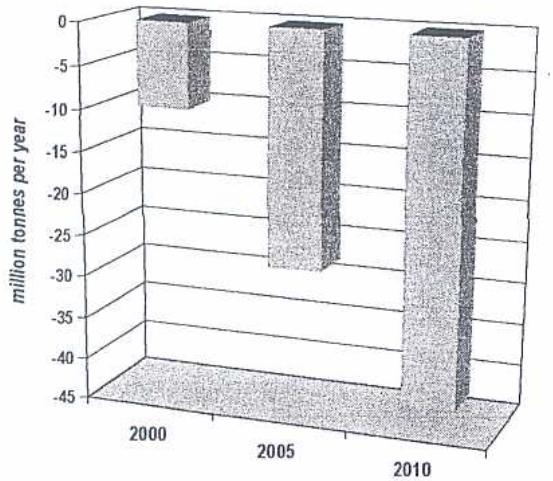
Growing transportation fuel demand

Global transportation fuels demand is significantly influenced by global events affecting economic activity and confidence. Hence demand growth has historically been erratic. World consumption of refined products grew by an annual rate of 1.4% during the 1990s. However, if the Former Soviet Union and Eastern Europe are excluded, the growth rate is higher at 2.4% per annum.

In this period all light products (transportation fuels and petrochemical intermediates) exhibited stronger growth, with global demand expected to average approximately 2% per annum. We are seeing a shifting demand/supply balance, especially for middle distillates. In Europe, for example, the deficit for road diesel is forecast to be around 45 million tonnes by 2010.

Figure 1: Road Diesel Deficit

Source: TotalFinaElf, WEFA Conference, June 2001



Much of the investment in coking in the USA in the past 10-15 years has been driven by the wish to process lower value crudes from Latin America. In broad terms about 50% of the potential economic benefit from a coker comes from using cheaper crude (the other 50% comes from the higher value of the upgraded products).

The bigger the spread between heavy and light products, the more incentive refiners have to invest in the necessary hardware to process cheaper feedstocks to gain competitive advantage. The heavy crude oils produce a higher portion of heavy, highly contaminated materials, which historically have been disposed of to fuel oil. However, these stocks can be upgraded to more valuable products using mature technologies such as fluid catalytic cracking (FCC), hydrocracking and delayed coking, thereby helping to correct finished product imbalances to improve refinery margins. Typically, a delayed coker will convert 65% of its feed into transportation fuels, the other 35% being coke.

Coke market

Fuel grade coke is an internationally traded product and competes with coal in the market place. Its higher heating value over coal (typically 20% higher) can encourage its use, with traditional power stations able to blend around 20% into coal feed without the need for significant modifications. The high sulfur content of fuel grade petroleum coke usually means that it can only be used on power plants with flue gas desulfurisation. Coke traders consider that the future market for fuel grade coke is strong although it is generally regarded as a low value, distress product.

Anode grade coke, used in aluminum smelting, is a robust market and fetches a far higher price than fuel grade ($300+ per tonne). To a large extent the production of anode grade coke is feedstock driven requiring the processing of a low sulphur, low metals crude. Overall refinery economics, in general, dictate whether purchasing this higher quality, more expensive crude, to make anode coke is justifiable.

The demand for needle coke, used in the steel industry, has been fairly flat over the last 20 years. It is unlikely any new needle cokers will be built for economic reasons.

The delayed coking option

Delayed coking is a mature process which remains for many the preferred residue upgrading option because of its ability to handle the heaviest contaminated crudes. Globally, approximately one third of installed residue upgrading plant is by delayed coking.

Today, around 50% of the worldwide delayed coking capacity is concentrated in the US with more than 2,000,000 B/D of installed capacity. In the last 15 years, delayed coking capacity has grown by 56% in the USA, followed by hydrocracking (37%) and FCC (14%).

A recent paper by Foster Wheeler (Ref 2) compared the economics of a number of residue upgrading schemes:

- Delayed coking/fluid catalytic cracking
- Integrated Gasification Combined Cycle (IGCC)
- Atmospheric residue hydrotreatment and residue catalytic cracking (RFCC)

In summary, if transportation fuels command a higher value to the refiner than power, the refiner is most likely to opt for a delayed coking or RFCC-based scheme.

Schemes based on FCC/delayed coking, hydrocracking/delayed coking appeared to provide the lowest capital and operating costs. All three schemes offered a positive internal rate of return.

Coking offers refiners much more flexibility in feedstock and crude selection, allowing the refinery scope to take advantage of spot markets. Coking offers the refinery the opportunity to move towards zero fuel oil production whilst meeting future product demand growth from low-value residuals rather than additional crude processing.

Ref 1) EPC 2nd Bottom of the Barrel Technology Conference, Istanbul, 8-9 October 2002. Keynote address by Nexant/Chem Systems.

Ref 2) Advances in residue upgrading technologies offer refiners cost-effective options for zero fuel oil production. Graham Phillips, Fang Liu, Foster Wheeler 2002 European Refining Technology Conference, Paris.

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This article has been published in Petroleum Economist, September 2003.

Residual markets

For most refiners fuel oil is usually an undesirable byproduct. Unlike light products (such as gasoline and middle distillates), fuel oil usually commands a price below the cost of crude thereby effectively depressing overall refinery margins.

Residual fuel oil demand declined by 20% during the 1990s even though bunker fuel use increased over the same period. At a recent bottom of the barrel conference (ref 1) Nexant/Chem Systems reported that a global 50% fall in residual fuel markets would necessitate around 200 heavy residue destruction projects with current crude slates. In Europe, legislation regarding the sulfur content of fuel oil may reduce the market size by 50%, leaving bunker markets as the main outlet. If the pace of market decline were to accelerate, many refiners might face 'stay in business' investment decisions, converting residuals by means of capital intensive processes with unexciting rates of return.

Some forecasters, however, believe that residual fuel oil demand has now leveled out and could even increase by around 0.5% per annum. This is being caused by a combination of US national gas shortages, the early phasing out of nuclear power in certain countries and growth in demand for bunkers. However, this growth rate is four times lower than the forecast global growth in light product demand.

Crude supply & price differentials

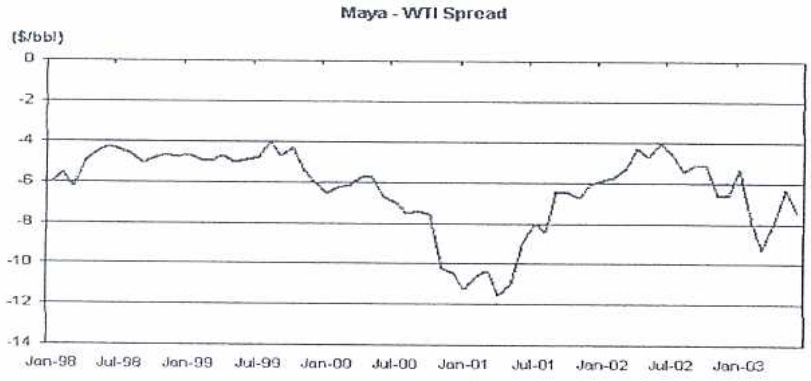
Directionally, world crude supply is expected to become heavier and more sour.

Light crude (34 API or higher) represents around 50% of crude currently processed. Although production of light sour crude is expected to increase by 9 million b/d by 2015, the production of light sweet crude is expected to increase by only 1-2 million b/d over the same period.

The pace of decline in light sweet availability will be influenced by production levels in West and North Africa, the North Sea and elsewhere. The availability of light condensates could also have a major influence on light feedstock supplies. Refiners have to some degree been able to avoid investment in upgrading by crude substitution, especially in market conditions in which reduced light/heavy price differentials have prevailed. However, fuel specifications are becoming so stringent that this solution is not sufficient to meet the new specifications and residue upgrading is required.

Heavy crude release to the market has been held back by adherence to OPEC quotas (which encourage sales of higher price light crudes). Heavy sour crude makes up only a small percentage of current production but is increasing.

Light/heavy crude differentials can be explained largely by two key factors - supply, estimated by the relative proportions of these grades in the output slate (the supply side), and demand for heavy products, particularly residual fuel oil (the demand side). These factors pull in different directions, with spreads widening as the relative output of heavy crude rises and narrowing with stronger fuel oil demand. There is no reason to suspect that the volatility in differentials will disappear and directionally, one would expect differentials to widen.



Appendix B: XRD Analysis of Coke Samples to Determine the Degree of Graphitisation

sasol
reaching new frontiers

Materials Characterization
Analysis Note: **XRD2007-0188**

To: J. Clark

From: E. du Plessis
S. Lubhelwana

Date: 23 December 2007

Pages: 3

Copy: B. Anderson

XRD Analysis of Coke Samples to Determine the Degree of Graphitisation

1. Background

A sample of green petroleum coke and the sample of the same material but graphitised at 2100 °C were received. Sample names are given in Table 1.

Table 1 – Sample names

Sample Name	XRD Code
Green petroleum coke	XD2314
Graphitised petroleum coke	XD2315

2. Experimental Details

Each sample was ground using a pestle and mortar. The sample was then packed into a stainless steel holder using the side loading technique. A Philips X'Pert Pro multi-purpose diffractometer (XRD-2 system) was used to carry out the analyses. A flat stage configuration was used. Three scans of each sample were acquired at ambient temperature and atmospheric pressure conditions. Instrument settings were as follows:

Tube voltage	:	40 kV
Tube current	:	40 mA
Source	:	Cobalt (wavelength 1.78897 Å)
Soller slit	:	0.04 rad.
Beam mask	:	10 mm
Fixed divergence slit	:	1 °
Anti-scatter slit	:	2 °
Filter	:	Iron
Detector	:	X'Celerator
Detector active length	:	2.121 °
Scan from	:	5 °2θ
Scan to	:	55 °2θ
Scan axis	:	Gonio
Scan mode	:	Continuous
Step size	:	0.0167 °2θ
Time per step	:	50 seconds
Scan duration	:	20 minutes

The degree of graphitisation and the stacking height were calculated using the following formulae:

Degree of graphitisation = (3.44 – d_c) / (3.44 – 3.354)

Where **d_c** is the calculated d value of the sample

3.354 is the d-value of pure graphite

3.44 is the d-value of turbostratic carbon

Stacking height = ((0.89 x λ) / (β x cos θ)) x (180 / π)

Where λ = 1.78897 Å

β = FWHM (in degrees)

θ = Bragg angle of the (002) reflection, (in degrees)

π = 3.14159

X'Pert HighScore Plus software was used to determine the values of d_c, β and θ.

3. Results

The diffractograms are shown in Figure 1. Results of the degree of graphitisation and the stacking heights are given in Table 2.

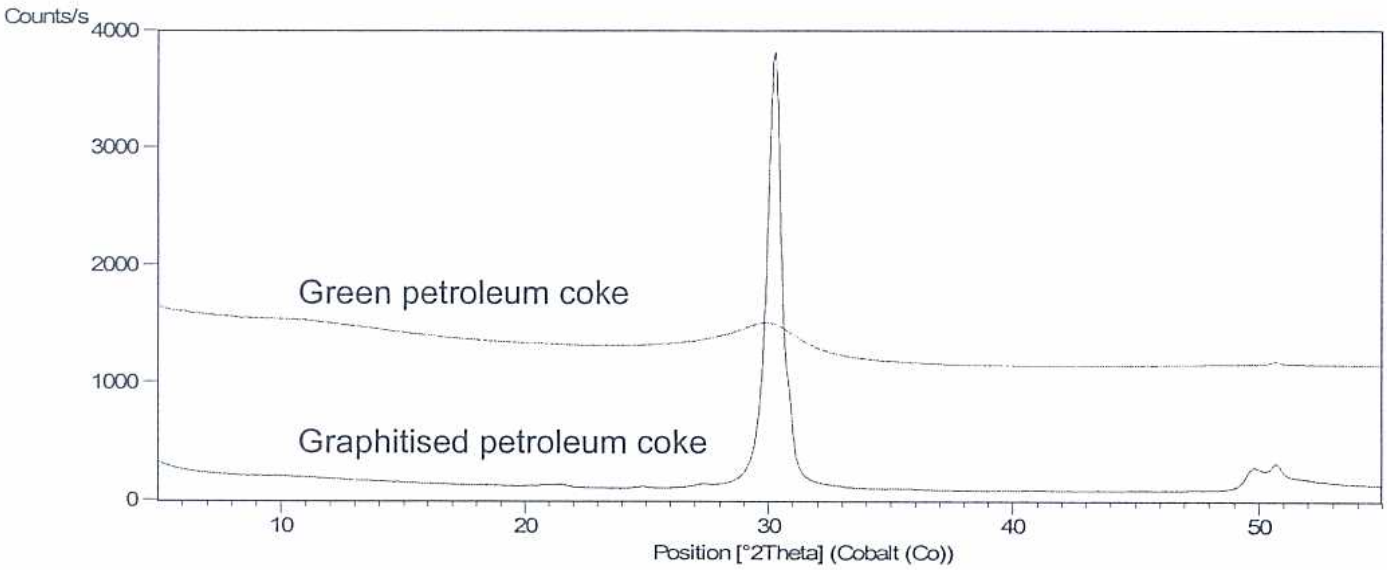


Figure 1 – Diffractograms of green and graphitised petroleum coke.

Table 2 – Sample names

Sample Name	**Degree of graphitisation (%)**	**Stacking height (Å)**
Green petroleum coke	*	28(1)
Graphitised petroleum coke	9.1(5)	136(2)

* The degree of graphitisation could not be determined for the green petroleum coke, since the d-value was larger (3.49 Å) than that of turbostratic carbon (3.44 Å).

Appendix C: Address by the Minister of Environmental Affairs and Tourism, Marthinus van Schalkwyk to the Energy Security and Climate Change meeting, Washington DC, 27th of September 2007

SA: van Schalkwyk: Energy Security and Climate Change meeting (27/09/2007)

Send to Colleague
Print Article

Published: 27 Sep 07 - 8:12
Date: 27/09/2007
Source: Department of Environmental Affairs and Tourism
Title: SA: van Schalkwyk: Energy Security and Climate Change meeting

Opening statement by Marthinus van Schalkwyk, South African Minister of Environmental Affairs and Tourism at the major economies meeting on Energy Security and Climate Change, Washington DC

On behalf of South Africa, I would like to thank you for creating this opportunity to deliberate on our common challenges. Energy and climate security present them as the horns of the greatest dilemma humanity may yet have faced. The fact that these challenges are twins and inextricably linked is now clearer than ever, through the efforts of science.

We must conclude international negotiations by 2009 on the climate regime after 2012. A road map for multilateral negotiations to achieve this must be agreed in Bali. 2008 will be an important milestone in the run-up to an agreement, by 2009, that builds on the United Nations Framework Convention on Climate Change (UNFCCC) and its Kyoto Protocol. At COP14 in Posnan we must take stock of and receive reports from the different contributions to the multilateral process, including this one. This meeting today is therefore very timely. Dedicated efforts will be required over the next year to ensure that we prepare a meaningful input to feed back into the UNFCCC negotiations.

Based on the established principle of common but differentiated responsibilities, we understand that we must all do more and act with a greater sense of urgency. In working towards a fair, effective, flexible and inclusive climate regime beyond 2012, the message from a developing country perspective is clear: We take our responsibilities seriously. We are already making a meaningful contribution within our respective capabilities. We are willing to do more. But the trigger must come from the north.

Besides broadening participation to include the world's largest historical emitter, the United States (US), the creation of a more empowering technology and financing framework will be a precondition. We therefore welcome this initiative by the United States as a first step towards assuming their global leadership role and full responsibility in the multilateral solution that reflects equity across nations and generations.

From the United Nations Secretary-General's meeting on 24 September there is an emerging consensus that a road map for negotiating the future regime should be launched in Bali and be concluded by 2009. Therefore, we look forward to urgently advancing and concluding this interaction between us as one important contribution to the United Nations negotiations by the end of 2008. The central challenge is to build bridges to enable the transition from the fragmented status quo to a coherent regime where all Annex I parties take on absolute and binding emission reduction targets. Given the challenges that face us, I would suggest that all of us in this meeting carefully consider the scope and substance of our agenda and what we can meaningfully contribute to the UNFCCC negotiations.

We should also remind ourselves that the majority of countries that will be hardest hit by climate change are not at this table today. We cannot design a climate change regime that works only for the 15 or 20 major economies. Ultimately, multilateralism must prevail. An ambitious and equitable framework must work for all parties. It must balance our stabilisation and sustainable development objectives and our mitigation and adaptation responses. It must deal with the unintended consequences of these responses. And it must be underpinned by an empowering technology and financing framework that allows developing countries to reach economic and human development goals quicker and cleaner than developed countries did. These are the key building blocks.

The balance between sustainable development and stabilisation, as articulated in Article two of the United National Framework Convention, will have to underpin the strengthening of the climate regime. The development of any long term global emission reduction goal that serves as yardstick to guide our overall climate efforts must strike this fundamental balance. It must be based on sound science and broad consensus, and it must inform ambitious and binding mid-term targets for all developed countries.

In April the Intergovernmental Panel on Climate Change (IPCC) reminded us that existing technology and policies, together with new developments in the pipeline, can address the climate problem at a cost that is relatively affordable. The challenge is to accelerate technology development, commercialisation and wider deployment and to up-scale existing investment and financing by orders of magnitude.

Though long term technology research and development will remain an important part of our work, the urgency of the challenge requires of us to use all available tools to our best advantage and for the common good. Equity requires of all countries to shoulder their responsibility towards future generations, in balance with taking historical responsibility for the problem. South Africa, like other developing countries, needs sustainable development in order to address poverty and unemployment. Mindful

that thirteen million South Africans do not yet have access to modern energy resources, ensuring universal access to energy remains a critical priority.

Given that the energy sector is the single largest source of emissions in South Africa, mitigation and technological interventions are aimed at energy efficiency, diversifying energy sources away from coal, promoting energy security and also the research and development of new technologies that will lead to a cleaner, more sustainable, low carbon energy future.

From our perspective, a number of critical issues must be resolved at a multilateral level to enable us to address climate change whilst meeting our energy and sustainable development objectives. This includes innovative ways to address the costs of deploying more expensive advanced and cleaner technologies, which in turn is closely related to the vexing issue of intellectual property protection; as well as multilateral funding to support higher levels of research, development and deployment. In considering these issues, we need to focus on a suite of technologies, funding mechanisms, investment structures and policy tools.

The further development of carbon markets holds the potential to provide significant incentives for the diffusion of technologies. An urgent priority is to secure the global carbon market by sending a clear market signal about the climate regime after 2012. Ambitious targets for all developed countries are critical to create the demand required to fuel the carbon market and to create meaningful financial flows to stimulate investment in low carbon economic growth in developing countries. But carbon funding alone will not be enough, and we will also need to mobilise financing and investment beyond carbon markets.

In addition to participation in Kyoto carbon markets, South Africa supports a strategic approach of sustainable development policies and measures, or so-called Sustainable Development Policies and Measures (SDPAMs) for developing countries. The SD-PAMs approach makes it possible for developing countries to pledge measurable, reportable and verifiable mitigation actions, supported by technology and enabled by finance, and consistent with their sustainable development objectives. These would be measurable mitigation actions, but of a different kind than quantified targets for developed countries.

Chair, we need a step-change in the pace of negotiations. Addressing only emissions intensity or long term Research and Development (R&D) will not be sufficient. Global emissions will need to peak and decline. By 2009 we will need a common understanding that all developed countries need to be playing on the same field, with quantitative mitigation targets, and that major developing countries need to be playing on a matching field, one which involves recognition and positive incentives for their measurable action.

Chair, in conclusion, I would like to reiterate that the outcomes of our interaction should contribute to the wider agenda and broader engagement under the UNFCCC. And we must ask how we can contribute to building the bridge from where we are today, to a strengthened regime based on the UNFCCC and its Kyoto Protocol. We are looking to the United States to play a global leadership role. No nation has the inherent right to hold to ransom the future of all nations. We need a clear and credible signal from the north and for our part we stand ready to take on our fair share of responsibility.

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Appendix D: Address by the Minister of Environmental Affairs and Tourism, Minister Marthinus van Schalkwyk, to the International Emissions Trading Association Forum in Washington DC, 26th of September 2007

SA: Van Schalkwyk: International Emissions Trading Association Forum (26/09/2007)

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Title: SA: Van Schalkwyk: International Emissions Trading Association Forum

Address by South African Minister of Environmental Affairs and Tourism Marthinus van Schalkwyk, at the seventh International Emissions Trading Association (IETA) Forum on State and Development of the Greenhouse Gas Market, Washington DC

The pace of climate change negotiations is out of step with the urgency indicated by science. With the first commitment period of the Kyoto protocol ending in 2012, we are approaching a key point in the increasingly urgent task facing us.

Achieving climate stability requires individual nations to rise above short term self-interest for the benefit of the long term common good. And though we have different responsibilities, we all have a common responsibility to act in accordance with our national capabilities.

In working towards a fair, effective, flexible and inclusive climate regime beyond 2012, the message from a developing country perspective is clear: We take our responsibilities seriously. We are already making a meaningful contribution within our respective capabilities; we are willing to do more. But the trigger must come from the North. Besides broadening participation to include the world's largest historical emitter, the United States, creating a more empowering technology and financing framework will be a precondition. A core of the solution underpinning any future agreement must be a balance between sustainable development and climate imperatives, and between historical responsibility for the problem and taking responsibility for the future.

When we meet in Bali in December this year, we should agree on a process to conclude negotiations, by 2009, on a strengthened climate regime that builds on the United Nations Framework Convention on Climate Change (UNFCCC) and its Kyoto protocol. This process should be outlined in a Bali road map.

Chair, success by 2009, and beyond, will depend on our collective political will to strike a balance between five key areas of work, namely adaptation, mitigation, managing the unintended consequences of climate policies and measures for the economies of other countries; technology development, diffusion and commercialisation, and also financing and investment.

No agreement on the international climate architecture will be complete, or politically feasible, if adaptation is not accorded much higher priority in our deliberations. Moving from vulnerability assessments to the implementation of those adaptive activities indicated in such assessments is critical. This will require financial resources to be up-scaled by two to three orders of magnitude. New sources of funding could come from both market and non-market sources, for example, the proceeds of the auctioning of emission allowances in Annex B countries, involuntary levies against emissions, user charges and/or the extension of the two percent Adaptation Fund levy to all three Kyoto Protocol flexible mechanisms.

Chair, turning to mitigation, there are three strands that have to be woven into one multilateral framework.

* firstly, more ambitious and quantified emission reduction targets for all developed countries under the Kyoto Protocol
* secondly, re-engagement of the United States of America (USA) in the full multilateral process and binding emission reductions
* thirdly, recognition of, and incentives for enhanced mitigation action by developing countries.

In this context, initiatives such as the United States hosted Major Economies Meeting are welcome as meaningful contributions to the multilateral process. The outcome of this initiative should contribute to the building of bridges to enable the transition from the fragmented status quo to a coherent regime where all Annex I Parties take on quantified emission reduction targets.

Chair, the science tells us that greenhouse gas emissions must peak and decline within the next 10 to 15 years. We cannot delay taking real action. Therefore, commitments by some Annex I Parties which focus on voluntary "pledge and review", or emissions intensity or long term research and development, will not be an adequate substitute for absolute emission reduction targets.

Chair, carbon markets will remain an important element in the climate architecture after 2012. In this regard, three issues deserve some attention, namely:
1. broadening the scope of the Clean Development Mechanism (CDM),
2. de-fragmenting the status quo
3. ensuring a more equitable geographic spread of CDM projects.

Long term ambitious commitments and much stricter mid-term targets for emission cuts by all developed countries would be critical to fuel demand in the carbon market. This would also ensure that we maintain price levels, it would provide adequate time horizons for investors, and at the same time it would increase investment in low carbon economic growth in developing countries. Should the regime evolve to include new gasses or asset classes after 2012, there should be a concomitant increase in stringency of emission reduction targets.

An all-encompassing global carbon market regime which includes all developed countries is the first and ultimate aim. However, it may be that the market does not evolve this way in the short term. In this instance, it is essential to create linkages between the various national or regional cap-and-trade carbon markets, as a first step leading to full de-fragmentation.

On the supply side, several approaches for extending the architecture of the CDM have been suggested. This includes proposals to extend the CDM to economic sectors and/or policies. Common to these proposals is the recognition that we can achieve more for both the atmosphere and sustainable development under an enhanced CDM. Likewise, a number of proposals have been made to appropriately scale the CDM to also incentives smaller mitigation projects.

South Africa recognises that the evolution of the Clean Development Mechanism and the further creative development of market mechanisms could provide up-scaled incentives for developing countries to enhance their climate action. But then this should be based on the modification of the existing architecture, drawing on the valuable lessons learned during the first commitment period, rather than a newly designed framework.

Chair, whilst the development of large scale CDM projects is important, many of the economies in Africa have small to minor mitigation potentials. We must therefore find a way to seize the opportunities that exist to develop appropriate small scale mitigation projects, simple in structure and finance, but with high contributions to sustainable development.

Finally, Chair, we should also recognise that carbon markets can assist in driving investment in low carbon technologies up to a point. In addition to participation in Kyoto carbon markets, South Africa supports a strategic approach of sustainable development policies and measures, or so-called sustainable development policies and measures (SD PAMs), for developing countries.

An SD-PAM would be a commitment to implement a policy or measure that makes the development path of a country more sustainable, and with climate co-benefits. Because SD-PAMs focus on large-scale policies and measures and are not limited to projects or programmes, the co-benefits may be substantial.

Funding for implementation could come from both climate and non-climate sources; and from public as well as private investment. Some SD-PAMs can also be designed to provide market-based opportunities, linking them to this potentially large source of climate-friendly investment. But policy actions should ideally be linked to other incentives that address incremental cost gaps and facilitate the deployment of low carbon technologies on preferential terms.

The SD-PAMs approach makes it possible for developing countries to pledge measurable, reportable and verifiable mitigation actions, supported by technology and enabled by finance, and consistent with their sustainable development objectives. These would be measurable mitigation actions, but of a different kind than quantified targets for developed countries.

Chair, in conclusion, we realise that we must all act with a greater sense of urgency. We are looking to the United States as the world's largest historical emitter to play a global leadership role. No nation has the inherent right to hold to ransom the future of all nations. We need a clear and credible signal from the North and for our part; we stand ready to take on our fair share of responsibility.

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Appendix E: Changes ahead for ship fuel

World: Global

Changes ahead for ship fuel

Cleaner ship fuel is on the way after a report alleged that pollution caused by ships is reponsible for tens of thousands of deaths per year. AP Moller-Maersk blamed for more greenhouse gases than the whole of Denmark.

by Thrasy Petropoulos Thursday, February 21, 2008

It is so thick that it has to be heated to become mobile and is ranked the dirtiest type of fuel. Marine fuel oil - or bunker fuel, as it is known in the trade - is responsible for moving 90 percent of world trade by volume. However, it has so far escaped emissions-cutting regulations.

Indeed, shipping was omitted altogether from the Kyoto Protocol and the European Union's emissions trading scheme because of the difficulty in proving which countries are responsible for which emissions.

But with recent reports claiming that by 2012 up to 80,000 people a year will die as a result of shipping air pollution, as well as that the industry's contribution to global greenhouse gas emissions has been significantly underestimated, the International Maritime Organisation (IMO) appears set to tighten up fuel regulations

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The aviation industry, which was similarly not considered by the Kyoto Protocol, was last month included in draft amendments to the EU's emissions trading scheme. And the EU has since told the IMO - the shipping industry's regulating body - that it will announce its own measures by the end of the year if it does not impose industry-wide regulations specifying the use of lower sulphur fuels or pollution abatement technology aboard ships.

A source at the IMO's marine environmental committee told the Athens News that EU-imposed measures could potentially prove counter-productive because they could lead to "different regulations at different ports and the

possibility of ships having to carry different grades of fuel or having to switch on and off their abatement technology". This, he said, could lead to inconsistency and confusion.

He added, however, that the marine environment committee was considering a draft amendment to Annex VI of the IMO's Marpol Convention, which governs marine pollution. The amendments will address the issue of sulphur and nitrogen oxides released in the combustion of bunker fuel.

"Most of the issues surrounding the revision of Annex VI have been agreed upon," the source told this newspaper on condition of anonymity. "They have been under revision for almost three years and include many elements that have never been contested. But the area of exhaust fumes has been quite contentious."

Where nitrogen oxides (NOx) are concerned, he said, a two-tier approach was being considered. The first would come into effect by January 2011 and involves a 15- to 20-percent reduction in NOx emissions for new engines compared to 2000 levels. The second - and significantly more ambitious - tier specifies an 80-percent reduction beginning by 2016. The longer-term limit would only apply in specially designated areas, however.

"This has been agreed upon," he said. "It might be revisited by the committee, but we don't expect that."

Exposure to high levels of NOx can cause pulmonary complications, such as asthma and reduced lung function. Mono nitrogen oxide eventually forms nitric acid, a component of acid rain.

Low-sulphur zones

However, as far as the reduction of sulphur oxides is concerned, the prognosis is not so straightforward.

"There are only two ways to reduce sulphur," the source said. "One is by burning low-sulphur fuel, and the other is to remove the sulphur pollution from the exhaust gases. The second involves old land-based technology used in power stations and industrial applications, but it is a new technology for ships and it isn't widely commercially available.

"The first method requires cleaner fuel from the oil industry, which involves more refining. The bill for this will be passed on to the shipping industry because they are the customers. The option of a total switch to [further-refined] distillate fuel has been estimated at 126 billion dollars. And there are other considerations. Many see the burning of distillate on the high seas as unjustified because it will use more energy and, therefore, produce more CO2 in the refining process."

Furthermore, he noted, pollution from particulate matter is an issue that affects only coastal areas. For this reason, so-called SECAs (sulphur emission control areas) have already been designated by the IMO in parts of the North and Baltic seas, and the US is reportedly considering similar restrictions on ships visiting areas of its shoreline.

However, according to the Hellenic Marine Environment Protection Association (HELMEPA), the extension of these low-sulphur zones may drain other resources. "There is concern over whether sufficient quantities of a better-quality fuel would be available to support

the proposed options," a representative of the organisation said.

She added: "While it is known that small-diameter airborne particles generated by the combustion of residual and distillate fuels cause air quality problems, it should be noted that adverse health effects are a function of multiple sources and are not solely from shipping. Use of better-quality fuel oils in shipping will certainly cut down the emissions of particulate matters and sulphur oxides. However, we believe that all possible alternatives - better quality of fuel oils, gas treatment technology etc - must be evaluated and left to the discretion of the shipping industry."

Deadly polluter

A report published last December in the American Chemical Society journal Environmental Science & Technology estimates that by 2012 approximately 80,000 people will be killed yearly by cancer, cardiovascular and other illnesses prompted by particulate matter pollution generated by high-sulphur level fuels used in shipping.

It goes on to say that the use of abatement technology or low-sulphur fuels could lower that death toll by up to 60 percent. Current EU rules limit the sulphur content of car fuel to 15 parts per million, against 45,000 parts per million found in bunker fuel.

The report, which has been seen by this newspaper, was considered by the IMO in the drafting of the amendments to its marine pollution regulations.

Furthermore, according to the UK's Guardian newspaper, a soon-to-be published UN study

has found that the annual CO2 emissions from shipping are 1.12 billion tonnes per year, more than twice the previous estimate. It also warns that these emissions will rise by 30 percent by 2020.

Of all industrial emitters, only electricity producers (24 percent) and manufacturing plants (11 percent) pump more greenhouse gases into the atmosphere.

To put these numbers into perspective, the Danish media last week reported that the country's largest shipping conglomerate, AP Moller-Maersk, emits more greenhouse gases than the rest of the country combined.

Indeed, its container ship Emma Maersk, which is the largest of its kind in the world, consumes 200,000 litres of fuel a day - "equivalent to the needs of a small Danish city", according to reports. Annual emissions from the Maersk fleet are said to total between 40 and 50 million tonnes of CO2.

Thrasy Petropoulos writes for Athens News and appears here with permission.

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