UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

THE MODIFICATION OF WAXY OIL FOR PREPARING A POTENTIAL FEEDSTOCK FOR NEEDLE COKE PRODUCTION

by

John Graham Clark

A thesis submitted in partial fulfilment of the requirements for the degree

Philosophiae Doctor in Chemical Engineering

in the

Institute of Applied Materials
Department of Chemical Engineering
Faculty of Engineering, the Built Environment and Information Technology

University of Pretoria
Pretoria

July 2011

Promoter: Professor Brian Rand

DECLARATION

I declare that this dissertation is my own unaided work. It is being submitted for the Degree of Philosophiae Doctor at the University of Pretoria, Pretoria. It has not been submitted before for any degree or examination to any other University

……

(Signature of Candidate)

On this 18th day of October 2011

DEDICATION

This doctoral thesis is dedicated to my mother

Catherine Janet Clark

ABSTRACT

This research study determines the potential to increase substantially the anisotropy of a coke from an aliphatic Waxy Oil produced by Sasol Synfuels at Secunda, South Africa. Experimental modifications included filtration, distillation and thermal treatment, followed by distillation with the aim of producing a carbonised product similar to needle coke. The substantial concentration of an iron oxide catalyst (up to 2%) in Waxy Oil is increased by an order of magnitude upon carbonisation and calcination due to low coke yield and reactivity factors. The catalyst also promotes oxidative polymerisation of the residue, acts as a barrier to mesophase formation and promotes multi-phase graphitisation. Filtration of Waxy Oil using a 0.5 µm sintered metal filter reduces the ash content to 0.006% and increases the anisotropy of the carbonised product to 54% flow domains compared with 22% for the carbonised product of virgin Waxy Oil. Thermal treatment followed by distillation of Waxy Oil reduces the effect of organic reactivity promoters (mainly multi-alkylated aliphatics/aromatics and oxygenates), while increasing the concentration of thermally stable (C_{18} to C_{30}) normal alkanes to 85% compared with 38% in the filtered Waxy Oil. Compared with the filtered Waxy Oil, thermally stabilised Waxy Oil reduces the amount of the pre-carbonisation residue (from 98.7 to 43.0%), while "static" carbonisation thereof increases the green coke yield (from 19.8 to 36.3%) and increases the anisotropicity (from 54 to 100% flow domains). The carbonisation mechanism of filtered and thermally treated Waxy Oil involves initial cracking of high molecular weight normal alkanes (C_{18} to C_{30}), thus concentrating the molecular weight of normal alkanes (C_{18} to C_{22}). This is followed by a slow cyclisation step involving both self condensation and cyclo addition reactions to form two- to six-ring cyclo-alkanes or hydro-aromatics. The hydro-aromatics are dehydrogenated rapidly to form methyl and di-methyl three- to six-ring substituted aromatics. Further thermal degradation dealkylates these molecules to form stable four- to six-ring "pre-mesogens". The mesospheres are nucleated from the isotropic matrix and grow to more than 0.050 mm in diameter, with a volume of 2.61×10^{-3} mm^3. Subsequent coalescence of the mesospheres produces mesospheres with diameters of over 0.200 mm and volumes of 41.82×10^{-3} mm^3. The resultant microstructure of the solid carbon is composed of flow domains more than 400 µm in length. Although needle cokes have historically been produced from aromatic residues, this research is the first to show that a coke with a similar microstructure can be produced from a totally aliphatic residue. The research thus provides potential for the development of a needle coke from a totally unique Waxy Oil residue with negligible sulphur (< 0.008%) and nitrogen (< 0.09%) contents. This is the first academic study of the chemistry of Waxy Oil.

Keywords: Waxy Oil, Anisotropic, Thermal treatment, Needle coke, Mesophase

ACKNOWLEDGEMENTS

It is with great humility that I wish to acknowledge and thank the people who aided in my doctoral studies.

This work is based on research supported by the South African Research Chairs Initiative of the Department of Science and Technology and the National Research Foundation, whose support is gratefully acknowledged.

I would like to express my thanks and appreciation to my supervisor, Professor Brian Rand (University of Pretoria), who constantly checked my work and gave his expert opinion as to ideas which could be tested. Brian, your valuable input as my supervisor will never be forgotten.

I would also like to thank Sasol Synfuels Marketing for financial support of my studies, especially Dr Flip Hayes who acted as my industrial supervisor. Flip's knowledge of both the technical and marketing aspects of the coking industry proved invaluable in the creation of this thesis.

I would also like to thank the personnel at INCAR in Spain where I did a great deal of the research for this thesis. Your friendly and helpful attitude contributed greatly towards the original knowledge gained during this project. I would especially like to thank Drs Rosa Mendez, Ricardo Santamaria, Alba Centeno Perez and Clara Blanco. I truly appreciate the assistance of Antonio José Martin Fernandez and Daniel Barreda Garcia.

I would further like to acknowledge and thank people who throughout my career in the delayed coking industry I consider to have been my mentors. In this list I include Messrs Piet Ligthelm, Gregor van Deventer, Jo Spieth and Quentin Beukes, and Drs Flip Hayes and John Chang.

I would like to thank my family for their interest in and support of my doctoral studies. I would especially like to thank my wife Karen for her continuous encouragement and for checking my thesis for errors, but mostly for the time over weekends and at night when I got time to study. In this respect I would also like to thank my daughter Megan for the time I had to study instead of playing in the garden with her.

I would like extend my appreciation to Dr Ricardo Santa-Maria and Mr Deon van der Westhuizen for proofreading my thesis.

Further, I would like to acknowledge the support and kindness of my friends at Pizza Viali, especially Marco, Louis, Gavin, David, Brian, Raymond, Deon, Linda, Nikita, Barry, Vincenzo, Nicky and Michael.

While it would be almost impossible to name everybody who in some way contributed towards this thesis, I would also like to thank the following people:

- Professor Walter Focke (University of Pretoria)
- Drs Wilhelm Frohs and Thomas Mueller (SGL Carbon Ltd, Germany)
- Mr David Grace (SLFC)

- Dr Jaco van der Walt (NECSA)
- Mr Etienne Schuin (Sasol Technology – Research and Development)
- Mr Ben Ashton (Sasol Technology – Research and Development)
- Dr Esna du Plessis (Sasol Technology – Research and Development)
- Messrs Johann Snyman and Ewie Du Plooy (Synfuels laboratories)
- Messrs Siyanda Lubhelwana and Werner Barnard (Sasol Technology – Research and Development)
- Mrs Vivien du Cann
- Mr Johan Joubert (Sasol Technology – Research and Development)
- Mr Allen Hall (University of Pretoria)
- Mrs Beverlie Davies (for editing the thesis)

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS AND SYMBOLS

Symbol	Description
amu	atomic mass units
µm	microns or x 10^{-6} metres
Å	Angstrom or x 10^{-10} metres
CCR	Conradson Carbon Residue
cSt	Centistokes
CTE	Coefficient of Thermal Expansion
CTP	Coal-Tar Pitch
DTA	Differential Thermal Analysis
DTG	Differential Thermal Gravimetry
EAF	Electric Arc Furnace
ETP	Ethylene Tar Pitch
FCC	Fluidised Catalytic Cracker
FCCDO	Fluidised Catalytic Cracker Decant Oil
FDMS	Field Desorption Mass Spectroscopy
FTIR	Fourier Transform Infra-Red
GC-AED	Gas Chromatography–Atomic Energy Detection
GCMS	Gas Chromatography Mass Spectroscopy
HDDC	Hydrogen Donor Diluent Cracking
He (density)	Real density
HGI	Hardgrove Grindability Index
HI	Heptane Insolubles
HPLC	High Performance Liquid Chromatography
I_{ar}	Aromaticity Index (FTIR)
IBP	Initial Boiling Point
LDMS	Laser Desorption Mass Spectroscopy
LSVR	Low-Sulphur Vacuum Residue
MIQ	Mass Insoluble in Quinoline
MIT	Mass Insoluble in Toluene
NMP	N-methyl-2-pyrrolidone
NMR	Nuclear Magnetic Resonance
OTI	Optical Texture Index
PAH	Polycyclic Aromatic Hydrocarbons
PDA	Photodiode Array
PSD	Particle Size Distribution
QI	Quinoline Insolubles
SDO	Synthol Decant Oil
SEM	Scanning Electron Microscopy
SRC	Solvent Refined Coal
TGA	Thermogravimetric Analysis
TI	Toluene Insolubles
VBD	Vibrated Bulk Density
VCM	Volatile Carbon Matter
VR	Vacuum Residue
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence