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The development of improved road tar binders from indigenous coal tars and aspects of their use

by

Ian L. Jamieson

VOLUME I

The development of improved road tar binders from indigenous coal tars and aspects of their use

Ian Laurence Jamieson

VOLUME I

A dissertation submitted to the
Faculty of Engineering, University of the Witwatersrand,
Johannesburg, for the Degree of Doctor of Philosophy

JOHANNESBURG, 1977

DECLARATION BY CANDIDATE

I, Ian Laurence Jamieson, hereby declare that the work presented in this thesis is my own and that it has not been submitted for a degree of another university.

Ian L. Jamieson

August 1977

ABSTRACT

The thesis deals with the development of improved road tar binders in South Africa and their application in surface treatments and in mixes used for pavement wearing courses and basecourses in this country.

This work is timely in view of the country's current economic problems. Locally produced tar binders are considerably less expensive than bitumen binders in inland areas; tar being produced in the Witwatersrand complex whereas locally refined bitumen is produced from imported crude oil. The annual expenditure on bitumen by the South African road industry is currently of the order of R26 000 000. However, previously it had been found that tar binders were less durable than bitumen.

From the average service life of bitumen constructions, estimates of economic service lives for the corresponding tar constructions have been made. The main object of the work was to compare the service performance of constructions containing the improved tars with the estimated "target" or "break-even" life. The study shows that tar surface treatments will exceed the surface treatment "target" life of 6 years and tar basecourses will exceed the basecourse "target" life of 12 years. At present it is not certain that the tar surface mixes will achieve the 12 year target life, though certain mixes are performing well (after $2\frac{1}{2}$ years) in an experimental pavement.

An important part of this work is a comprehensive investigation of the chemical nature of tars from all major sources in South Africa. A combination of sophisticated methods of chemical analysis has been used in this first-ever study of local tars and their characterisation has been possible. It is shown that coke-oven tars all conform closely to one type and vertical-retort tars all conform to another type. An important discovery is that Lurgi tar is closely related to the vertical-retort type and, in view of the widespread use of the latter in Europe in recent times, the potential value of Lurgi tar, which is available in large quantities in this country, is firmly established.

A correlation between change in composition (loss of oils) of coke-oven tars and the increase in their viscosity has been established for tars aged in surface treatments over a four year period,,so confirming that evaporation is the major weathering mode despite relatively strong oxidising conditions on the Highveld. This also confirms that the

replacement of previous tar compositions by low-volatile blends is acting against the root cause of their earlier unsatisfactory behaviour. Further improvements in durability have been achieved by the incorporation of polyvinyl chloride (PVC) in the tar whose presence permits the addition of extra quantities of heavy non-volatile oils in the blends. Tars containing 1,5 per cent PVC are still cheaper than bitumen in most inland areas of South Africa.

Original methods have been devised for studying the affinity of hydrocarbon types for the PVC and for quantifying the phenomenal cohesive properties (ductility-tenacity) of this binder. A comprehensive study of the properties of PVC/tars shows that PVC is more suitable than other commercial polymers, such as some types of acrylonitrile butadiene, for incorporation in surface treatment tars.

A large number of experimental sections of PVC/tar surface treatments have been constructed and their performance has been studied for periods of up to six years. Small-scale sections were used extensively and a mini binder-distributor was developed for the construction of these sections. The required target has been achieved in these experiments and also in full-scale experiments and work carried out under normal resealing practice. A number of practical recommendations have been made for the design and construction of PVC/tar single-surface treatments.

The use of tar/bitumen blends in surface treatments is discussed and the weathering (under local conditions) of blends produced overseas and locally has been studied. It is shown that their weathering depends upon the type of tar and the quantity of volatile tar oils used in the blend. Suitable viscosity grades have been proposed for use in South Africa based on their rheological properties and local road temperatures. Specifications for these grades are proposed.

Initial results from a full-scale double-seal experiment show that Lurgi tar may be used in the lower layers of these constructions. Sections in which the tar was used in both upper and lower layers are also performing well.

The high stiffness of tar mixes suggests that tar is ideal as a base-course binder but that thin tar wearing courses may have low fatigue lives unless very stiff foundations are provided. Dense surfacing mixes were used in an experimental pavement and the initial (after 1 year)

hardening of these binder is much less than would have occurred if they had been used in a single-surface treatment. It is not certain at this stage ($2\frac{1}{2}$ years after construction) whether the "target" life will be exceeded, although at present the stiffness of coke-oven and PVC/tar bound mixes is low. A Lurgi-tar-bound mix has a significantly higher stiffness.

In PVC/tar-bound mixes the main benefit of the polymer appears to be in the improvement in durability (again provided that heavy flux oils are used in the preparation of the binder) and PVC has no influence on stability other than that due to the increased Evt of the binder. Although PVC decreases the temperature susceptibility of viscosity of the tar, this is not reflected in improved mix stability-temperature relationships for PVC concentrations(in tar) of up to 5 per cent.

The effect of mix preparation on the increase in viscosity of the tar may depend to some extent on the aggregate grading and it was found in an investigation that there was a greater increase in tar viscosity during the preparation of a semi-gap-graded mix than during the preparation of a continuously graded mix. The results also show that viscosity changes are minimal during the handling, transportation and paving of the mix. Because of the higher mix temperature, the change in viscosity of bitumen during mixing was greater than that in the tar.

To ensure that the value from the development of improved tars is passed on to the local road industry, proposals are given, in an appendix, for revised tar specifications and these include recommendations for the use of tar binders and tar-bound materials.

Hydrocarbon emissions during paving operations have been examined and it is shown that the main constituents are non-carcinogenic volatile substances some of which are known to irritate the skin, eyes, nose and mouth. However, the concentrations of these non-carcinogenic substances in the air surrounding the paver-driver are below recommended danger levels. In view of the relatively low content of carcinogenic substances in tar-volatiles, an increased tolerance of benzene solubles in these emissions is suggested as an alternative to existing recommendations which the author regards as being unrealistic.

DEDICATION

To my nearest and dearest, namely my wife Phil with special thanks for her typing of this work, and to my children, Paula, Keith and Sheelagh.

PREFACE

This thesis is the canditate's own work except where acknowledged otherwise. Unless otherwise stated all measurements were carried out by the author or under his direct supervision.

The author claims originality and extension to existing knowledge in the following areas:

Part 1

The application of simple principles of economics to determine the "break-even" life of tar constructions.

Part 2

The comprehensive studies on the chemical characteristics of local tars, using the most advanced techniques, provide a further substantiation of the findings of other workers. As far as the author is aware this is the first time that Lurgi tar has been included in such a survey. The determination of the average structural parameters of coke-oven pitch extracts presents additional information on the variations that may be possible within this pitch type.

The GLC study of the composition of weathered tars is the most comprehensive of its kind and the correlations between oil losses and changes in Evt are believed to be the strongest affirmation ever obtained that evaporation is the predominant mode of weathering in coke-oven tars. Previously this conclusion has been made as a result of indirect investigations i.e. through noting the absence of appreciable amounts of oxidation products or through lack of evidence of other processes.

Part 3

The use of GLC subtraction-loop methods to study the affinity between polymers and hydrocarbons is unique. The results provide substantiation for the proposed mode of bonding between PVC and coal tar hydrocarbons. The modification of the ductilometer to determine the ductility-tenacity of polymer/tars is original. The mini binder-distributor is simple in principle and design but interest expressed by other workers in this development is some proof of its value.

The comprehensive series of road experiments is believed to be the most thorough study of any binder used for single-surface treatment maintenance. The practical recommendations arising from this work are the author's own.

First ever proposals are given for viscosity grades of tar/bitumen blends suitable for use in this country. The study of the precision of the sulphonation and GPC methods for determining the proportion of bitumen in tar/bitumen blends may be a useful addition to this subject. The work described in Part 3 Chapter 3 is thought by the author to be the first-ever evaluation of Lurgi tar as a road binder.

Part 4

The author knows of no other work in which the indirect tensile strength test and elastic (ultrasonic) modulus tests have been used to study variables in tar-bound mixes. While some of the results derived from the study of PVC/tar-bound mixes may be known to some workers, the author has found no published work on this subject. The same applies to the monitoring of tar viscosity during mix preparation and paving.

The stiffness monitoring tests on tar-bound mixes are also thought to be unique.

Part 5

While the nature and concentrations of hydrocarbons in emissions occurring during actual paving operations may previously have been studied (though the author has not been able to find any of this data) these results are original for the tar formulations used in South Africa.

ACKNOWLEDGEMENTS

I wish to thank Dr. S.H. Kuhn, Director of the National Institute for Transport and Road Research of the South African Council for Scientific and Industrial Research for permission to use results obtained during the Institute's research programme for this thesis.

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Mr. Neil Walker (Head of Materials and Design Branch),
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Close colleagues Tony Edler, Alan Brady, Ria Hattingh and Ciaran MacCarron . Tony carried out chromatographic and rheological measurements, prepared modified binders and was involved in many other facets of the work. Alan made most of the infra-red measurements and carried out most of the photomicrography. He also helped in the intrepretation of the chemical data and thanks are also due for many discussions on the derivation of organic structural parameters. Ria carried out elemental analyses and molecular mass determinations and her competence in recording all the data was an essential part of this study. Ciaran retrieved samples during and subsequent to the construction of experimental sections of road and his efforts during the Boksburg experiment were invaluable.

Mr. Nash and his staff, particularly Mr. Broadbent, Mrs. Findlay, Miss. Hasa and Mrs. Scallion for the numerous standard tests.

Mr. Sonny Greeff for routine field test measurements and traffic control during the field work.

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To others who gave temporary but valuable help during the construction of the road experiments the author's thanks.

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It is a pleasure to add my family to this list. To my mother far away in Scotland and other family members scattered among the Celtic fringe of the British Isles.

Finally acknowledgement is made to the people of South Africa who welcomed the Jamieson family in September 1966 and have treated us kindly since then. This goes with the author's sincere wish that the findings of this work will be implemented and so be of benefit to the national economy.

TABLE OF CONTENTS

VOLUME 1

		PAGE
INTRODUCTION		1
PART 1	STRATEGIC AND ECONOMIC ASPECTS OF TAR USAGE	3
PART 2	THE NATURE OF SOUTH AFRICAN COAL TARS	13
PART 3	TARS AS SURFACE TREATMENT BINDERS	78
PART 4	TAR BINDERS IN MIXTURES FOR BASECOURSES AND SURFACE COURSES	169
PART 5	TOXIC HAZARDS IN USING ROAD TARS	211
PART 6	PRACTICAL RECOMMENDATIONS RESULTING FROM THIS WORK	229
GLOSSARY OF TECHNICAL TERMS		233

VOLUME II

APPENDICES		240

INTRODUCTION

For many years coal tar as well as petroleum bitumen has been used for road construction in most parts of the world. At one time tar was regarded as the traditional road binder, but in the last decade or so its use has greatly diminished despite a general increase in road construction activities. This is particularly true in Europe and is associated with the declining availability of major sources of tar. As recently as 1970 McNeil, (1970) estimated that tar was used for the majority of surface treatment maintenance in Britain, but since this time its use for this purpose has decreased because of the almost complete absence of by-product tar from conventional gasworks which have closed due to the exploitation of the North Sea gas fields.

The opposite situation exists in South Africa where due to industrial expansion the amount of by-product tar is increasing. Furthermore, tar is considerably cheaper than bitumen which in South Africa is refined from imported crude oil, this country being without any known resources of petroleum.

At present most of the tar used by the South African road industry is for priming basecourses. Tar primes have been found to be excellent for this purpose (National Institute for Road Research, 1967). Past experience of road engineers in this country has been that generally tar is a less satisfactory road binder than bitumen. This has been associated with tar's greater susceptibility to weathering and higher temperature susceptibility of viscosity. It is evident that the economic benefits of substituting tar for bitumen in roads will only be realised if the service performance is equivalent or nearly equivalent.

In the project described in this thesis the author attempted to develop improved road tars, from indigenous materials, through a study of their chemical and rheological behaviour and the identification of their major weathering mechanisms. The ultimate aim was to evaluate the performance of improved tars in major types of construction by means of road experiments in which conventional petroleum-based binders were included for comparison. The major types of construction in which the use of tar may be considered are: surface treatments(for maintenance and new construction) and mixtures for wearing courses and basecourses. A necessary condition was that the improved tar should still have a real cost advantage.

The author's hypothesis is that indigenous coal tars can be used in most aspects of the maintenance and construction of South African roads with consequent direct savings in cost to public authorities and with benefit to the national economy.

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PART 1

Strategic and economic aspects of tar usage

INDEX TO PART 1

		PAGE
1.1.	STRATEGIC FACTORS	5
1.2	ECONOMIC FACTORS	7
1.2.1.	Tar and bitumen and South Africa's foreign exchange problem.....	11
1.3	REFERENCES.....	12

1 STRATEGIC AND ECONOMIC ASPECTS OF TAR USAGE

Resumé

Road bitumens used in South Africa are refined from imported oil, the supply of which is subject to political influences. Quantities of local crude tars are increasing due to expansion in local steel and oil-from-coal industries. From calculations of the cost of both road tar and bitumen at major centres in the country it is shown that in inland areas tar is considerably cheaper than bitumen. Savings in initial cost of constructing surface treatments and pavement layers with tar in the Witwatersrand area should be of the order of 20 per cent and 10 per cent respectively. In terms of these economic advantages it is shown that "target" lives are about 6 years and 12 years respectively in these constructions.

A complete substitution of tar for bitumen would save local road authorities on the Witwatersrand a total of R4 500 000 per annum. Total expenditure by the nation on bitumen is R26 000 000 per annum though it will not be possible to realise a saving of this order as long as crude oil imports are necessary for other purposes.

It has been mentioned that this work has been motivated by the prices of bitumen and tar. Furthermore, whereas this country has no oil resources, tar is produced from indigenous supplies of coal and therefore is of strategic importance. Before describing the development of the improved tar binders it is proposed to outline the strategic and economic factors in some detail. This has been attempted previously (Jamieson et al.1974) but recent events have altered the picture considerably and a further appraisal of the situation is appropriate.

1.1. STRATEGIC FACTORS

In recent times it has been apparent that the world will eventually be confronted with a shortage of petroleum oil. In view of certain political considerations it seems possible that South Africa may be affected sooner than other oil-importing countries.

The inevitability of the rapid exhaustion of oil resources is a result of the rate at which demand for oil is allowed to increase. Prior to the Middle East war, in October 1973, it was estimated that world oil consumption was increasing at a rate of 7 per cent per annum (Journal of the Institute of Fuel, 1973). Despite boycotts and attempts to conserve oil subsequent to the war, consumption has continued to increase at almost the same rate (Oil and Gas Journal, 1974). The world's proven resources are estimated to be 91 525 million tonnes (World Energy Conference, 1974) and this is calculated to be equivalent to about twenty year's supply, allowing for a growth in demand.

While other estimates of the world's reserves are more optimistic it is quite certain that costs to the consumer will increase. It is well known that about 70 per cent of the oil reserves are in the hands of Middle East countries whose governments are continually pressing for increases in price. Although new oil resources belonging to the western nations have been discovered these are located underneath the sea bed and their recovery is costly.

Because of the present problems in the oil industry the coal industry, which was slowly declining throughout the world, has been given a considerable boost. It has been announced that further oil-from-coal plants will be constructed in South Africa and the by-product tar obtained from these processes is of potential value to the road industry provided that it can be used to prepare a satisfactory road binder.

There are abundant supplies of coal in the country for energy raising purposes and for the production of liquid and gaseous fuels, but resources of coal suitable for the manufacture of metallurgical coke and consequent production of by-product coke-oven tar are less plentiful.

The latter is of greatest significance to the road industry because this is the most suitable type of coal tar for use in road construction. Crude coke-oven tar production at present is about 300 000 tonnes per year and may rise to 400 000 tonnes per year by the end of the decade. The amount of road tar produced from this quantity of crude will depend on refining capacity and the demands made by other industries. (It is possible that local resources of coking coal may eventually be diminished to such an extent that the

steel industry will have to resort to"form-coke" production which would use up most of the available by-product tar. However, it is considered likely that such a transition will not take place for some years and will be gradual rather than sudden.)

From estimates of future crude tar production from all sources in South Africa it has been possible to superimpose the expected crude tar production, over the period 1977 - 1985, on the current (1975) annual usage of bituminous binders, as shown in Figure 1 - 1. At a conservative estimate the total amount of crude tar produced per annum will exceed 400 000 tonnes by 1980. This material may have a number of industrial applications and the proportion processed into road tar depends on a number of factors, not the least of which is its suitability for road construction and maintenance operations. However, it has been stated that in future years an increased usage of local tars by the road industry is inevitable (Blight, 1974).

1.2. ECONOMIC FACTORS

The previous discussion mentioned that the political importance of oil has affected the price of petroleum bitumen in South Africa. However, although the price of bitumen has doubled since the Middle East War, the price of tar has also doubled. This is not solely because of the increased costs of coal and transportation but partly because coal-tar fuels can be used to replace petroleum oils for some industrial purposes, e.g. as a furnace fuel. The increase in the prices of tar and bitumen in recent years is given in Table 1 - 1.

TABLE 1 - 1

PRICES OF TAR AND BITUMEN ON THE WITWATERSRAND FROM 1972 TO 1976

Date	Bitumen	Tar
July 1972	R56/tonne	R25/tonne
October 1973	R76/tonne	R25/tonne
February 1974	R102/tonne	R38/tonne
January 1976	R116/tonne	R52/tonne
December 1976	R116/tonne	R56/tonne

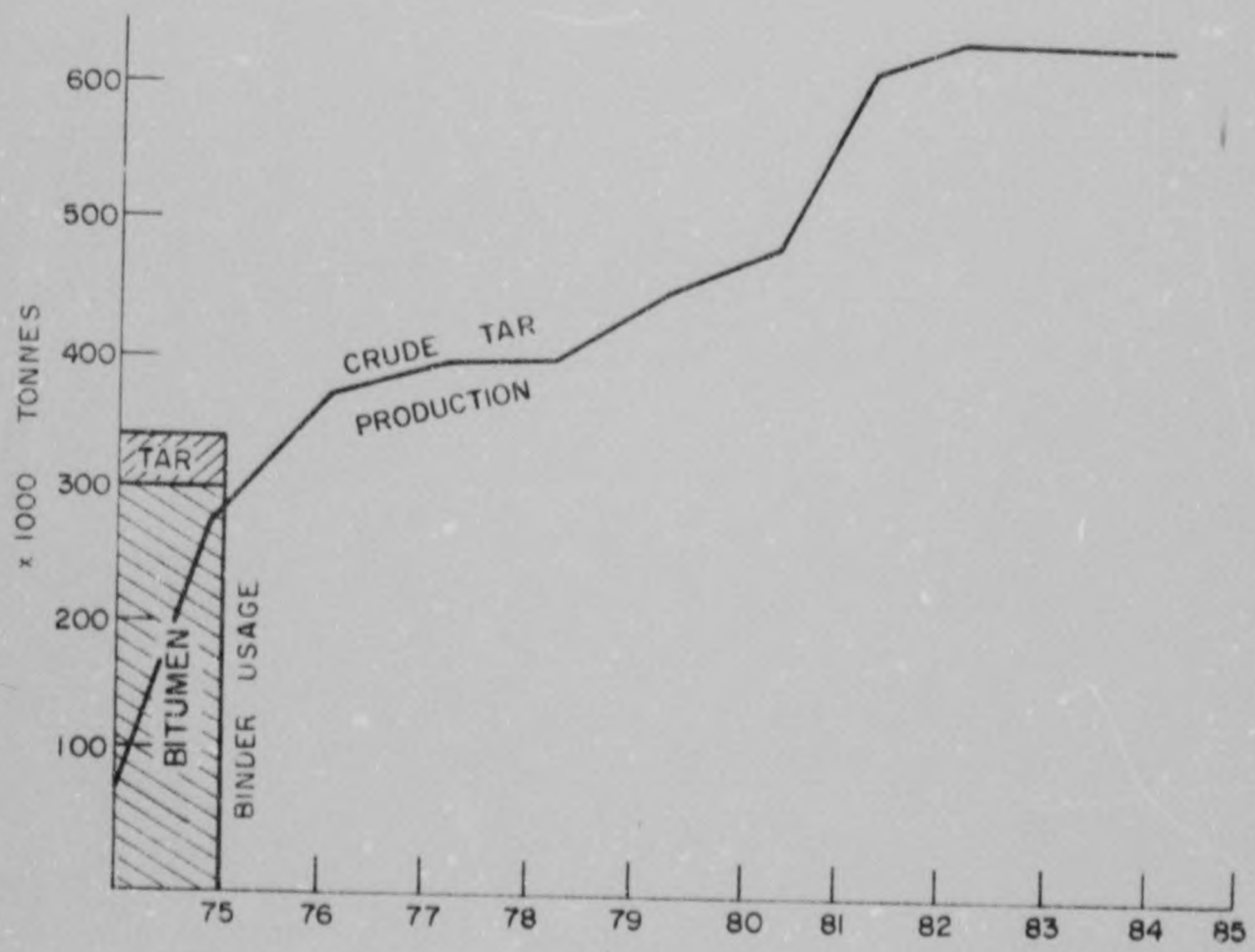


FIGURE 1-1
ESTIMATED CRUDE-TAR PRODUCTION 1975-1985 AND USAGE OF TAR AND BITUMEN IN 1975

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The present price difference between tar and bitumen on the Witwatersrand is R50/tonne and thus where tar can be used to replace bitumen large cost savings can be achieved (N.B. However, the price advantage will not be as big as indicated in Table 1 - 1 due to the difference in density*, tar - 1,23, bitumen - 1,002).

The cost advantage at a particular site will of course depend upon the distance over which each binder has to be transported from its point of supply. The location of plants producing tar in South Africa is shown in Figure 1 - 2 and crude oil is off-loaded at Durban and Cape Town for refineries situated there and at Sasolburg. Present sources of coke-oven tar are inland at Pretoria, northern Natal and the northern, central and eastern regions of the Orange Free State. If proposals for an ore-producing plant, including coke-ovens are accepted for the western Cape area, coke-oven tar will be available in these regions at a cost below that of bitumen. Lurgi tar is at present produced at Sasolburg and will be available in the eastern Transvaal when the second Sasol plant comes into production. This tar will also have a price advantage over bitumen in these regions.

Calculations of the cost of the two products, (tar and bitumen) at various centres in South Africa are shown in Figure 1 - 3 and indicate the widespread price advantage of tar in inland areas. It is emphasised that these prices have been calculated from recent prices at the nearest points of supply and the transportation costs have been taken as 5c per km. (The supply point for tar is Sasolburg-Vanderbijlpark and the supply points for bitumen are Cape Town and Durban.) Prices are in cents per litre at the spraying temperature of the binder (117°C for tar and 155°C for bitumen). There will be areas where due to local factors prices will differ substantially from those given here; e.g. in northern Natal tar from Washbank would be cheaper than indicated in Figure 1 - 3, and in addition it is customary to give discounts when large quantities of binder are ordered. With these provisos it is maintained that Figure 1 - 3 fairly reflects the relative costs of tar and bitumen at these centres in South Africa.

Similar calculations have been made in Part 3, Chapter 1 to compare costs of PVC/tar(containing 1,5 per cent PVC) with petroleum bitumen.

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* at 25°C

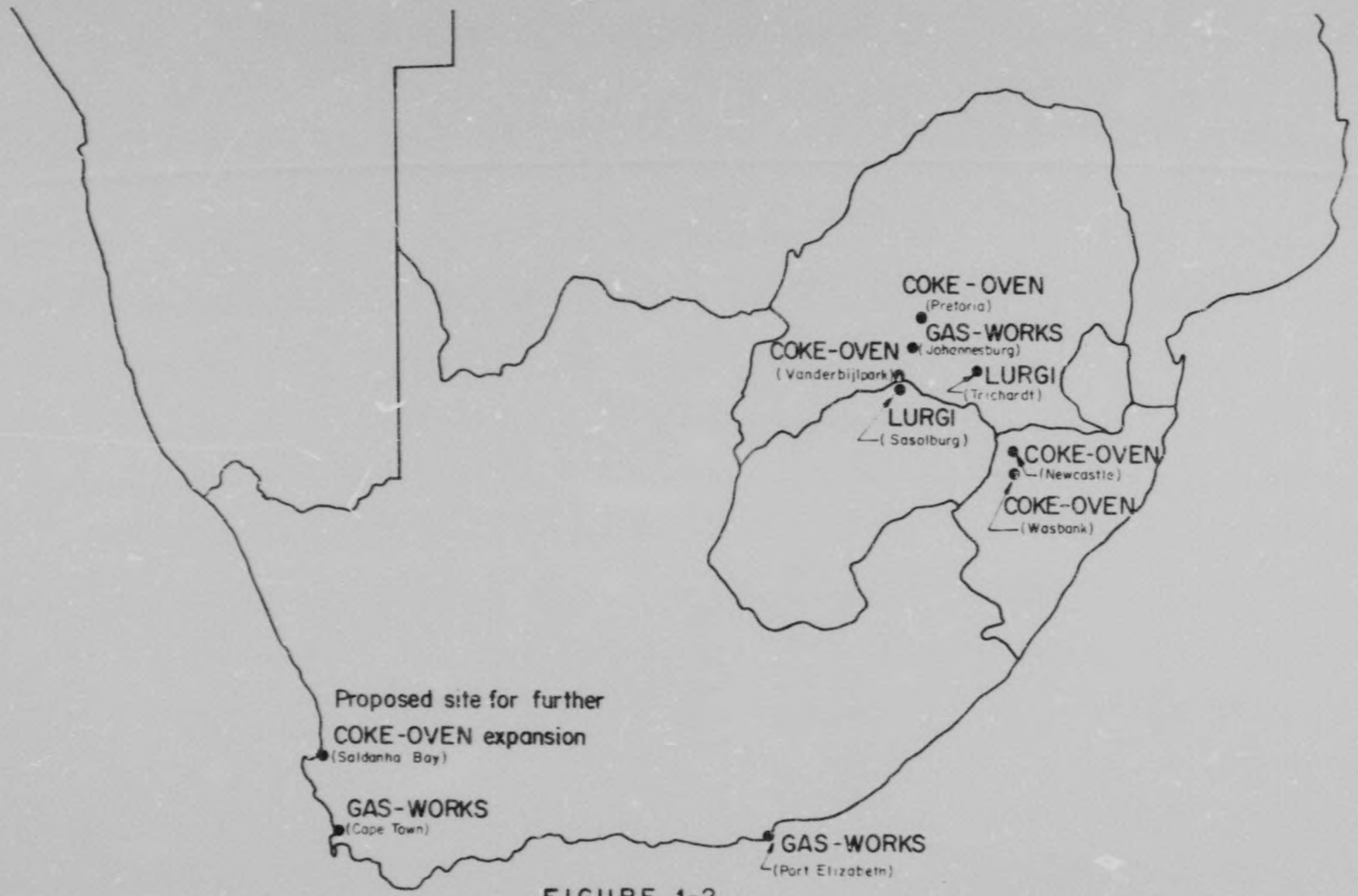


FIGURE 1-2

SOURCES OF TAR IN SOUTH AFRICA

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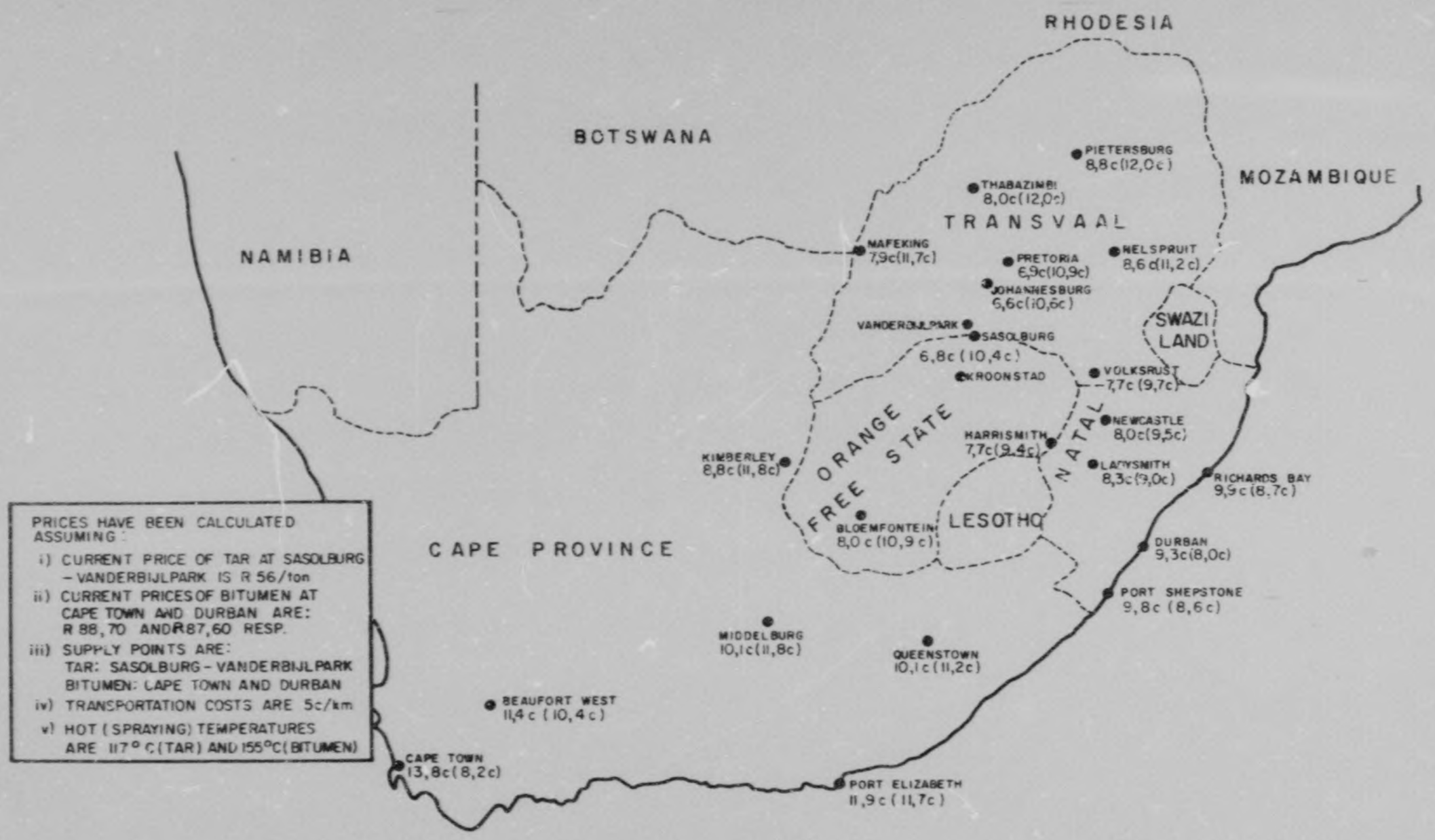


FIGURE 1-3

APPROXIMATE COST (CENTS PER LITRE HOT) OF TAR AND BITUMEN IN VARIOUS PARTS OF SOUTH AFRICA, DECEMBER 1976. (BITUMEN PRICES ARE IN PARENTHESES.)

An attempt has been made to indicate savings which may result through the use of tar as an alternative to bitumen in surface treatments and in mixes.

Example 1 Single-surface treatments

A Provincial Roads Department has estimated the cost of a single-surface treatment at R1 800/km for an 8 m wide road. Assuming prices of 10,6c per litre (hot) for bitumen and 6,6c/litre (hot) for tar and respective applications of 1,20 l/m^2 bitumen and 1,25 l/m^2 tar, the savings accruing through the use of tar rather than bitumen can be calculated:

The volume of bitumen required per km	= 9 600 litres
The volume of tar required per km	= 10 000 litres
9 600 litres of bitumen	= R1 018
10 000 litres of tar	= R660

Thus the cost per kilometre using tar would be only R1 442- a saving of R358 or almost 20 per cent of construction costs.

However, for a true comparison of the alternatives, performance aspects must be considered. The concensus of opinion it that a bitumen single-surface treatment on average lasts for 8 years. In view of the cost advantage it may be economically advantageous to accept a slightly shorter service life from a tar surfacing. The life required of a tar surfacing costing R1 442/km to "break-even" with a bitumen surfacing costing R1 800/km may be calculated using the concept of the equivalent uniform annual cost (EUAC).

If the interest is taken at 7 per cent per annum then the EUAC of a bitumen treatment lasting 8 years is:

EUAC = R1 800 x (CR - 7 - 8) (where CR-7-8 is the capital recovery
= R1,800 x (0,16747) factor)
= R301,45 (Winifrey, 1969)

The life required of a tar surfacing costing R1 442/km to "break-even" with a bitumen surfacing costing R301,45/km/year is

$$R1\,442 \times (CR\text{-}7\text{-}n) = R301{,}45$$

$$(CR\text{-}7\text{-}n) = 0{,}20905$$

By interpolation from tabulated values of CR-7 per cent factors n is found to be 6 years. Thus if the tar treatment lasts for longer than 6 years it is economically preferable to bitumen, if it lasts for less than 6 years bitumen is preferable.

Generalisations from this particular example cannot be made as the result is dependent on the cost of construction, the price of tar and bitumen, interest rates, and the estimated life of a bitumen surfacing. However, the price differential of 4 cents per litre is fairly typical for the Witwatersrand area where improved tar binders, close to their source, are most likely to be put to use. It would appear that in these areas a minimum service life for tar surface treatments of 6 years is necessary for them to be economically advantageous.

Example 2 Mixes for basecourses and surface courses

In mixtures for surfacings and basecourses the amount of binder required is greater than that used in single-surface treatments. Whereas 10 000 litres of tar per kilometre were required in Example 1 (8 m wide road at a typical application of 1,25 litres/m^2), in the case of a 25 mm thick tar-bound mix containing 6 per cent tar (typically) approximately 22 000 litres of tar would be necessary.

Using the price in Example 1, the binder costs per km (for 22 000 litres of binder) would be R1 452 for tar and R2 332 for bitumen. If we assume that the total cost of constructing a bitumen overlay is R3 500 /km/10 mm mix thickness for an 8 m wide road (i.e. approximately R19/tonne), then a 25 mm overlay will cost R8 750/km including the bitumen cost of R2 332. The cost of the tar overlay would be R7 870. The difference per km would be R880 and a saving of 10 per cent of construction costs and 37,7 per cent of binder costs would result.

Again for a true assessment of the relative economy of tar and bitumen mixes the service lives of the mixes must be taken into consideration. If a service life of 15 years is assumed for a 25 mm bitumen overlay, one can calculate the "break-even" life of a tar overlay and this will be found to be $12\frac{1}{2}$ years. Thus if the tar overlay lasts for more than $12\frac{1}{2}$ years it will be more economical than the bitumen overlay lasting for 15 years.

Although results are dependent upon the prices of tar and bitumen, and the service lives obtained when using these binders, it is believed that the above conditions are fairly typical for the Witwatersrand area. Hence for surfacing and basecourse work, tar mixtures should be able to perform satisfactorily for say 12 years.

When the total volume of bitumen used in areas close to supplies of tar is considered, it can be shown that by substituting tar for

bitumen local road authorities may save considerable sums of money. Figure 1 - 3 shows that tar is cheaper than bitumen in most areas of the country, and it is estimated that about two thirds of the total consumption of road bitumen in South Africa will occur in the heavily indutrialised Witwatersrand complex and adjacant regions. If the reasonable assumption is made that the average price advantage throughout this area is 2 cents/litre this would be equivalent to a saving of the order of R4 500 000 per annum.

1.2.1. Tar and bitumen and South Africa's foreign exchange problem

The potential savings which may result from replacing bitumen with tar take on a striking significance when related to the present problems of the national economy. Figure 1 - 1 shows that about 300 000 tonnes of bitumen are used annually on South African roads and at current prices in Durban and Cape Town this is equivalent to an expenditure, on an imported item, of the order of R26 000 000 every year. While it may prove to be inadvisable for the road industry to dispense with bitumen completely, this is the total value of the road binder market and it is against this background that the increased quantities of by-product tars must be viewed. This is especially significant in view of this country's balance of payments problem.

However, in view of South Africa's petrol needs it is unlikely that bitumen would disappear entirely from the road binder market, because for as long as it is necessary to import crude oil to refine engine fuels, the bitumen component of the crude must be disposed of profitably. It is not possible to obtain crudes without some bitumen component and in view of the world-wide imbalance in demand for " essential " petrol and diesel fractions and " less desirable " heavy oil and bitumen fractions there would appear to be little hope of South African refineries obtaining " light " crudes having a low bitumen content.

Should the demand for bitumen drop because of increased use of alternatives, such as tar or concrete, oil companies may have to implement measures to process bitumen into light hydrocarbon fuels. Because of the above-mentioned imbalance in demand, this trend has already begun with the installation in South African refineries of chemical plants to break down middle oils into " gasoline " hydrocarbons.

1.3. REFERENCES

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PART 2

The nature of South Arrican coal tars

INDEX TO PART 2

PAGE

2.1 THE ORIGINS OF TAR 15

2.2 A STUDY OF THE CHEMICAL CHARACTERISTICS OF CRUDE TARS AVAILABLE IN SOUTH AFRICA..... 18

2.2.1 The properties of crude tars..... 21

2.2.1.1 Use of unrefined crudes as primes..... 23

2.2.2 Examination of the oil component..... 25

2.2.2.1 Gas chromatographic studies..... 25

2.2.2.2 Infra-red spectroscopic studies..... 26

2.2.2.3 Proton magnetic resonance spectroscopic studies..... 32

2.2.3 Examination of the pitch component..... 39

2.2.3.1 Development of the solvent fractionation method..... 39

2,2.3.2 Method for the determination of molecular mass..... 40

2.2.3.3 Spectroscopic studies..... 41

2.2.3.4 Microscopic and X-ray investigations..... 42

2.2.3.5 Discussion of results; methanol, heptane and toluene extracts..... 42

2.2.3.6 Discussion of results; pyridine, quinoline and nitrobenzene extracts and nitrobenzene insolubles..... 45

2.2.4 Particular chemical characteristics of Lurgi gasification tars..... 46

2.2.5 Summary of findings from the chemical work..... 49

2.3 THE PREPARATION OF ROAD TARS..... 52

2.3.1 Distillation of crude tars..... 52

2.3.2 Blending of road tars..... 53

2.4 THE PHYSICAL AND RHEOLOGICAL PROPERTIES OF ROAD TARS AS COMPARED WITH THOSE OF PETROLEUM BITUMEN..... 55

2.4.1 Physical characteristics..... .55

2.4.2 Rheological properties..... 56

2.5 A STUDY OF THE WEATHERING OF ROAD TARS IN THE HIGHVELD CLIMATE..... 61

2.6 REFERENCES..... 70

2.1. THE ORIGINS OF TAR

Road tars are prepared from the crude tar condensate derived from carbonisation processes i.e. processes in which coal is heated in enclosed retorts at a high temperature.

Basically four types of coal tar are produced in South Africa:

1 Coke-oven tar; a by-product from the process by which coal is converted into metallurgical coke that is required for the manufacture of steel.

2 Lurgi-gasification tar; a by-product from a process whereby coal is gasified and the carbon monoxide and hydrogen produced are used for the synthesis of petroleum hydrocarbons.

3 Gas-works tar; a by-product of the conversion of coal into industrial and domestic fuel gas.

4 Miscellaneous and low-temperature tars; small amounts of tar derived from various other processes. Producer-gas tar is fairly common and is a by-product obtained from gas-producing units operating in industrial plants. (Low-temperature tars are derived from processes in which the coal is only partly carbonised usually at temperatures well below 800°C.

Local sources of types 1,2 and 3 have already been shown, in Figure 1 - 2.

Each of the types of tar, listed above, is formed in a specific type of plant and under particular physical conditions. This results in distinct differences in the chemical composition and physical properties of each tar. The hydrocarbon types that are the primary product of the thermal decomposition of coal may be different in each case. These may be either the pyrolysis products of the actual coal structure or resins and waxy inclusions derived from the original coalification process (McNeil, 1966a). The secondary reactions in which these primary products are involved are complex and they occur to a greater or lesser degree depending upon:

1 the design of the oven or retort

2 the oven temperature

3 the residence time of the primary products in the vicinity of the hot coke the hot wall of the oven and other parts of the plant. (Wilson, and Wells, 1950).

It appears that the main factor affecting the chemical nature of the by-product tar is the carbonising conditions ; the type of coal used has only a slight influence, although it will determine the yield of tar per unit mass of coal (McNeil, 1966b).

AUTHOR'S NOTE

Part 2.2 deals in detail with a fundamental chemical investigation in which all major sources of tar in South Africa are included. The reader who does not wish to follow this work may study only the resume' or the summary in Part 2.2.5 to avoid losing the continuity of the main discussion.

2.2. A STUDY OF THE CHEMICAL CHARACTERISTICS OF CRUDE TARS AVAILABLE IN SOUTH AFRICA

Resumé

Combined sophisticated analytical techniques are used to characterise South African tars. The nature of the oils is determined and the aromatic character; aromatic ring condensation, alkyl substitution and phenolic content of oil and pitch components are quantified. It is shown that one method based on first principles is appropriate for determining the average structures of fractions.

This first ever comprehensive study of local tars shows that coke-oven tars all conform closely to one type and vertical-retort tars to another. Lurgi tar is closely related to the latter tars and hence its value to the local road industry is established. However, coke-oven tars are more suitable for the manufacture of road tars than the vertical-retort tar type.

Unrefined gasification crudes are shown to conform nearly to specifications for primes.

Coal tar, like petroleum bitumen, is an extremely complex mixture of hydrocarbons containing small amounts of oxygen, sulphur and nitrogen. In tar the heaviest constituents have molecular masses of about 3 000 whereas it has been suggested that in bitumen the heaviest constituents may have masses of the order of 10 000 (Snyder, 1967, 1969).

As previously mentioned, crude tars recovered from different industrial carbonisation processes are formed under different physical conditions. This results in differences in the types of hydrocarbon, which comprise tars. The reactivity and stability of these hydrocarbon types will profoundly influence the weathering resistance of the binder and will also determine its rheological behaviour. These important factors determine its suitability as a road binder.

Although Bartle (1972) has estimated that the known constituents of tar now number about 1 000 this is only a small proportion of the total. These have been variously reported (Coal Tar Research Association, 1965). Of this number most are in the oily or lower molecular mass part of the tar. Less is known of the constitution of the pitch fractions, which comprise more than half of the refined road tar. This situation has

arisen because the constituents are similar in their chemical reactivity and thus their separation and identification is difficult. (In studying comparisons of tars reported in the literature, cognisance should be taken of the fact that the evidence may be mainly obtained from analyses of the oil fractions.)

Despite these limitations it has been possible to make chemical distinctions between tars of different origin. Tars produced in coke-ovens are more aromatic than tars produced from gas-making processes (continuous vertical-retort processes), and whereas in coke-oven tar over 90 per cent of the distillate oils consist of hydrocarbons of the benzene, naphthalene and anthracene series, similar oils from continuous vertical-retort tars may contain up to 25 per cent of phenolic materials and a similar amount of paraffins (Wilman, 1966).

The composition of continuous vertical-retort and also low-temperature tars varies more widely than that of coke-oven tar (Lang and Eigen, 1967). Karr et al. (1967) have shown that an increase in carbonisation temperature from 500 to 650°C greatly increased the yield of aromatic hydrocarbons, and both parent benzene and naphthalene and their alkyl derivatives were increased in quantity.

Recently, powerful new analytical techniques have been developed and considerable advances have been made in the characterisation of tars and petroleums and in the identification of constituents and constituent groups. South African produced tars have not previously been subjected to these techniques and the author considered that such a study was necessary as a basis for improving the quality of road binders derived from these tars. Specific objectives were:

(i) To make broad assessments of the differences between locally avaliable tars derived from coke-oven, Lurgi and vertical-retort processes.

(ii) To assess the variation in chemical characteristics of tar derived from coke-ovens.

(iii) To provide sufficient information on Lurgi tar to assess its potential as a road binder by comparison with data obtained on coke-oven and vertical-retort tars.

Local crude tars used in this study are as follows:-

Local coke-oven tars from the works of the South African Iron and Steel Corporation at Pretoria, Vanderbijlpark and Newcastle, and as received by Dundee Road Tar Products from the Vryheid works of Coronation Colliery.

Lurgi tar from the Sasol Corporation's works at Sasolburg.
Vertical-retort tars from continuous vertical-retorts at the municipal gas-works of Johannesburg and Port Elizabeth and of Capegas Ltd., Cape Town.

In addition a number of crude-tar samples were received from overseas and these were subjected to certain of the tests to give comparisons. These were:
Imported coke-oven tars from Lindu Company (Holland), Koppers Australia Pty. Ltd., Koppers Company Incorporated (USA), Scottish Tar Distillers (Scotland) and Wankie Colliery Ltd. (Rhodesia).
Imported medium-temperature tars Rexco tar from Midland Yorkshire Tar Distillers Ltd. (United Kingdom) and Coalite tar from Coalite and Chemical Company Ltd. (United Kingdom).

When samples were requested from manufacturers it was emphasised that they should be taken from typical distillation feedstock. The coke-oven crudes had probably all been through a dehydrator and the imported medium-temperature tars may have been subjected to some pretreatment to remove light hydrocarbons. Of the local gasification crudes, the Johannesburg crude was dehydrated but the samples from Capegas and Port Elizabeth crudes were not subjected to dehydration or any other form of pretreatment.

Because of the extreme complexity of crude tars, methods used for their examination usually involve a preliminary separation into groups having similar chemical or physical properties. Thus in the case of gasification or low-temperature tars they may be separated into acidic, basic and neutral constituents (Maher, 1963) (Andre et al., 1967), or divided by distillation into various oil fractions, or fractionated according to their solubility in various solvents (Mallison, 1944, 1950; Dickinson, 1945; Krenkler, 1949; Smith, 1966; and Bartle et al., 1969). In this investigation it was decided to make a separate examination of oil and pitch components. It was proposed that the oils would be removed by vacuum distillation and the resultant pitch residue fractionated by a solvent method. From knowledge of the constitution of coke-oven tar oils, it was estimated that the vacuum distillation method used would afford a separation at a constituent molecular mass of about 200.

The full separation scheme is shown in Figure 2 - 1. However,

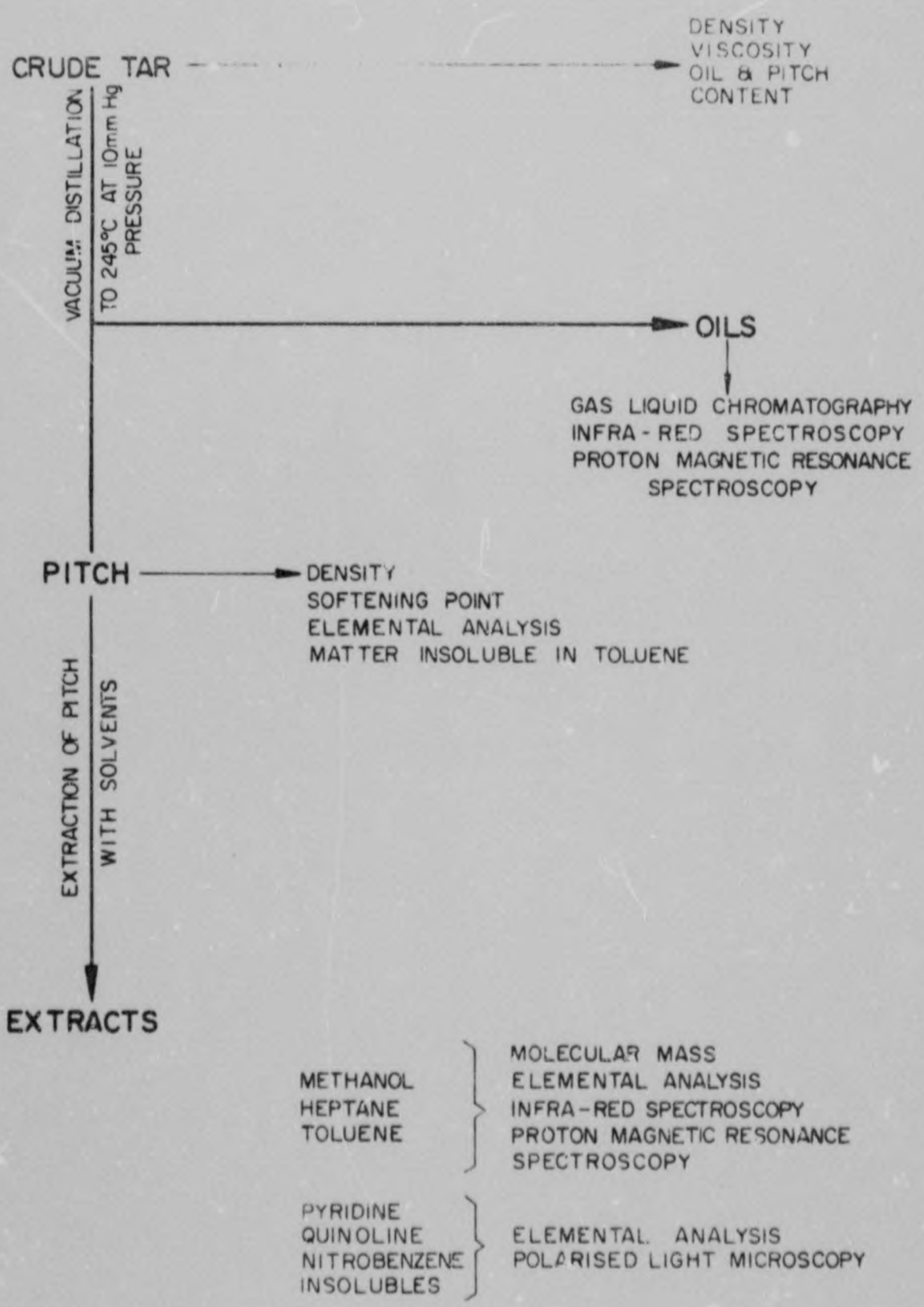


FIGURE 2-1

SCHEMATIC REPRESENTATION OF THE INVESTIGATION OF CRUDE TARS.

before the examination of the oil and pitch components is discussed the properties of crude tars as such will be described and the suitability of unrefined vertical-retort crude tars for priming basecourses will be considered.

2.2.1 Properties of crude tars

The density and viscosity of various local and overseas crude tars are shown in Figure 2 - 2. The viscosity is expressed as the equiviscous temperature (Evt)*. These properties were determined according to STPTC** methods RT1 and RT 2 (STV method) respectively.

Coke-oven crudes have a substantially higher density than gasification crudes and the densities of local and overseas coke-oven crudes were similar in this respect. The density and viscosity (Evt) were not necessarily related but as is well known the density is a good guide to the origin of a tar. However, for a particular crude or crude type the density increases as the Evt increases and thus where density is used for identifying a crude source, cognisance must be taken of this factor.

A breakdown of the crude composition was ascertained during the vacuum distillation procedure used to separate the oil and pitch fractions. ASTM method D1160+ was used for this purpose and the distillate volume was recorded at the reduced pressure equivalents of well-recognised distillation cut-point temperatures. (These were interpolated from the nomogram prepared by Bell, 1948). These fractions were:-

Equivalent at 100 kPa (760 mm Hg)	Vacuum 1316 Pa (10 mm Hg)
0 - 200°C	0 - 70°C
200 - 270°C	70 - 130°C
270 - 300°C	130 - 155°C
300 - 340°C	155 - 190°C
340 - 400°C	190 - 245°C

The compositions of local crude tars and overseas crudes are given in Figures 2 - 3 and 2 - 4 respectively. In no case was there any measurable quantity of water in the samples though traces could be detected in the distillate in some cases. The coke-oven tars had a

---

* The Evt scale is described in Chapter 2.3 and Chapter 2.4.2.

** Standardisation of Tar Products Tests Committee (Watkins, 1967).

\+ A description of this method, including an assessment of its precision in testing Lurgi tars, is given in Appendix L.

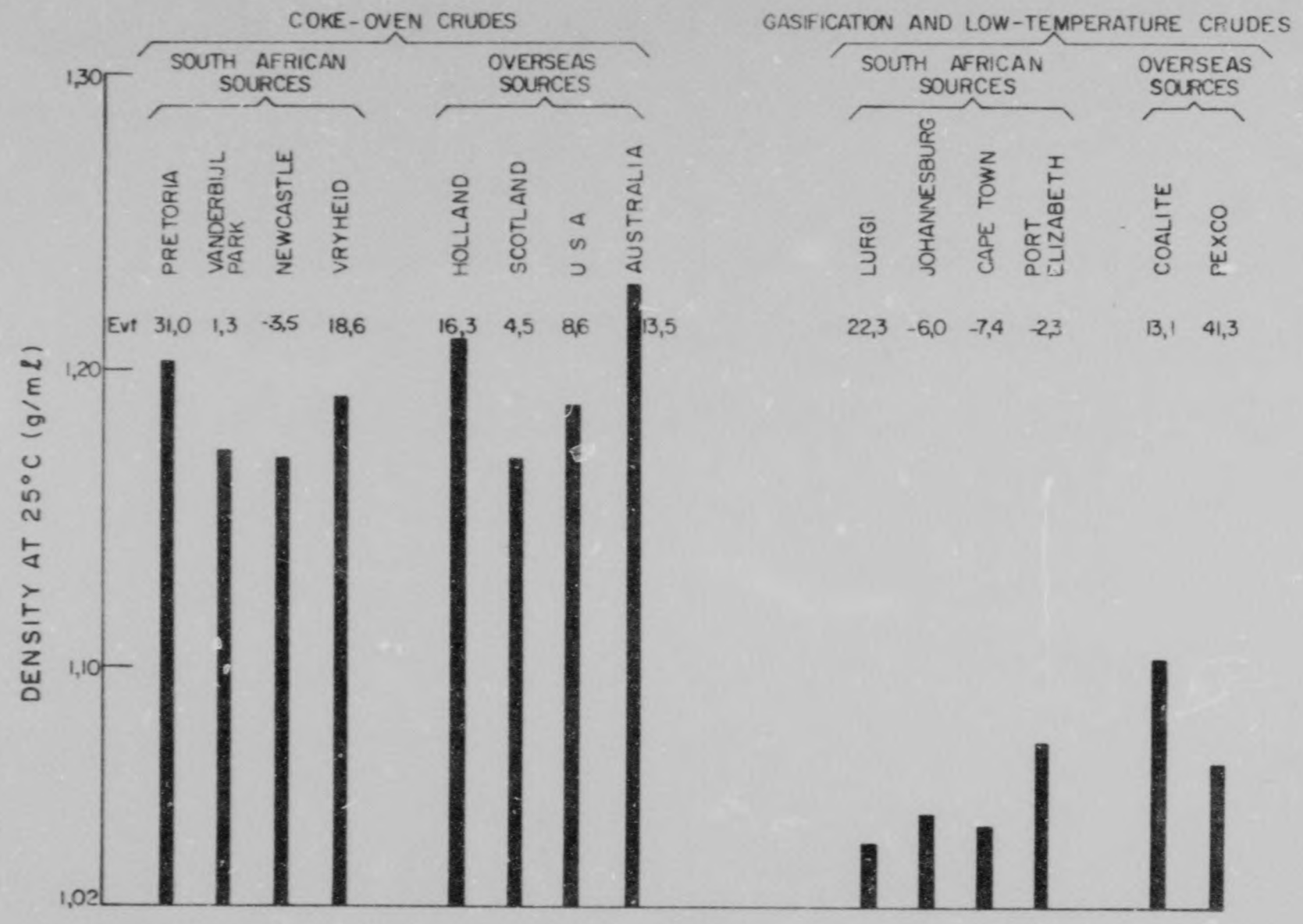


FIGURE 2-2

THE DENSITY (AT 25°C) OF CRUDE TARS FROM VARIOUS SOURCES.

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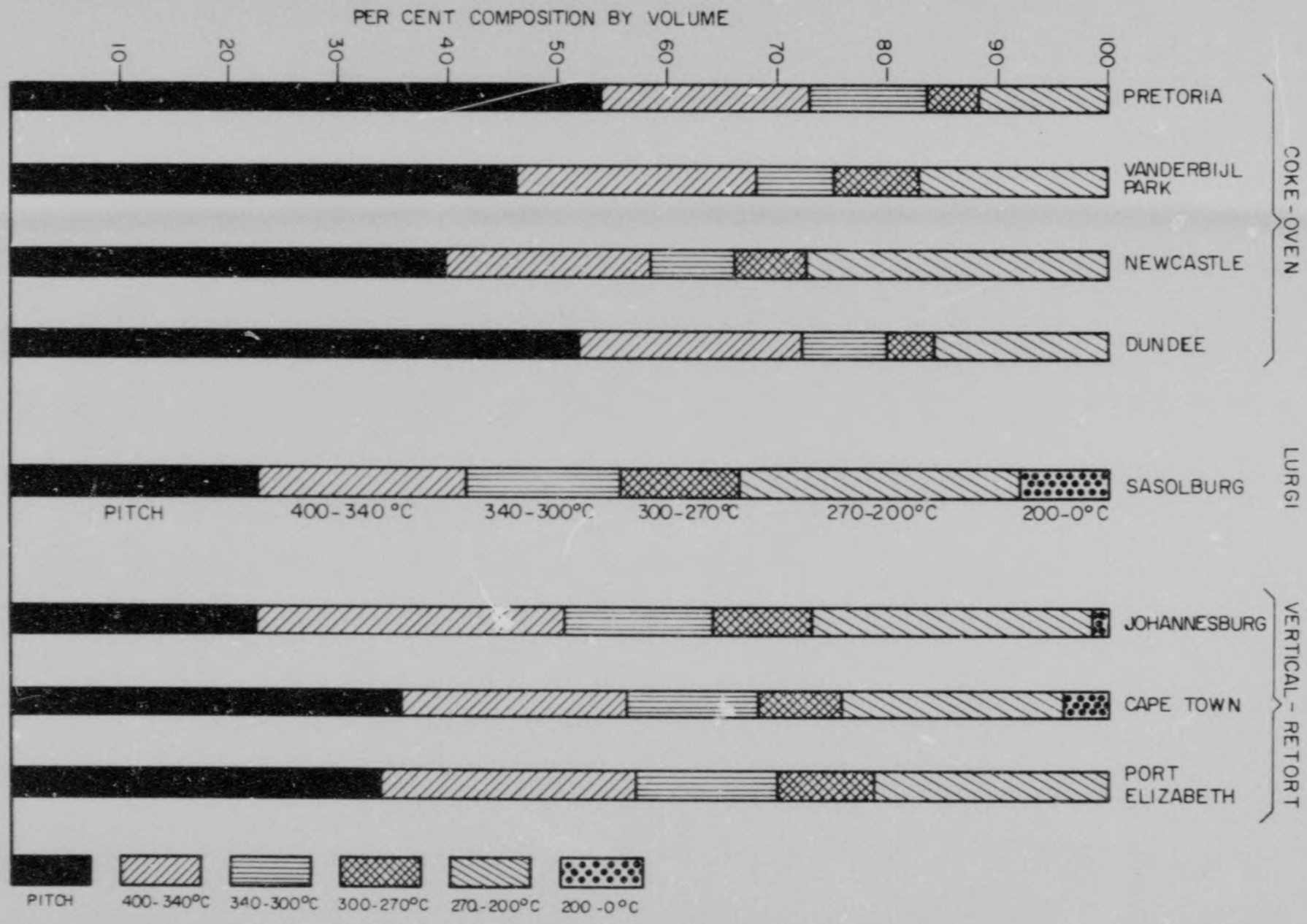


FIGURE 2-3
COMPOSITION OF SOUTH AFRICAN CRUDE TARS (PER CENT BY VOLUME.)

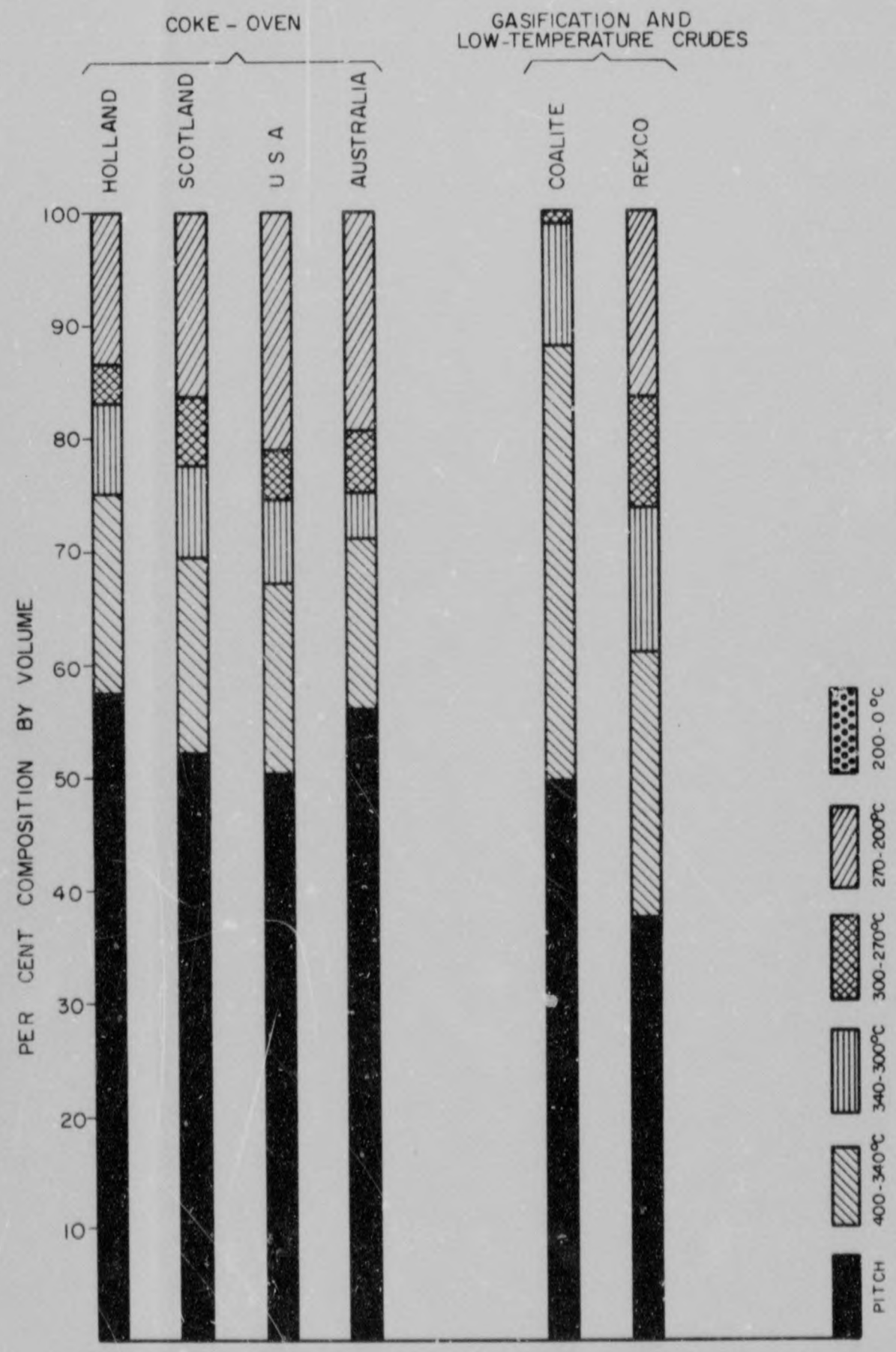


FIGURE 2-4

COMPOSITION OF CRUDE-TAR SAMPLES RECEIVED FROM OVERSEAS.

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higher pitch content than gasification and low-temperature crudes and there was a tendency for the density to increase with increasing pitch content as shown in Figure 2 - 5. The Coalite crude was an outlier in this regard and it may be that this crude had been "topped" (lighter fractions removed) prior to sampling. The greater proportion of the oils in the gasification tars occur mainly in the anthracene and heavy-oil fractions 300 - 340°C and 340 - 400°C respectively.

The softening point of each of the distillation residues was determined (STPTC method RT 3) and these results are presented in Figure 2 - 6. In general coke-oven pitches are harder than those derived from gasification and medium temperature crudes.

These results are in general agreement with data published by workers in America (Wilson and Wells, 1950) and the United Kingdom (McNeil, 1966a) in which coke-oven tar was found to have a higher density and to be composed of heavier constituents than tars originating from vertical-retort and other gasification sources. (An exception is the tar recovered from horizontal gas-retort processes in which the physical conditions are more akin to those in a coke-oven. The primary products of carbonisation pass through hot zones, where secondary reactions occur, instead of being conducted away from the hot zone as in the Lurgi and vertical-retort moving charge processes. This type of retort is not used anywhere in South Africa and in the rest of the world is almost, if not entirely obsolete.)

The Pretoria coke-oven crude had the highest Evt and pitch content of all local crudes examined. It is believed that certain ovens were dry-charged and where this practice is used this may decrease the proportion of light oils in the crude tar and thus increase its density.

From these results it would be expected that local coke-oven crudes would have the following composition and properties;

Density at 25°C (g/ml)	1,16 - 1,21
Oil Fraction as determined by vacuum distillation 1316 Pa (10 mm Hg pressure)	
Equivalent stop-points at 100 kPa	Per cent by volume
0 - 200°C	trace only
200 - 270°C	15 - 22
270 - 300°C	7 - 12
300 - 340°C	8 - 17

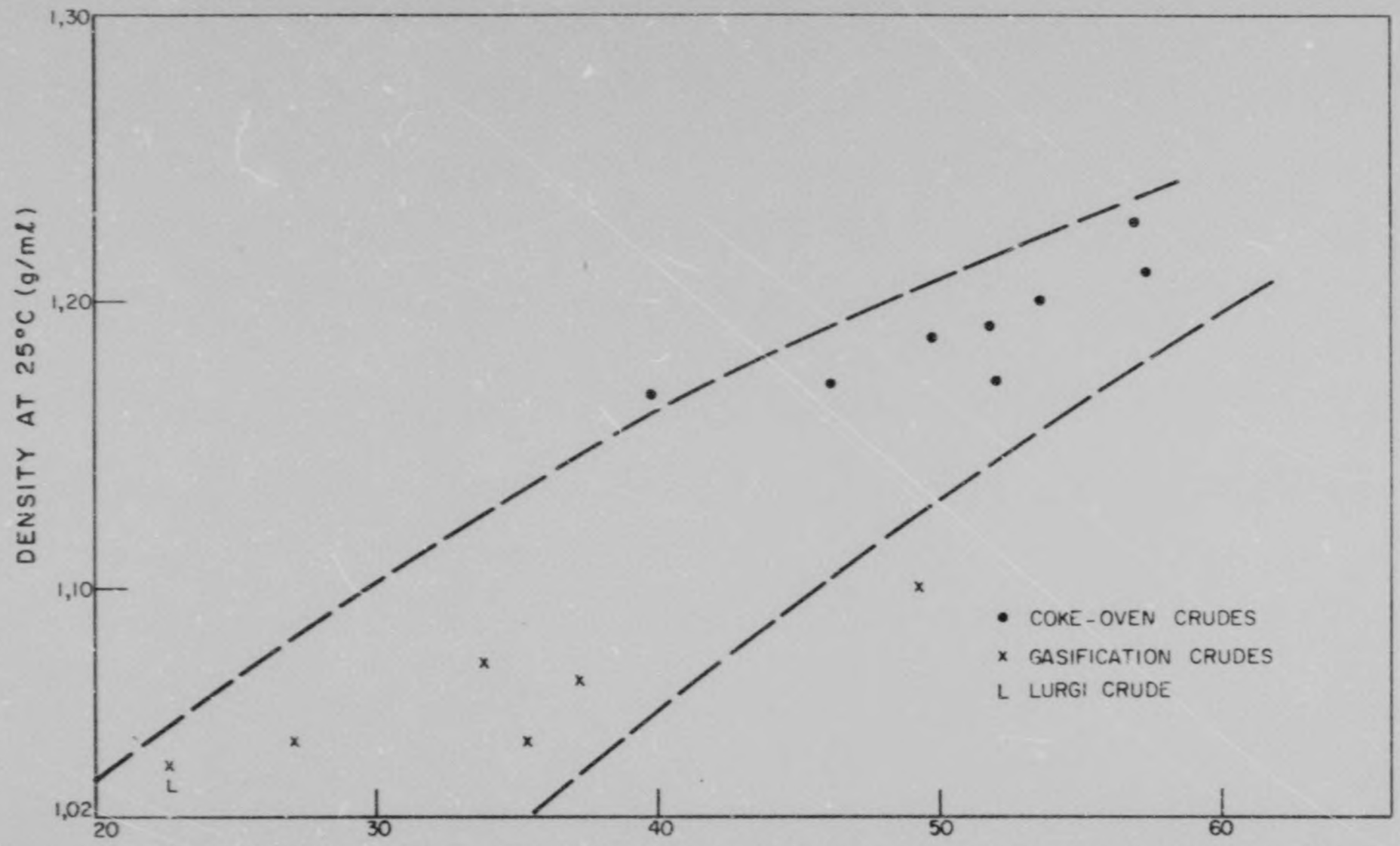


FIGURE 2-5

DENSITY AND PITCH CONTENT OF CRUDE TARS.

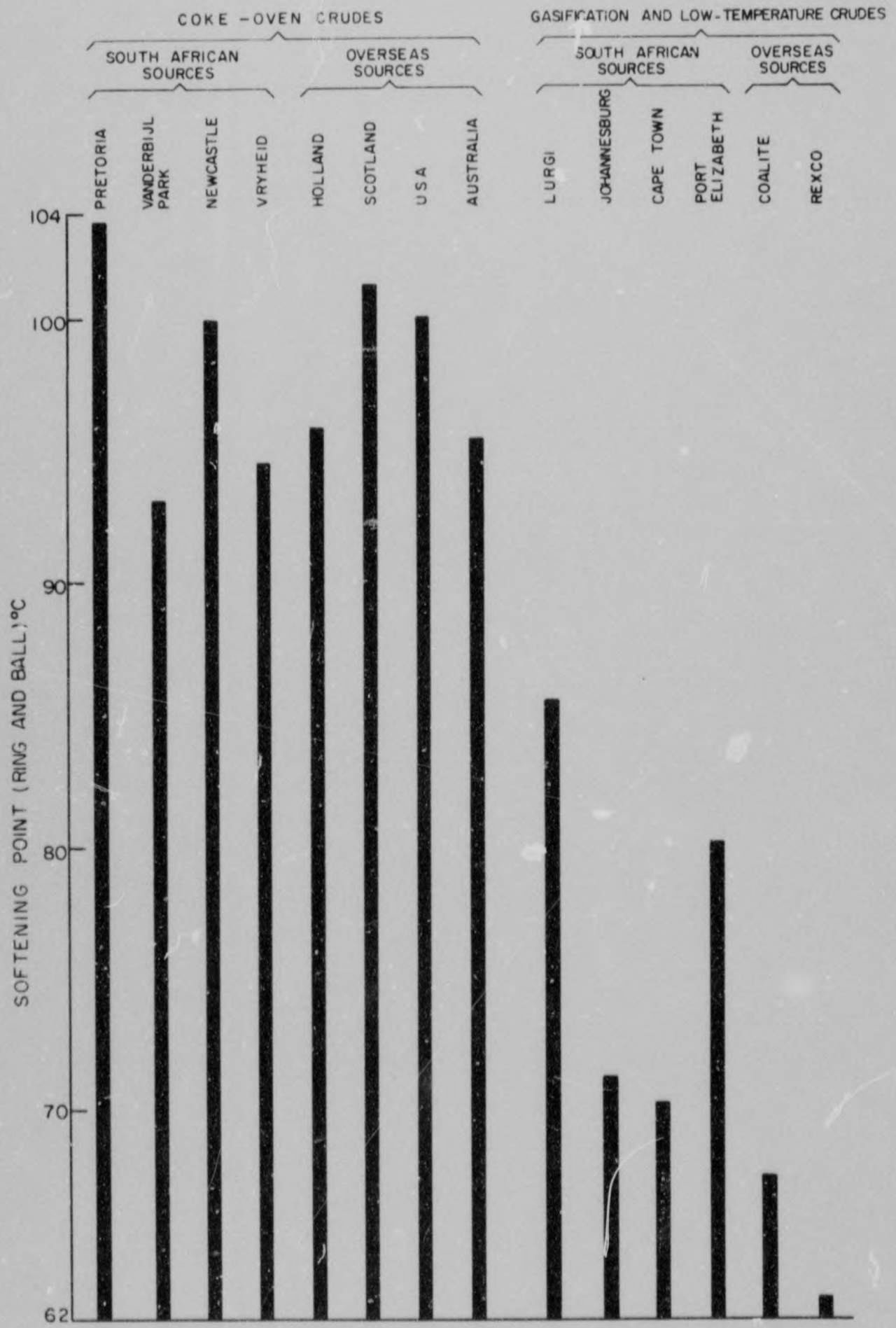


FIGURE 2-6

SOFTENING POINT OF DISTILLATION RESIDUES OF VARIOUS CRUDE TARS (DISTILLED AT 10 mm Hg PRESSURE TO 245°C)

300 - 340°C	8 - 17
340 - 400°C	30 - 36
Total oils	39 - 52
Pitch residue per cent by mass of crude	48 - 61
Pitch softening point °C (ring & ball)	93 -103

2.2.1.1. Use of unrefined crudes as primes

It has been mentioned that coal tars have proved excellent as basecourse primes (National Institute for Road Research, 1967).

At present the vertical-retort crudes from the gas-works at Johannesburg, Cape Town and Port Elizabeth are not processed into road tar grades. At Cape Town and Port Elizabeth these are the only tars produced in these areas and there is some value in determining whether the unrefined crudes would make acceptable primes. The three vertical-retort tars have been examined by the tests which comprise the current specification for tar primes prepared from low- and medium-temperature crudes, SABS 749:1971. These results are given in Table 2 - 1. The crudes comply with the requirements, excepting for their viscosities (Evt) which are low. This may not seriously affect their performance as primes and it is suggested that this could be evaluated using equipment similar to that described by Brink and Klenyan (1974). The excess light oils could be removed by some simple means of warming the crude.

TABLE 2 - 1

PROPERTIES OF SOUTH AFRICAN VERTICAL RETORT TARS AND THE SPECIFICATION REQUIREMENTS FOR ROAD TARS PRIMES (SABS 749:1971)

Property	Gas-works			SABS 749:1971
	Johannes-burg	Cape Town	Port E' beth.	
Evt (°C)	-6,0	-7,4	-17,5	3 - 12
Density at 25°C (g/ml)	1,047	1,046	1,155	1,05-1,14
Water content per cent by mass	-	-	-	0,5 (max.)
Distillation fractions				
Up to 200°C	4,8	3,4	1,7	3,0 (max.)
200 - 270°C	19,5	20,6	18,2	15-30,0
270 - 300°C	8,8	6,5	6,2	5-15,0
200 - 300°C	28,3	27,1	24,4	40,0 (max)
300 - 340°C	10,7	12,3	12,2	5-20,0
* Softening point of residue °C (r&b)	<35	<35	<35	80,0 (max.)
Phenol content (per cent by mass)	15,2	13,5	12,2	15 (max.)
Matter insoluble in toluene (per cent by mass)	3,6	3,5	5,3	10 (max.)
Viscosity STV (seconds)	8	7	-	40-100
Test temp.(°C)	30	30	30	30
Standard tar viscometer cup orifice (mm)	4	4	4	4

* The softening point of the residue was too low to be determined

2.2.2 Examination of the oil component

The total oil fraction was examined by gas-liquid chromatography infra-red spectroscopy and proton magnetic resonance spectroscopy.

2.2.2.1 Gas Chromatographic studies

Gas-liquid chromatography is a particularly useful tool for studying the constitution of tar-oils. The principles of this technique are described in Appendix A. Chromatograms of the coke-oven oils have been described previously (Jamieson, 1974a and see Appendix A Figure 3) and these were prepared using columns (2,1 m x 4 mm I.D.) packed with 3 per cent E 30 on diatomite C. These chromatograms are reproduced in Figure 2 - 7 and the series of peaks represents a separation of the main constituents of the tar-oils in order of increasing boiling points from right to left. This Figure suggests that all coke-oven tar-oils may be composed of the same major constituents in almost identical proportions.

Attempts to obtain chromatograms of non-coke-oven tar-oils using these columns were less successful, and instead of a series of well defined peaks as shown in Figure 2 - 7, a number of smaller peaks and "humps" resulted. Because of this, a high-resolution capillary column (wall-coated open tubular column) was invoked. This was a 100 m x 0,5mm I.D. stainless steel column coated with stationary phase SE 52. (This is similar to E 30 but has a slightly higher maximum operating temperature; 275°C as compared with 250°C). Capillary chromatograms of local coke-oven Lurgi and vertical-retort tars, and Coalite tars are shown in Figure 2 - 8 and the operating conditions are also described in this Figure. These were obtained using a Perkin-Elmer GC 900 instrument fitted with flame ionisation detectors. The inlet carrier stream with volatile sample was split in a ratio of 14:1. The most important feature shown by Figure 2 - 8 is that in coke-oven tar-oils a few (about seven) constituents predominate whereas Lurgi, vertical-retort and Coalite tar oils are composed of more even proportions of a larger number of constituents.*

The constituents of local coke-oven tar oils have been identified previously (Jamieson, 1974a) and these are mainly unsubstituted 2-, 3-, and 4-ring aromatic hydrocarbons. The identification of all the constituents

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* This assumes that the detector response is similar for all tar-oil constituents (which is a reasonable assumption as flame ionisation detectors were used) and that the peaks in the coke-oven tar chromatograms represent single constituents.

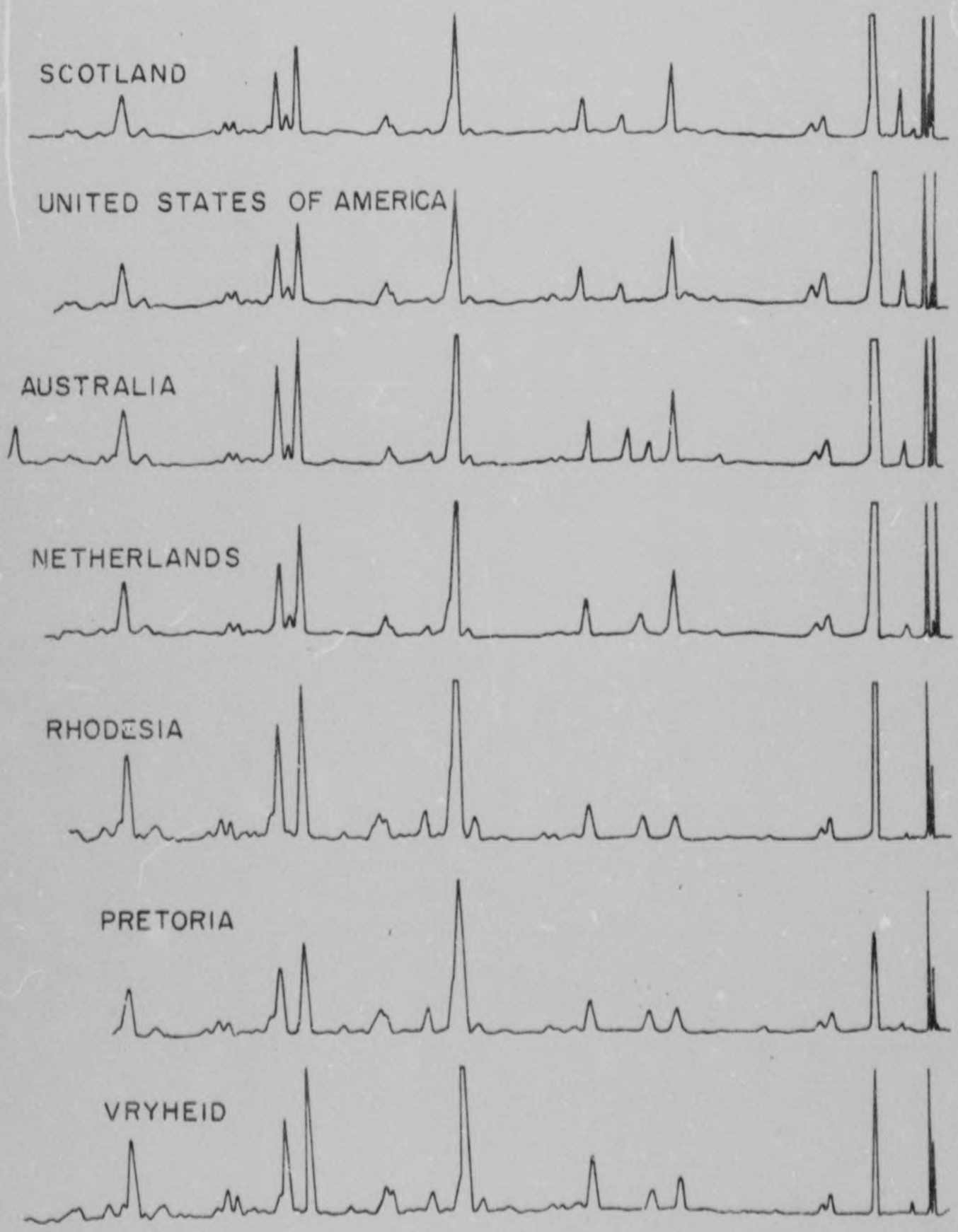


FIGURE 2-7

CHROMATOGRAMS OF CRUDE COKE-OVEN TAR OILS OBTAINED FROM VARIOUS SOURCES (FROM JAMIESON 1974a)

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NOTE : 100 m x 0,5 mm ID CAPILLARY COLUMN COATED WITH SE 52.
FLOW RATE 1,6 - 0,8 ml/min 1 µl 20 % SOLN. IN CS_2 SPLIT 14 : 1
TEMP. INJECT. 275 °C, COLUMN 100 - 275 °C AT 1,5 °C/min 24 mins AT 275 °C

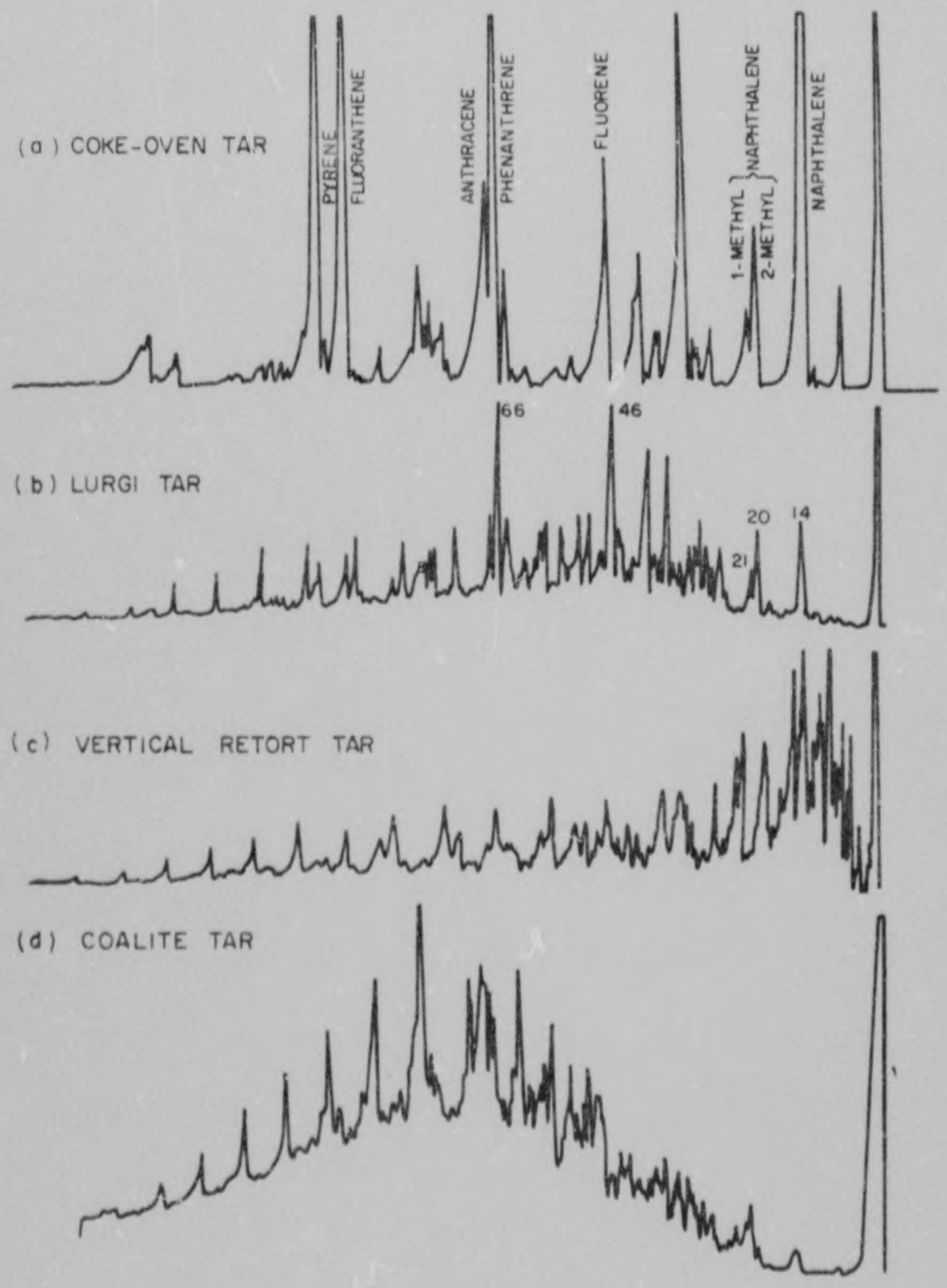


FIGURE 2-8

"CAPILLARY" CHROMATOGRAMS OF (a) COKE-OVEN TAR, (b) LURGI TAR, (c) VERTICAL-RETORT TAR, ALL PRODUCED IN SOUTH AFRICA AND (d) A LOW-TEMPERATURE TAR PRODUCED IN EUROPE.

of each of the non-coke-oven tar oils was not attempted as this would have been less useful than a general characterisation in terms of constituent types. The identities of some constituents of Lurgi-tar oils were determined by a combination of gas chromatography and infra-red spectroscopy as described in section 2.2.4. Spectroscopic methods, particularly infra-red spectroscopy and proton magnetic resonance spectroscopy, have been found to be of value in characterising complex substances such as tars and bitumens.

2.2.2.2 Infra-red spectroscopic studies

A description of this technique is given in Appendix B.

The infra-red examinations were performed on a Pye SP1100 double beam scanning spectrophotometer. The spectra were obtained by painting CS_2 solutions of the oils onto KBr (potassium bromide) discs evaporating off the solvent and placing the discs in the energy path of the instrument. Spectra typical of each oil type are shown in Figure 2 - 9 and the main features of the coke-oven, Lurgi and vertical-retort tar-oils are summarised in Tables 2 - 2, 2 - 3 and 2 - 4 respectively.

It may be that infra red examinations of such complex mixtures are less reliable than results obtained on pure hydrocarbons because of the uncertainty of the significance of absorbtion band intensities. Nevertheless, using this technique it has been possible to make important suggestions as to the character of the various oils.

All the oils exhibit an aromatic character (aromatic C - C quadrant) stretching at 1600 cm^{-1}). The aromaticity varies from oil to oil and is strongest in the coke-oven tar (most intense bands in the 3020 - 3060 cm^{-1} region due to aromatic C-H stretching and in-plane and out-of-plane quadrant bending at 620 cm^{-1} and 480 cm^{-1}). The strong intensities at the 620 cm^{-1} and 480 cm^{-1} wavenumbers together with the C-H wagging intensities at 820 cm^{-1} , 780 cm^{-1} and 750 cm^{-1} (2,3 and 4 adjacant hydrocarbons respectively) and the presence of only a weak band ascribable to lone hydrogens (900-835 cm^{-1} regions) indicates that coke-oven tar-oil constituents are mainly unsubstituted

There are major differences in the 3600 - 3000 cm^{-1} region, coke-oven oils exhibiting a sharp band at 3435 cm^{-1} whereas non-coke-oven types show broad bands characteristic of hydrogen bonding. The sharp band at 3435 cm^{-1} is probably N-H stretching as in molecules containing pyrole type structures, e.g. carbazole.

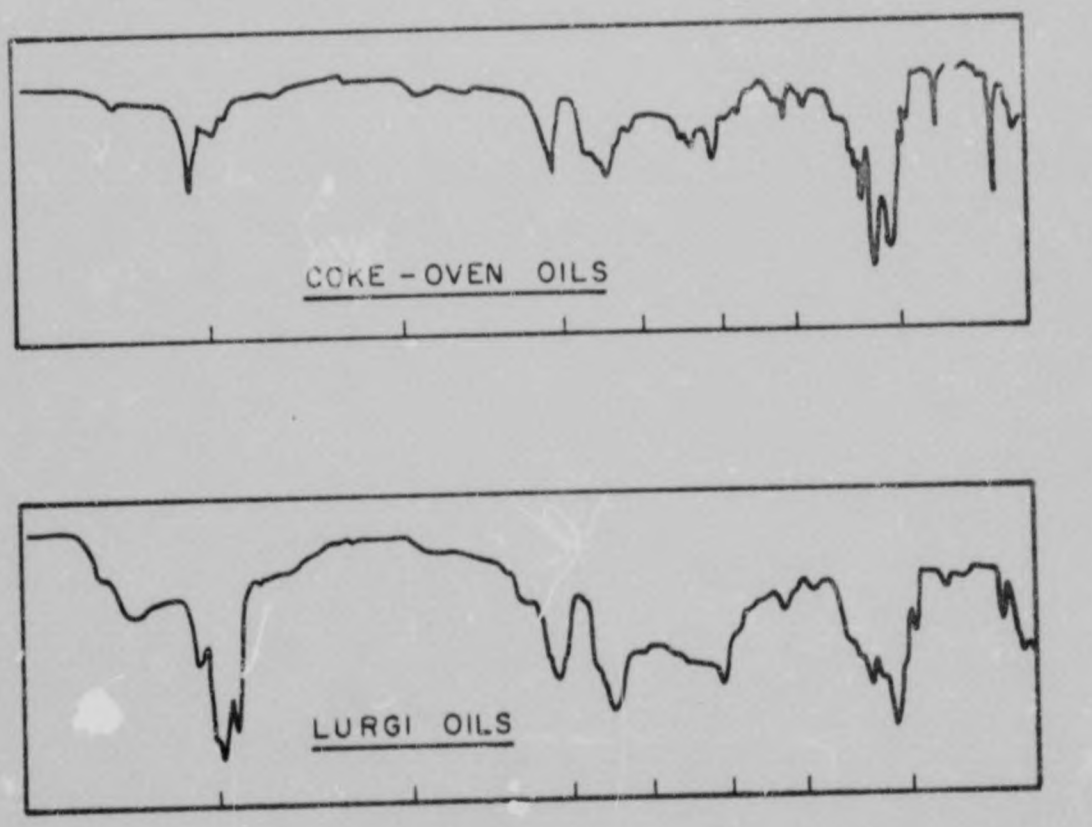


FIGURE 2-9

INFRA - RED SPECTRA OF VARIOUS TYPES OF TAR - OIL .

TABLE 2 - 2

CHARACTERISTICS OF IR SPECTRA OF COKE-OVEN TAR- OILS

Wave number (cm^{-1})	Band intensity	Assignation	Comment
3435	Very weak	N-H stretching	Pyrole type as in carbazole. Substantiated by addition of carbazole to tar solution
3040	Medium	Aromatic C-H stretching	Considerable aromatic character
2960,2875	Weak	CH_3 type C-H stretching	Low intensity may be due to low paraffinic character
2935	Weak	CH_2 type C-H stretching	
1460,1385	Weak	CH_3 deformations	
2000,1700	Very weak	Aromatic C-C out-of-plane bending vibrations	Very weak bands may indicate that aromatics are largely unsubstituted
1600	Medium	Aromatic C-C quadrant stretching	Strong aromatic character
900,650	Very strong	Aromatic C-H wagging	The predominance of bands due to 4 adjacent hydrogens and low intensity of bands due to one adjacent hydrogen (900-835 cm^{-1}), may indicate that aromatics are predominantly unsubstituted
	820 cm^{-1} weakest of bands	2 adjacent hydrogens	
	780 cm^{-1} strongest band	4 adjacent hydrogens	
	750 cm^{-1} stronger than 820 cm^{-1} but weaker than 780 cm^{-1}	4 or 3 adjacent hydrogens	
620	Strong	Aromatic ring quadrant bending	Aromatic character
480	Medium	Aromatic ring out-of-plane bending	Aromatic character

TABLE 2 - 3

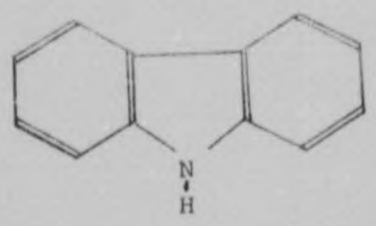
CHARACTERISTICS OF IR SPECTRA OF LURGI TAR-OILS

Wave number (cm^{-1})	Band intensity	Assignation	Comment
3600 - 3200	Broad but weak	Hydrogen bonded OH	Some phenolic constituents present, presence of a C=O stretching band (circa 1700 cm^{-1}) indicates the possibility of some carboxylic acid or ester groups.
3060 - 3040	Medium	Aromatic C-H stretching	Aromatic character
2960,2875	Medium	CH_3 type C-H stretching	The intensity indicates that there is considerable paraffinic character.
1460,1385	Weak	CH_3 deformation	
2935,2860	Strong	CH_2 type C-H stretching	
1700	Weak	C=O bond stretching	Carbonyl probably carboxyl group
1600	Medium	Aromatic C-C quadrant stretching	Aromatic character
900-600	Weak to medium 820 cm^{-1} Weak 750 cm^{-1} Weak	Aromatic C-H wagging 2 adjacent hydrogens 4 or 3 adjacent hydrogens.	The low intensity of these bands and the absence of any strong bands due to one adjacent hydrogen (900-835 cm^{-1}) may indicate that oils are a mixture of paraffinic and aromatic constituents and aromatics are predominantly unsubstituted

TABLE 2 - 4

CHARACTERISTICS OF IR SPECTRA OF VERTICAL-RETORT TAR- OILS

Wave number (cm^{-1})	Band intensity	Assignation	Comment
3600 - 3200	Broad medium intensity	Hydrogen bonded OH	Phenolic constituents. Intensity indicates that they may be present in some quantity. Absence of C=O stretching band (circa $1700 cm^{-1}$) precludes the presence of significant amounts of carboxylic acid or ester groups.
3060, 3040	Weak	Aromatic C-H	Aromatic character
2960, 2875	Strong	CH_3 type C-H stretching	The intensity indicates that there is considerable paraffinic character
1460, 1385	Weak	CH_3 deformation	
2935, 2860	Strong	CH_2 type stretching	
1600	Medium	Aromatic C-C quadrant stretching	Aromatic character
900 - 650	Weak-medium	Aromatic C-H wagging	The low intensity of these bands and the absence of any strong bands due to one adjacent hydrogen (900-835 cm^{-1}) may indicate that oils are a mixture of paraffinic and aromatic constituents and aromatics are predominantely unsubstituted.
	820 cm^{-1} Weak	2 adjacent hydrogens	
	750 cm^{-1} Weak	4 or 3 adjacent hydrogens	



Carbazole

This was confirmed from spectra of coke-oven tar-oils containing additions of carbazole. The broad absorption bands in the spectra of non-coke-oven types were ascribed to the presence of appreciable quantities of phenolic types of constituents. In the case of the Lurgi oils a small band at 1700 cm^{-1}, which is a characteristic region for abscrptions due to carbonyl groups, indicated the presence of constituents containing carboxylic acid or ester groups.

The oils were washed with sodium hydroxide* to remove the phenolic matter and the spectra of the "washed" oils was redetermined. The spectra of the "washed" and "unwashed" oils in the region 2 000 - 4 000 cm^{-1} are given in Figure 2 - 10.

The phenols and pyridine base contents of these oils were determined by the method described in the footnote. The results are given in Table 2 - 5.

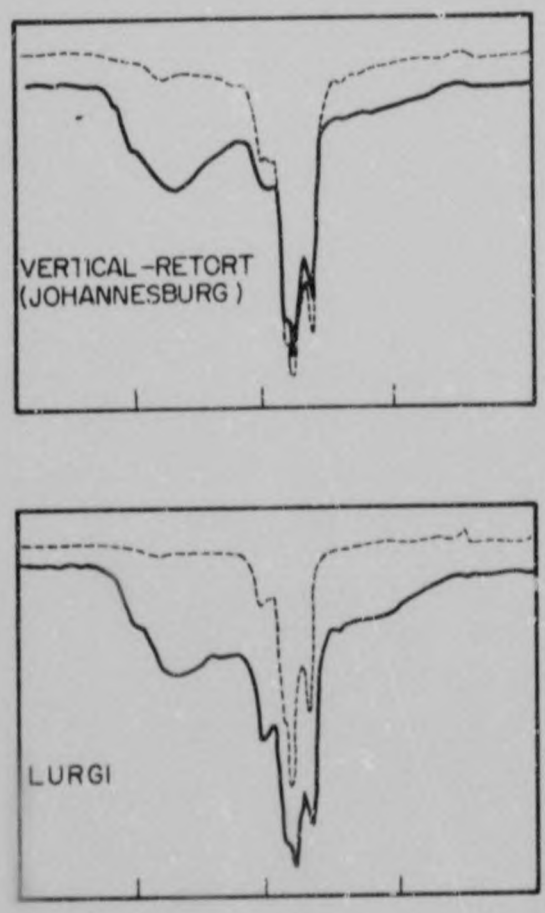
TABLE 2 - 5

PHENOLS AND PYRIDINE BASES IN LURGI AND VERTICAL RETORT TAR OILS**

Oils	Phenolic matter (Per cent by volume)	Pyridine bases (Per cent by volume)
Lurgi	26	0,79
Vertical-retort		
Johannesburg	36	0,56
Cape Town	29	0,53
Port Elizabeth	38	0,56

* 100 ml of oils in a separating funnel were washed with 50 ml of 10% (by mass) of NaOH solution and the aqueous layer run off. The last washings were examined for the presence of phenolic matter by acidification with concentrated Hydrochloric acid. Finally the phenol oils were washed with two 50 ml quantities of distilled water. 10 ml of the residue were separated, warmed to drive off moisture and subjected to infra-red examination.

** Values given by coke-oven tar oils (Vanderbijlpark) were low by comparison; Phenols 0,9%, Bases 0,5%.



WITH PHENOLS (ORIGINAL OILS) ——————

PHENOLS REMOVED - - - - - - - -

FIGURE 2-10

EFFECT OF REMOVAL OF PHENOLS ON THE 3000 cm^{-1} - 4000 cm^{-1} REGION OF THE INFRA-RED SPECTRA OF TAR OILS.

These values are similar to those reported by Wilman (1966) for vertical-retort tars.

The oils are particularly rich in crude tar acids which are of considerable value to the chemical industry.

The infra-red spectra show that there are major differences in the aromaticity of the different tar-oils, coke-oven tars being more aromatic than vertical-retort and Lurgi tars. The Lurgi and vertical-retort tar-oils have similar aromaticity. The relative aromatic character of the oils may be expressed by calculation of the optical density ratios of the bands at 3050 cm^{-1} (aromatic C - H) to 2935 cm^{-1} (CH_2 stretching). These values have been calculated and are shown in Table 2 - 6

TABLE 2 - 6

OPTICAL DENSITY RATIOS OF TAR-OILS

Tar oil	Ratio $\frac{O.D.\ 3050\ cm^{-1}}{C.D.\ 2935\ cm^{-1}}$
Coke-oven	
Pretoria	3,13
Vanderbijlpark	1,69
Newcastle	2,94
Vryheid	3,57
Lurgi	
Sasolburg	0,10
Vertical retort	
Johannesburg	0,07
Cape Town	0,07
Port Elizabeth	0,11

The paraffinic content of the non-coke-oven tar oils is shown by the intense C - H stretching bands characteristic of CH_3 groups (2960 and 2875 cm^{-1}) and CH_2 groups (2930 and 2860 cm^{-1}). From the infra-red spectral

evidence alone it is not clear to what extent the methyl and methylene groups are present as substantially paraffinic compounds or as alkyl substituents attached to aromatic groups. Previously Wilman (1966) found that in coke-oven tars the numbers of alkyl substituents per average molecule range from 0,5 - 2,0 for coke-oven tars to 2, 5 - 6,0 for vertical-retort tars; in both cases the number of alkyl substituents increases with increasing molecular size. The typical spectra in Figure 2 - 9 show that the coke-oven tar oils examined also have a lower paraffinic content than the non-coke-oven types but to make a more accurate estimate of the hydrogen distribution the infra-red data must be considered in conjunction with results given by proton (nuclear) magnetic spectroscopy (Proton NMR).

2.2.2.3 Proton magnetic resonance spectroscopy

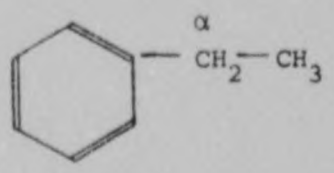
A brief description of the technique of proton magnetic resonance spectroscopy is given in Appendix C.

Using this technique it is possible to distinguish between hydrogen situated in the following environments:

H_A = Aromatic and phenolic hydrogen

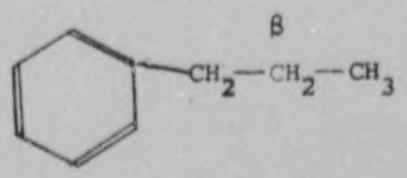
H_α = Hydrogen attached to carbon atoms placed next to an aromatic ring

e.g. in ethyl benzene



H_β = Hydrogen in paraffinic methylene and on carbon atoms two positions away from an aromatic ring

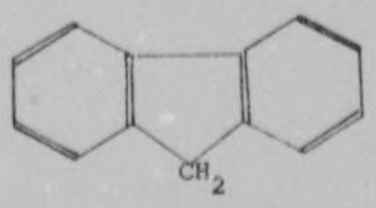
e.g.in propylbenzene



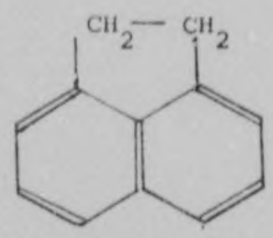
H_δ = Hydrogen in paraffinic methyl groups and/or attached to carbon atoms three positions away from an aromatic ring.

H_F = Hydrogen in methylene groups situated between two aromatic rings.

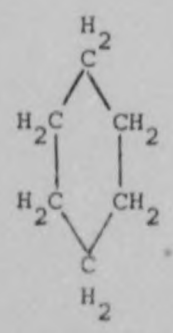
e.g. in fluorene



H_{AC} = Hydrogen in methylene groups as in acenaphthene or indenes
e.g. Acenaphthene



H_I = Hydrogen in cyclic methylene structures as in cyclohexane
e.g. Cyclohexane



A more detailed description of the hydrogen present in coal tars has been given by Bartle and Smith (1965) and is shown in Appendix C, Table 1. Equivalent ranges in the convention given by the apparatus used for this work are:

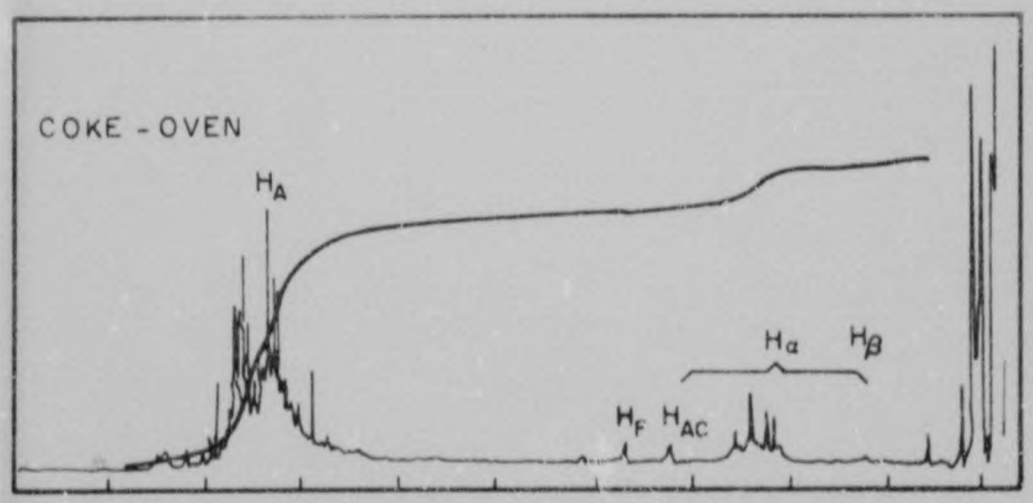
H_A	=	9,2	- 6,2	p.p.m.
H_α	=	3,0	- 1,17	"
H_β	=	1,17	- 1,00	"
H_γ	=	1,00	- 0,50	"
H_F	=	4,34	- 3,42	"
H_{AC}	=	3,42	- 3,17	"
H_I	=	1,40		

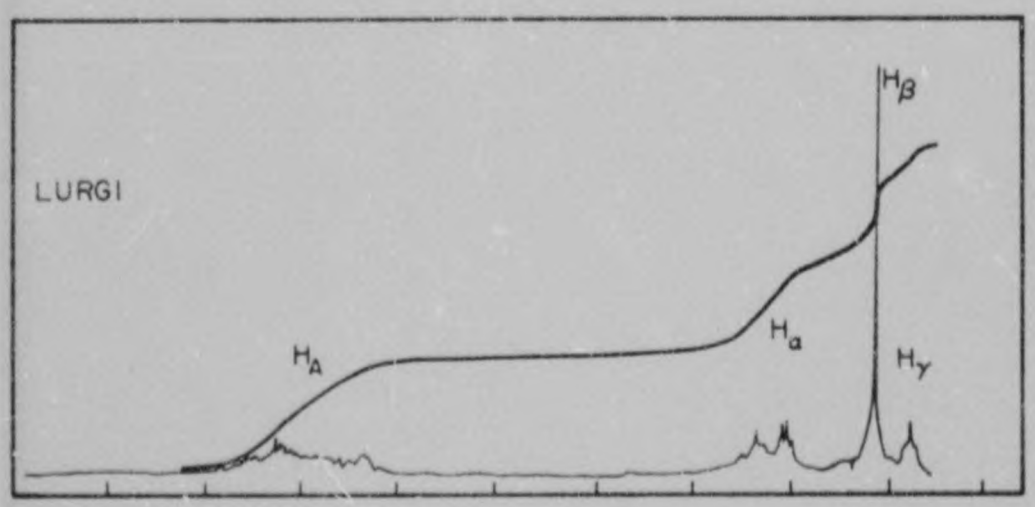
The proton magnetic resonance spectrum of each of the local tar-oils was determined in a solution of carbon disulphide (CS_2). These measurements were carried out by the National Chemical Research Institute of the CSIR using a Varian HA instrument at a field strength of 100 MHz. Typical spectra for coke-oven, Lurgi and vertical-retort tar-oils are shown in Figure 2 - 11. Although aromatic H_A type protons were present in significant amounts in all three types they predominated in the coke-oven tar oils, whereas in the non coke-oven tar oils there was an even distribution between H_A, H_α , and H_β protons.

---

* Individual peak positions are reported in Hertz relative to the standard used. The Delta (δ) system is used when accurate resonance positions are known.

$$\delta = \frac{\text{(Chemical shift in Hz)}}{\text{Spectrometer frequency}} \times 10^6$$





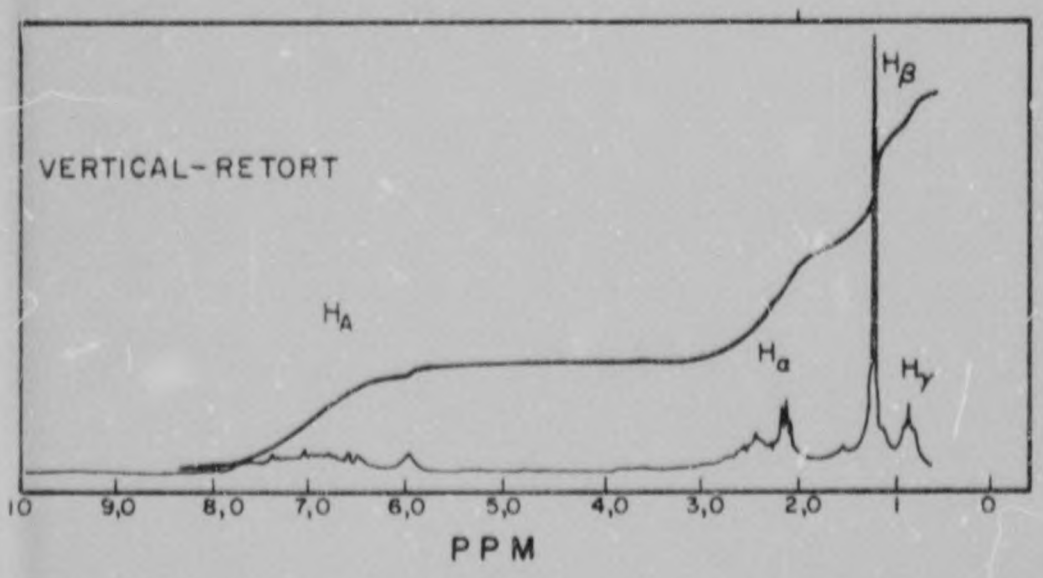


FIGURE 2-11

PROTON NMR SPECTRA OF TYPICAL TAR OILS.

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The coke-oven tar oils also contained detectable quantities of CH_2 groups as fluorene types [+] (H_F) and acenaphthene types [+] (H_{AC}). These were hardly detectable in the vertical-retort or Lurgi oils. The proportions of the various hydrogen types were determined, by normalising peak area integrals (which are also shown in Figure 2 - 11) and these are shown in Table 2 - 7 in which the hydrogen distribution of the most common types are given as ratios H_A/H_α / H_β. These results are in good agreement with results given by solvent extracts of road tars of coke-oven and vertical-retort origin reported by Bartle and Smith (1965).

Brown and Ladner (1960) and Brown, Ladner and Sheppard (1960) examined coal extracts by proton magnetic resonance techniques and showed that if the atomic ratio of hydrogen to carbon in the non-aromatic system is known the proton NMR data can be used to provide important information on chemical structure. If this ratio is x for carbon groupings and y for the indirectly attached groupings, then it is possible to estimate three useful parameters:

$$F_a \quad \text{(the ratio of aromatic carbon to total carbon)} = \frac{\frac{C}{H} - \frac{H^*_\alpha}{x} - \frac{H^*_O}{y}}{\frac{C}{H}} \qquad ---(1)$$

$$\sigma \quad \text{(degree of substitution, fraction of outer edge carbons occupied by substituents)} = \frac{\frac{H^*_\alpha}{x} + \frac{O}{H}}{\frac{H^*_\alpha}{x} + \frac{O}{H} + H^*_A} \qquad ---(2)$$

$$\frac{H_A}{C_A} \quad \text{(atomic hydrogen to carbon ratio of the hypothetical unsubstituted material)} = \frac{\frac{H^*_\alpha}{x} + H^*_A + \frac{O}{H}}{\frac{C}{H} - \frac{H^*_\alpha}{x} - \frac{H^*_O}{y}} \qquad -(3)$$

Where $\frac{C}{H}$ and $\frac{O}{H}$ are atomic ratios determined directly from the elemental analyses, Elemental analyses [++] of the oil and pitch components

---

+ The identity of these peaks was confirmed by comparison with spectra of fluorene and acenaphthene.

++ Carbon, hydrogen and nitrogen contents were determined by the National Chemical Research laboratories of the CSIR using a Perkin-Elmer elemental analyser A 240. The precision of this apparatus was established from six determinations on one sample and mean values of 91,8 per cent carbon, 4,7 per cent hydrogen and 1,7 per cent nitrogen were obtained, with standard deviations of 0,80, 0,15 and 0,15 respectively. The sulphur contents were determined by a modification of the method given in BS 1016 Part 8. Ash contents were determined from the residue in the sulphur content determinations. The oxygen was calculated as the difference between C,H,N,S, ash and 100 per cent. All results are given in Appendix D.

TABLE 2 - 7

THE DISTRIBUTION OF HYDROGEN IN LOCALLY AVAILABLE TAR OILS

Tar-oil	Hydrogen distribution (ppm)						Hydrogen distribution in types H_A, H_α, H_β		
	H_A (7 - 5)	H_α (3,17-1,17)	H_β (1,17-1,00)	H_γ (1,00-0,50)	H_F (3,1)	H_{AC} (2,7)	H_A :	H_α :	H_β
Coke-oven oils									
Pretoria	82,5	11,6	1,1	0	2,1	1,6	86,7	12,2	1,1
Vanderbijlpark	84,1	11,4	1,3	0	1,9	1,3	86,9	11,8	1,3
Newcastle	81,1	11,8	2,9	0	1,8	1,6	84,7	12,3	3,0
Vryheid	81,8	11,1	2,8	0	1,6	1,6	85,5	11,6	2,9
Lurgi tar oils									
	35,5	32,0	23,3	8,1	1,1	0	39,1	35,3	25,6
Vertical retort oils									
Johannesburg	24,1	29,2	32,1	11,1	0	0	28,2	34,1	37,7
Cape Town	25,7	33,5	25,2	12,4	0	0	39,6	34,3	26,1
Port Elizabeth	35,8	31,0	23,6	9,6	0	0	30,4	39,7	29,9

of each crude are given in Figure 2 - 12, and Appendix D, and:

$H^*_\alpha = \frac{H_\alpha}{H}$ the fraction of total hydrogen as α hydrogen

$H^*_0 = \frac{H_0}{H}$ the fraction of total hydrogen on other non-aromatic carbon

Nitrogen and sulphur are excluded from these calculations as they comprise only a small fraction of the material. It is also assumed that 60 per cent of all oxygen is present in phenolic groups and that the remaining 40 per cent is present in substituents attached to the aromatic molecules. This cannot be true of tar oils in which heterocyclic oxygen is known to be present (e.g. diphenylene oxide)

De Walt and Morgan (1962) modified these equations for application to tars by defining a certain region as $H_\alpha 2$ representing fluorene type methylene bridges by the term $\frac{H^*_\alpha 2}{z}$ Thus equation (1) becomes:

$$F_a = \frac{\frac{C}{H} - \frac{H^*_\alpha 2}{z} - \frac{H^*_\alpha}{x} - \frac{H^*_0}{y}}{\frac{C}{H}} \qquad (4)$$

The term introduced into equation (2) is $2\,\frac{H^*_\alpha 2}{z}$ as each CH_2 bridge represent two substituents. The oxygen is expressed as 0,6 of total oxygen and $(H_A + H_{Ph})^*$ is substituted for $H^*_A + \frac{O}{H}$

$$\sigma = \frac{H^*_\alpha 2 + \frac{H^*_\alpha}{x} + 0{,}6\,\frac{O}{H}}{H^*_\alpha 2 + \frac{H^*_\alpha}{x} + (H_A + H_{Ph})^*} \qquad (5)$$

(where z = 2)

Similarly equation (3) becomes:

$$\frac{C_A}{H_A} = \frac{\frac{C}{H} - H^*_\alpha 2 - \frac{H^*_\alpha}{x} - \frac{H^*_0}{y}}{H^*_\alpha 2 + \frac{H^*_\alpha}{x} + (H_A + H_{Ph})^*} \qquad (6)$$

Since the estimates of hydrogen and atomic ratios represent average values the results of these estimations should be considered as averages of all molecular species in the samples examined.

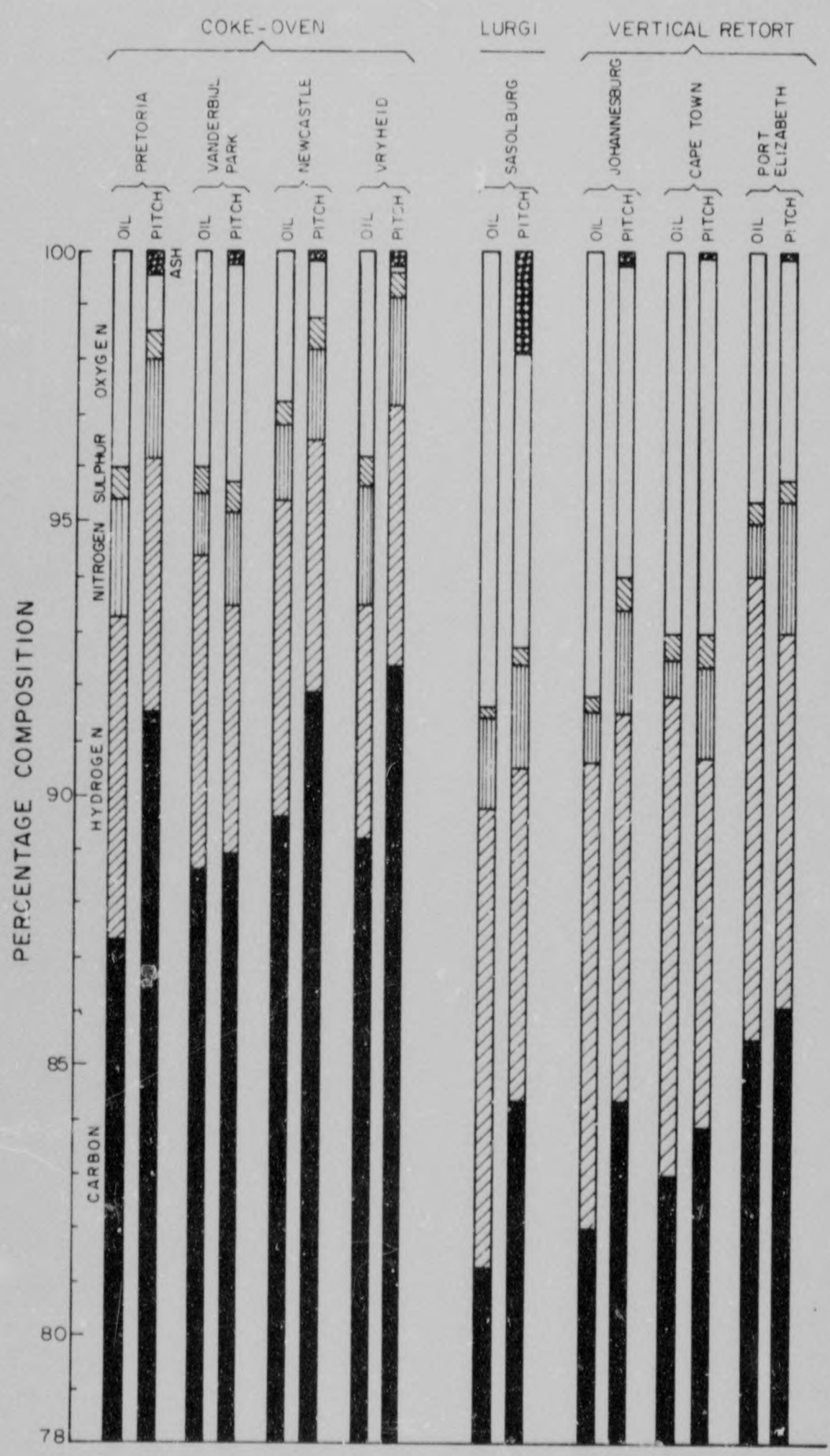


FIGURE 2-12

ELEMENTAL ANALYSES OF LOCAL TAR OILS AND PITCHES.

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The value of z is 2 but values of x and y are more difficult to estimate, De Walt and Morgan arbitrarily assigned values of 2,5 and 2 respectively.

The author set out to determine the non-aromatic carbon to hydrogen ratio and this was first attempted from the infra-red spectra of the local tar-oils by measuring optical densities at 2962 cm^{-1} (CH_3 type assymetric C-H stretching) and 2935 cm^{-1} (CH_2 type C-H stretching). As shown in Table 2 - 8 this gave rise to high CH_2/CH_3 ratios. (Calibrations were prepared using a series of alkyl benzene (ethyl to n-decyl benzene as shown in Appendix B). Le Tourneau (1965) and Le Roux (1969) have questioned the accuracy of such methods due to the influence of molecular configurations on absorbtion band intensities. Consequently the author developed a procedure which is an extension of a method suggested by Williams (1958) and used by Smith et al. (1974) in the characterisation of petroleum pitches. The author's calculations allow for the presence of CH_2 groups as methylene bridges of the fluorene and acenaphthene types. The method is described in detail in Appendix C.2.

Values of the non-aromatic carbon to hydrogen ratio given by the author's method are not in good agreement with the results derived from the interpretation of infra-red spectra as shown in Table 2 - 8.

TABLE 2 - 8

HYDROGEN TO CARBON RATIOS IN THE NON AROMATIC PORTION OF THE TAR OILS AS INTERPRETED FROM INFRA-RED SPECTRA AND FROM FIRST PRINCIPLES USING PMR DATA

Tar-oil	As detd. from IR spectra			As calculated from PMR spectra. 12/F (see F values App.C Table 111.)
	CH_2/CH_3 Ratio	Equivalent Atomic H/C ratio		
Coke-oven				
Pretoria	8,1	C_9H_{19}	2,11	2,68
Vanderbijlpark	7,1	C_8H_{17}	2,13	2,54
Newcastle	11,2	$C_{13}H_{28}$	2,15	2,43
Vryheid	7,1	C_8H_{17}	2,13	2,75
Lurgi				
Sasolburg	6,1	C_7H_{15}	2,14	2,32
Vertical retort				
Johannesburg	5,1	C_6H_{13}	2,17	2,32
Cape Town	5,1	C_6H_{13}	2,17	2,43
Port Elizabeth	9,2	$C_{11}H_{24}$	2,18	2,25

Using the author's method and assuming that the average molecular mass of all the oils is 151* (based on the concentrations of known constituents in coke-oven tar oils), values of the main structural parameters were calculated for each of the tar oils. These are shown in Appendix C (Table III) and typical values of the most important parameters are given in Table 2 - 9.

TABLE 2 - 9

VALUES OF THE MAIN STRUCTURAL PARAMETERS OF COKE-OVEN TAR OILS (VANDERBIJLPARK) CALCULATED BY THE AUTHOR'S METHOD

Parameters	Value
Ratio of aromatic to total carbon .	0,946
No. of aromatic ring carbons per average molecule	10,55
Per cent alkyl substituents on non-bridging aromatic carbons	4,58
No. alkyl substituents per average molecule	0,6

These results are in good agreement with actual values calculated from oil constituents. For example, the number of substituted outer edge positions in the constituents given in the footnote is 4,1 per cent of total outer edge positions, which is close to the value (4,6 per cent) found in Table 2 - 9. The average number of alkyl substituents per molecule (0,6) is close to that (0,5) found by Wilman (1966), in the lower molecular mass hydrocarbons of road tars of coke-oven origin. In view of the satisfactory results obtained by the author's method with oils of known constitution the procedure was used to determine structural parameter values for the pitch extracts, as described in section 2.2.3.5

---

* The major constituents of the Vanderbijlpark coke-oven tar oils were:

Phenol + Cresols + Xylenols	3,1 per cent
Naphthalene	30,1 per cent
1- and 2-Methylnaphthalenes	6,1 per cent
Dimethylnaphthalenes	7,5 per cent
Acenaphthene	1,1 per cent
Diphenylene oxide	3,2 per cent
Fluorene	4,6 per cent
Anthracene + Phenanthrene	12,8 per cent
Fluoranthene	4,0 per cent
Pyrene	2,7 per cent
Total	75,2 per cent

Values of structural parameters for all the tar oils were determined and the more significant results are shown in Figure 2 - 13. These results confirm the evidence obtained by infra-red spectroscopy.

This approach has yielded considerable information on the nature of tar oils derived from local crude tars. The particular points of importance are:

(1) Coke-oven tar oils are of one chemical type and Lurgi and vertical-retort oils of another.

(2) The four local coke-oven tar oils show little variation in constitution.

(3) The variation in the constitution of the vertical-retort tar oils was also only very slight though somewhat greater than was the case with the coke-oven oils.

(4) The similarity between the Lurgi-tar-oils and the vertical-retort tar-oils may be new information resulting from this work.

2.2.3 Examination of the pitch component

The elemental analyses* of pitches obtained from local crudes are given in Figure 2 - 12, and in greater detail in Appendix D. The coke-oven tars have higher carbon contents than the non-coke-oven types.

The first stage in the chemical examination of the pitch was the development of a solvent fractionation method.

2.2.3.1 Development of the solvent fractionation method

Numerous solvent extraction methods have been developed over the years and some have been applied to crude tars and road tars as well as to electrode pitches (Thomas, 1960). These have been previously reviewed by the author (Jamieson, 1974a). Of particular note is a method, developed at the CTRA**, subsequently used by a group of workers including Wilman (1966) and Bartle and Smith (1965). In this method the tar is dispersed in dioxane and a fraction is precipitated by addition of n-heptane. The precipitate is then successively extracted by n-heptane, methanol, benzene, dioxan and pyridine. The various fractions are recovered and examined by procedures such as those used in this study. A method developed by Smith (1966) is based on the partition of pitch components between polar and non-polar solvents, and is of less value for the examination of coke-oven pitch which is mainly composed of neutral constituents.

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* Carbon, hydrogen and nitrogen contents were determined as described in the footnote on page 34

** Coal Tar Research Association

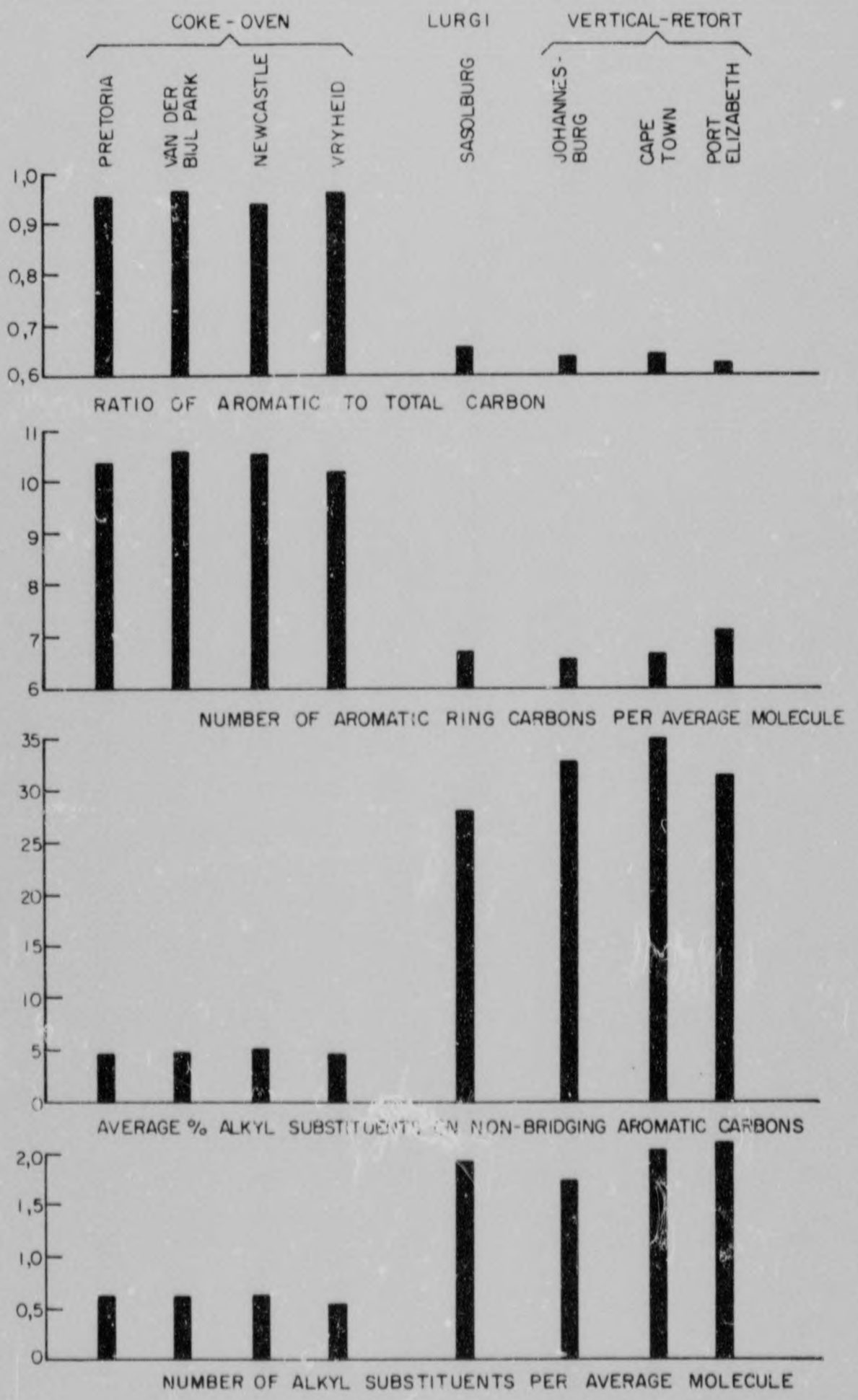


FIGURE 2-13

STRUCTURAL PARAMETER VALUES DETERMINED FOR LOCALLY DERIVED TAR OILS.

The author developed a method based upon the solubility of coke-oven pitch in a series of solvents which gave a fairly even partition of the coke-oven pitches. It was intended that this would result in a separation of fractions, increasing, progressively, in molecular mass. The development of the method is described in Appendix E. The following solvents were used in the order given: methanol, n-hexane + n-heptane (referred to hereafter as the n-heptane fraction) toluene, pyridine, quinoline and nitrobenzene.

The results of the solvent fractionation of local coke-oven, Lurgi and vertical-retort pitches and a petroleum bitumen are shown in Figure 2 - 14. The extracts increased in hardness with increasing power of the solvent, methanol to nitrobenzene. The methanol and n-heptane fractions were soft pastes while the other fractions were sufficiently hard to permit them to be ground into a powder.

2.2.3.2 Method for the determination of molecular mass

As has been mentioned previously the pitch component would be expected to comprise molecules of mass 200 and upwards to a maximum of 2 000 to 3 000 (Bartle, 1972). In recent years the development of gel-permeation chromatography (GPC) has permitted advances to be made in solving this problem. The author adapted a simple GPC procedure for the purpose (an osmometric method was investigated and discarded as the instrument was unreliable, and ebulliometric methods were unsuitable because of the relatively large quantities of material required). The GPC method is a modified version of the procedure used for the determination of the proportions of tar and bitumen in tar/bitumen blends, which is described in Part 3, Chapter 3, and in Appendix A.2.2.

In gel-permeation chromatography molecules are separated according to their hydrodynamic volume which depends on their size and shape. A solution is passed through a gel of pore-size distribution selected according to the molecular size distribution of the sample. Large molecules can enter only a small fraction of pores and therefore pass through the column more rapidly than small and compact molecules which diffuse into the pores of the gel.

Smith et al. (1974) have described the use of the technique for measuring the molecular mass distributions of petroleum feedstocks. Reerink and Lijzenga (1975) summarised some of the difficulties in applying gel permeation

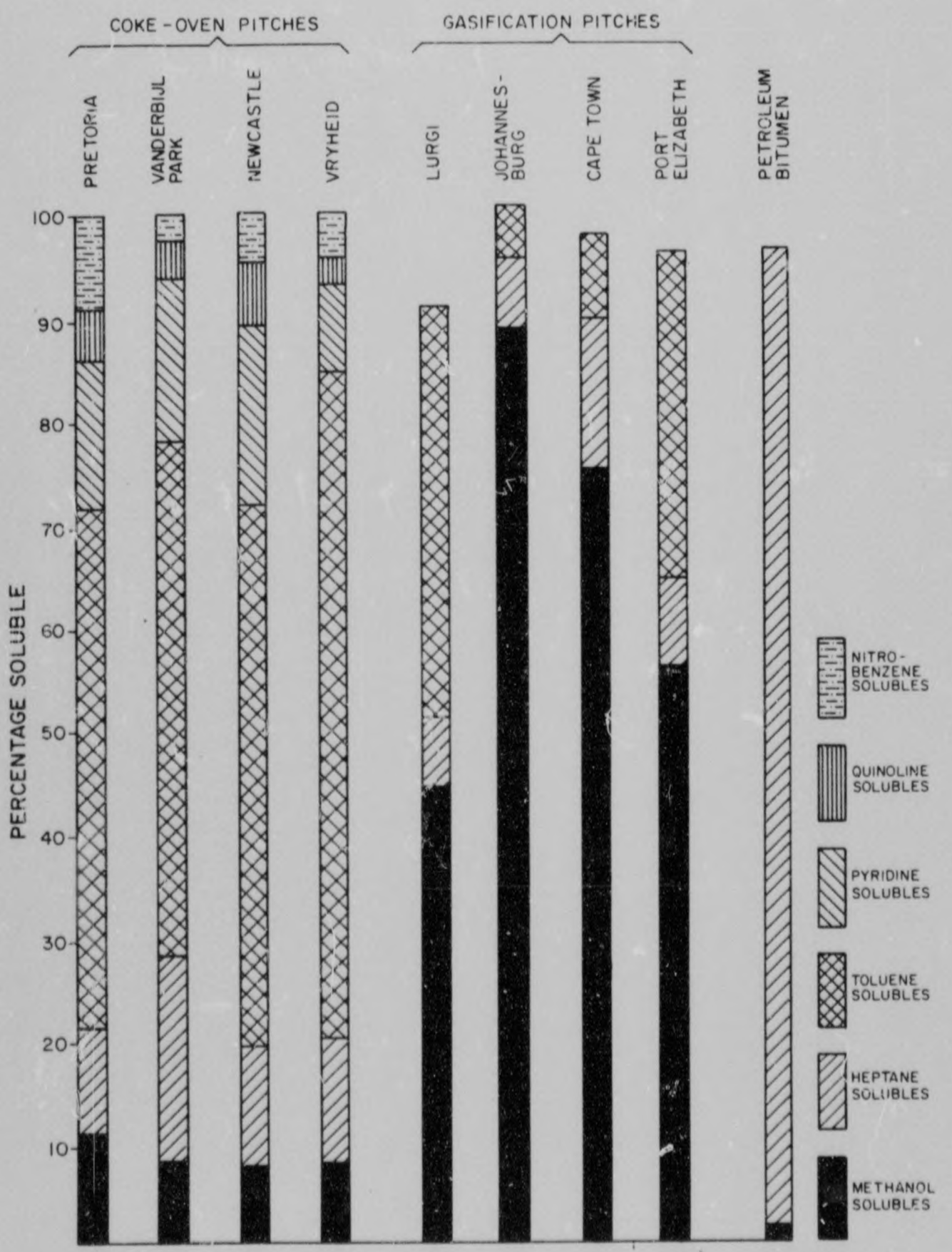


FIGURE 2-14

SOLVENT FRACTIONATIONS OF PITCHES DERIVED FROM SOUTH AFRICAN CRUDES AND A PETROLEUM BITUMEN

chromatography for such purposes, and pointed out that the class of hydrocarbon influenced the retention volume, paraffins and polyaryls differing appreciably from cata-condensed aromatics.

The author's method is described in Appendix A 2.1 and average masses of the methanol, n-heptane and toluene extracts are shown in Table 2 - 10.

TABLE 2 - 10
THE MOLECULAR MASSES OF THE PITCH EXTRACTS

Pitch	Methanol	n-Heptane	Toluene
Coke-oven pitches			
Pretoria	310	310	960
Vanderbijlpark	290	310	-
Newcastle	300	330	960
Vryheid	290	280	-
Lurgi pitch			
Sasolburg	310	310	-
Vertical retort pitch			
Johannesburg	310	310	960
Cape Town	-	320	-
Port Elizabeth	320	320	-

The masses of the methanol and n-heptane extracts are similar to corresponding results obtained by Bartle et al. (1969). In order to get a comparison of parameter values of the toluene extracts of pitches of different origin, it was assumed that these extracts of coke-oven pitches had the same value (960) as that determined from a vertical-retort pitch. In fact, the GP chromatogram of the former indicated a wide range in the masses of the constituents and it was difficult to get an accurate mass value.

2.2.3.3 Spectroscopic studies

Infra-red spectra were obtained as described in Appendix B. These were similar to the spectra of the tar oils (Figure 2 - 9) though there was a decline in resolution and spectral features.

As in the case of the IR spectra, there was some loss in resolution of proton magnetic resonance spectra of the extracts though they were similar to those given by the respective oils (Figure 2 - 11). The structural parameter values were calculated and these are given in Appendix C (Tables IV, V and VI).

2.2.3.4 Microscopic and X-ray investigations

The pyridine, quinoline and nitrobenzene extracts and nitrobenzene insolubles were examined by reflected polarised light microscopy and x-ray diffraction spectroscopy in an attempt to study the carbonaceous mesophase content in these fractions. This mesophase has been identified in coal tar pitch extracts and other hydrocarbons (White, 1974) as a distinct stage in the conversion of organic precursors into graphite. It has been commonly reported in publications dealing with the pyrolysis of pitches and was previously associated with the quinoline insoluble matter (Dubois et al. 1970).

Polarised light microscopy is suitable for the identification of this matter because the strong optical anisotropic characteristics begin with the parallel alignment of the mesophase molecules and the polarised light response of a polished section can be used for their identification.

The microscopic investigations were performed by mounting the carbon in Araldite moulds under reduced pressure, 200 mm Hg, and using the mixture of six parts adhesive Araldite to one part hardener and allowing to set at room temperature for 24 hours. The samples were ground for approximately one hour which was adequate to expose sufficient of the carbon surface for microscopy. A Struers, Scientific Instruments, diamond-paste grinding machine was used for this purpose. The rough grinding was done on a 600 grade Struers adhesive grinding paper. This was followed by a rough polishing for one hour with 7 µm diamond paste. Finally the samples were polished with Struers C grade polisher.

The polished samples were examined under a Leitz Wentzar Orthoplan microscope using reflected light and crossed Nicol prisms. The specimens were photographed under these conditions.

2.2.3.5 Discussion of results; methanol, heptane, and toluene extracts

The solvent fractionation analyses shown in Figure 2 - 14, indicate that there are substantial differences between the composition of pitches obtained from the different sources. As in the case of the oils, the coke-oven pitches tend to form one type and the Lurgi and vertical-retort pitches comprise another, particularly in respect of their solubility in methanol and toluene. The petroleum bitumen comprises a third type having a low solubility in methanol and being almost

completely soluble in n-heptane.

Insofar as the solubility of the pitches in methanol, n-heptane and toluene may be taken as an indication of the content of polar molecules, paraffinic molecules, and aromatic molecules respectively, it may be said that coke-oven pitches mainly consist of neutral aromatic molecules, that gasification pitches consist of molecules containing polar groups, and bitumens consist of non-polar paraffinic groups. Coke-oven pitches have a similar content of polar and paraffinic material and in all cases the toluene-soluble extract comprises the greatest proportion of the pitch.

Further detailed information is given by the infra-red and proton magnetic resonance spectra of the various extracts.

As in the case of the tar oils the aromaticity of the methanol, n-heptane and toluene extracts was assessed from the ratio of the optical densities at 3050 cm^{-1} and 2935 cm^{-1}. The aromaticity of the oils (reported in Table 2 - 6) and of the solvent extracts of the corresponding pitches are shown in Figure 2 - 15. In all cases the coke-oven pitches appear to be less aromatic than the oil fractions. As would be expected, the n-heptane fraction was the least aromatic of the pitch extracts and the methanol extract was most aromatic in the majority of cases.

The results of the examination by proton magnetic resonance spectroscopy were not in complete agreement with the conclusion drawn from the infra-red study as regards the relative aromaticity of the oils and the various pitch extracts. The values of the structural parameters are given in Appendix C, Tables lV-Vl. These results show that in each case the proportion of aromatic carbon (F_a) in the oils was more than that in the methanol or heptane extracts but less than that in the toluene extracts. It has been mentioned that other workers (Le Tourneau, 1965 and Le Roux, 1969) have found that infra-red methods are unreliable for determining the proportions of paraffinic groups in complex substances. The aromaticity of the pitch extracts may be demonstrated from the ratio $H_A/H_\alpha/H_\beta$ as illustrated in Figure 2 - 16. These results indicate that, as in the case of the tar oils, in terms of aromaticity the coke-oven pitches form one type whereas the Lurgi and vertical-retort type form another. The aromatic character of the coke-oven pitch extracts was greater than that of the vertical retort pitch extracts, while the bitumen had very little aromatic character.

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