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INVESTIGATION INTO THE POSSIBILITY OF PRODUCING ORGANIC CONTROLLED RELEASE FERTILIZERS FROM OXIDISED COAL

William Letlape Tsatsi

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

Johannesburg, 2005

DECLARATION

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

_____.

(Signature of candidate)

_____. day of _____. (year)_____.

Abstract

Fertilizers are defined in the broadest sense as products that improve the levels of available plant nutrients or chemical and physical components that directly or indirectly enhance plant growth, yield and quality. The aim of this study was to produce slow controlled release fertilizers from oxidised coal.

Two types of coals namely, Waterberg and Twistdraai (products, middlings) were utilised for the production of humic acids through slurry phase oxidation. The highest yields of humic acids were obtained in Waterberg and Twistdraai products samples. Subsequent to that, a nitrogen element was successfully inserted into the humic acid substrate. Humic acids are potential feedstock for modern manufacturing of organic fertilizers. The chemical substances regarded as hazardous to human consumption or those elements that negatively impact on the soil were significantly less detectable.

Dedication

To my dear mother, the late Ms Francis Moepeng Tsatsi who cherished education, my beautiful wife Minnete Tsatsi and wonderful kids: Boitumelo, Itireleng and Moepeng for their unconditional love and trust bestowed upon me!

Acknowledgements

My thanks to the following distinguished persons: Professor Rosemary Falcon and Dr Herman Louwrens for their guidance throughout the entire project. My gratitude also goes to Pat Skhonde, Kgutso Mokoena and Joseph Mpinga from Sasol Technology R&D for their continued support. I would also like to thank the entire management of Sasol Technology R&D for the financial assistance and support.

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NOMENCLATURE

Vs = volume of base used with the coal

Vb = volume of base for the blank

Vs = volume of acid used with the coal

Vb = volume of the acid for the blank

LOI = Loss of ignition

MMB = mineral matter basis

Chapter 1

1 INTRODUCTION

1.1 Background

Fertilizers are defined in the broadest sense as products that improve the levels of available plant nutrients or chemical and physical components that directly or indirectly enhance plant growth, yield and quality.

Fertilizers may be divided into two broad groups, organic and inorganic. An organic fertilizer is derived from a living plant or animal source. These types of fertilizers are termed slow-release fertilizers. They are characterised by a slow release of nitrogen, longer residual time, low burn potential, low water solubility and higher cost. In slow-release fertilizers, nitrogen in an organic moiety is slowly released and become available for plant use because the organic nitrogen (NH_2) must be reduced (converted) by micro-organisms to ammonium (NH_4) or nitrate (NO_3). The NH_4 and NO_3 are readily useable and absorbed by plant roots. The other function is that of the hydrophobicity of the organic framework which slows down the leachability of the nutrients from fertilizers.

Inorganic fertilizers are manufactured from non-living materials. Rock phosphate for example, is a common source of phosphorus in inorganic fertilizers. This is immediately available to plants from the nutritional point of view. However, they have three disadvantages. They are subject to leaching (hydrophilicity, water-loving), which occurs when fertilizers are washed by rain or irrigation water to below the level of the plant roots. Nitrogen is particularly susceptible to leaching. In addition, a heavy application of inorganic fertilizers can ‘burn’ (acid formation) seedlings and young plants. A third problem associated with the use of inorganic fertilizers is that heavy applications can

build up toxic concentrations of salts in the soil and create chemical imbalances.

N-P-K represents the chemical symbols for three major nutrients (Nitrogen, Phosphate and Potassium) that make up the inorganic fertilizers.

Plants use nitrogen to manufacture chlorophyll which is important for new plant growth. Turf grass suffering a lack of nitrogen will turn light green or yellow, and leaves will die starting at the tips. The second element listed on a fertilizer package, phosphorus is an important plant nutrient because it assists in the aging of tissues and stimulates root growth. The element is normally available to plants in the form of phosphates. Potassium is the third of the “big three” nutrients. Potassium is essential in the manufacture of sugar, starches and proteins.

Fertilizers can also contain small amounts of other elements (trace elements) which are necessary for healthy plant growth. These substances are iron, calcium, magnesium, sulphur, manganese, zinc, boron, copper, molybdenum and chlorine.

The low cost and the easy production of inorganic fertilizers made it difficult for the organic fertilizers to be attractive and hence man became distracted from the importance of organic fertilizers. Large industrial companies took advantages of the N-P-K discovery and extensively marketed these products in such a way that little impact was left for the organic fertilizers. The usages of the inorganic fertilizers, has in some other ways caused serious environmental problems. The environmental impacts aroused from the leaching of these water-soluble acidic N-P-K fertilizers during erratic rainfalls into the rivers, defeating their value as good fertilizers.

As stated earlier, slow-release fertilizers are expensive to produce and an opportunity, therefore, exists to produce organic fertilizers from feed stocks that contain organic materials that are cheaper and are able to supply the plants with nitrogen characterised by the slow rate of release. This type of organic material can be obtained from coals. These organic materials are termed humic substances. They can be extracted from oxidised coal using alkali solutions such as NaOH and others, depending on the organic composition, rank and grade of the coal.

1.2 Motivation

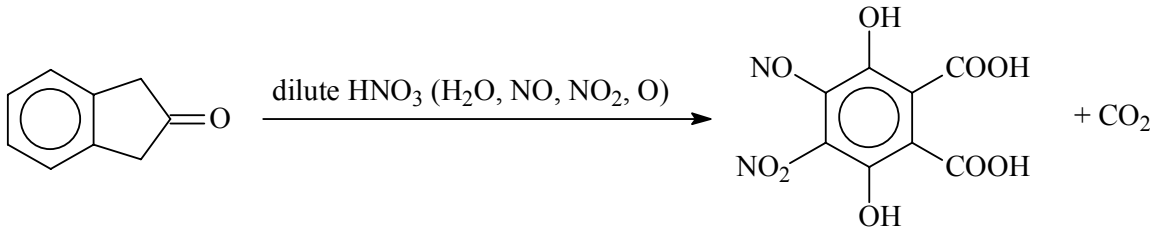
Sasol has yearly an excess of fine coal available as a result of an imbalance between its gasification of coarse coal and a limited installed capacity of boiler capacity for the fine coal fraction. The Twistdraai export plant also produces a portion of discard fines as a by product from the beneficiation process. The excess of fine coal is stored in SASOL's dedicated fine coal storage dams for future recovery, for purposes such as froth flotation and fine coals pelletisation. Waste fine coal is also available outside Sasol. The opportunity therefore, exists to utilize these fine coals as valuable source of carbon for organic fertilizers or development of organic materials as feed stocks.

1.3 Aim

In the past, black soil in the form of compost was used to improve the physical condition of the soil. The presence of organic materials in the compost played an important role in the conditioning of the soil. The aim of the study is to produce an organic molecular substance from oxidised coal and bind nitrogen (N) to it in such a way that, the release of nitrogen (N) can be controlled if the final product is used as fertilizers with appropriate characteristics.

1.4 Objectives

For the purpose of this study different coal types would be oxidised at different elevated temperatures. Subsequent to that humic acids which are regarded as organic materials would be extracted from the oxidised coals using alkaline solutions. Nitrogen element would be inoculated into humic acids through nitration and finally the nitrogen content will be increased by the ammoniation process of the resulting material. The following reactions were proposed in accordance with the basic organic chemistry for both nitration and ammoniation:



$$R\text{-}COOH + NH_3 \longrightarrow R\text{-}COONH_4$$

$$R\text{-}OH + NH_3 \longrightarrow R\text{-}ONH_4$$

Schematic reaction of nitric acid oxidation of coal, representative model, and ammoniation of the resulting material

The nitration process (proposed mechanism above) was used to bind the nitrogen onto the rings of the aromatic structure of the humic acids. Further more it was hoped that the proposed ammoniation process would follow the path outlined above.

It was presumed that after inserting nitrogen via nitration and subsequently ammoniating the resulting material, organic nitrohumic acid salts would be

formed and the reverse reaction will occur in the soil during their application as fertilizers in the presence of water. The release of these ammonium groups will be somehow controlled by the hydrophobicity of the organic part of the salts and thus the process will be slowly occurring. The synthetic process will also increase the salt index of the humic acids giving them one of the required properties of fertilizers.

Chapter 2

LITERATURE REVIEW

2.1 Introduction

In the 19th century good crop production was derived from dark, black soils rich in organic or composted organic materials which boosted the soils fertility compared to other humus poor soils [Humus Theory]. By the 20th century researchers became aware of the major inorganic elements that were responsible for plant growth. Inorganic mineral NPK containing fertilizers became the pillars of the agronomic nutrition throughout the developed world. Subsequent to that the introduction of cheaper ways of manufacturing the inorganic NPK containing fertilizers made the major roads of the "Humus theory" to become less important [Chen and Aviad, 1990].

Most fertilizers used today improve crop yields and are made from inorganic materials. They carry the connotation of being useful for problem soils or soils needing treatments to produce maximum yields [Hoffmann et. al 1992]. Inorganic fertilizers are significantly water soluble and contain potential polluting elements such as nitrate nitrogen which can more readily be leached from the soil, contaminating surface and ground water thereby reducing the effectiveness of the fertilizer as plant nutrient. Controlled or slow release fertilizers, which overcame this problem, are available; however, they remain expensive to produce.

Studies have shown that the addition of organic soils amendments or soil conditioners containing humic substances (HSs) benefit plant growth. They are natural compounds that are widely distributed in nature. Their structure, composition and properties have still not been clearly elucidated. The properties of HSs are determined by their composition, which results from the humification of living matter. HSs are intermediate phases in the humification process and traditionally are divided into several groups: fulvic acids (FAs),

humic acids (HAs) and humin [Pokoma′ et al. 2001]. Humic substances may be extracted from various substrata (compost, manure, peat, brown and brown–black coals, etc).

2.2 Different processes used to extract humic substances (HSS) from a variety of coals

2.2.1 Humic/fulvic acids extracted from leonardite

The naturally oxidised lignite (rich in available humic substances) is termed leonardite, after A.G. Leonard of North Dakota Geological Survey [Patti et al, 1988]. In this process humic acids are extracted from the natural oxidised lignite by alkali solutions. The 'Enersol' product is marketed by American Colloid of Chicago. Even though there are no documented field trials on this product, it is highly accepted because of popularity amongst Italian farmers and those from America [Brownell et al.1987; Irion et al, 1988].

Another process utilising alkali solutions patented by 'Actagro' of Fresno, California solubilizes humic acid fractions from leornadites, which are mixed with liquid phosphate fertilizers. [Marihart V.P.; Actargo, Personal Communications]. These fertilizers are used as 'starters', i.e. the solution is applied in early seasons for soil treatment and used as foliar sprayers. The claims of successful applications of Actargo product have been documented by [Brownell *et, al* 1987].

Borregaard LignoTech is a process that has been used to produce two highly purified extracted potassium humates namely Borresol HA-2 and Borresol HA-1 for agricultural use. Borresol HA-2 is a conventional potassium humate derived from leonardite and Borresol HA-1 is a modified potassium humate derived from leonardite. As spray dried powders, both offer a minimum total organic content of 70% (50% humic & 20% Fulvic) as determined by the

barium chloride method. In the liquid form, both products are offered with a minimum total organic acid content of 15% with the same humic/fulvic ratio [Detrick J 1997].

2.2.2 Humic extracts from common lignite and other coals

Common lignite has higher 'humic acids' content than bituminous coal. However a process called "Dry oxidative depolymerization of coal" is used to synthetically oxidised lignite and other coals to produce biochemically active humic substances. This process was developed by Eniricerche in Italy .The process convert almost any coal into a high yield of humic acids, lignite yield products with the highest abundance of chemically active functional groups [Rausa et al, 1992].

Nitric acid oxidation and Ammoniation of coal is another process that has the potential value of producing humic acids from oxidised coal. Berkonitz et al. 1970 found that this process could only be used for low rank coal. [Coca et al. 1984] down played the fact that nitric acid oxidation is only related to one type of coal. They affirmed that different types of coal may be used for this process, depending on the conditions given.

Mazundar, (1982); Muzundar et al. 1988, took this work in a different direction at the Central Fuel Research Institute of India, whereby extensive research using nitric oxidation and ammoniation of coal, which included the construction of a pilot plant. The end products were designated as 'ammonium polycarboxylate' (AMP) and composite ammonium polycarboxylate (CAMP). These products according to the results obtained outperformed urea a more conventional slow -release fertilizer.

In South Africa a relatively new process was developed and called "oxygen/air-driven wet oxidative conversion of reactive coal". The oxidation experiments were carried out in a two-litre-capacity auto clave. The typical

experiment was stirred at (1100r/min) slurry of 420g of 25μm median-sized bituminous South African coal. In this process humic acids with high yields (85% m/m) were obtained and fulvic acids were regarded as by-products [Dekker et al, 1990]. According to the authors this process is suitable for different kinds of coals and it is relatively inexpensive.

2.2.3 Humic acid structure and properties

Humic acids are a mixture of organic acids resulting from the controlled oxidation of carbonaceous matter. The structure is believed to be that of condensed cyclic rings, mostly aromatic in nature with carboxylic acid groups (-COOH), hydroxyl-substituted benzenecarboxylic acids, phenolic (-OH) and carbonyl (-C=O) groups and aliphatic. Humic acids are alkali – soluble but acid insoluble [Mehmet Yildirim et al (1997)]. Figure 1 below shows the model structure of humic acid [Stevenson 1982].

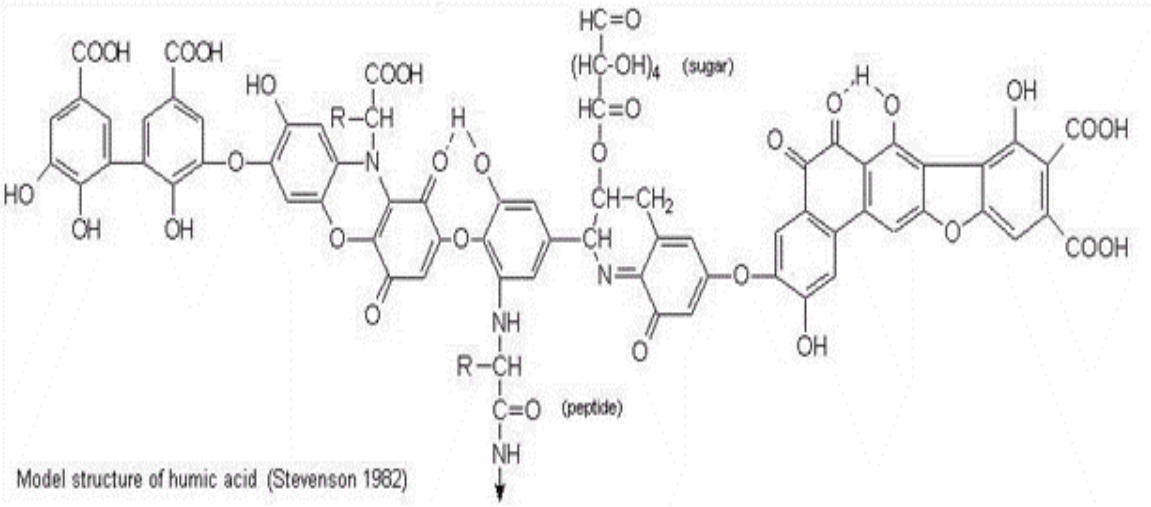


Figure 1: Model structure of humic acid [Stevenson 1982]

2.2.4 Oxidation process

The oxidation of coal attracted attention of researchers for three main reasons [Jacobus J Bergh et al (1997)]: first, to gain more knowledge about its auto ignition (a problem encountered in the storage and transportation of coal); second, to obtain information on the structure of coal; and third, to convert coal into acids, commonly grouped into humic (water-insoluble) and fulvic (water-soluble) acids.

It has been reported that preliminary oxidation of bituminous coal can influence not only the properties of the chars from carbonization [H Teng et al (1997)], but also that of the activated carbons by subsequent activation. Introduction of oxygen at 200 °C to the coal can effectively promote cross-linking reactions between the coal structures. The indication was that oxygen functional groups, either originally retained in the coal or introduced by oxidation, play an important role in reducing the caking of the bituminous coals, thus resulting in an increase in the surface areas. With the oxidation of coals, the resulting chars become more active in CO_2 (activation) than the unoxidised coals.

It was also found that the aromaticity increases with oxidation [D Lopez et al (1998)], which indicated that the non-aromatic part of the coal is the first to be affected. With the benzylic positions being the most reactive, they are the first to be oxidized to produce carbonyl groups and carboxylic acids; (Ar-CH_2-Ar) are very susceptible to self oxidation, generating groups such as Ar-CO-Ar. High temperature oxidation produce mainly carboxylic acids, esters and anhydrides, while the low-temperature oxidation hydroxyls, carbonyls and esters are found.

It was also reported that at temperatures higher than 150°C, humic acids are generated through coal oxidation. During coal oxidation at low temperatures, the concentration of these species (functional groups) increases significantly,

in particular hydroxyl groups. It was argued that at high temperatures (150°C) decomposition of carboxyl and carbonyl groups occurs, leading to the production of CO_2 and CO along two independent reaction part ways. These reactions were formulated as follows:

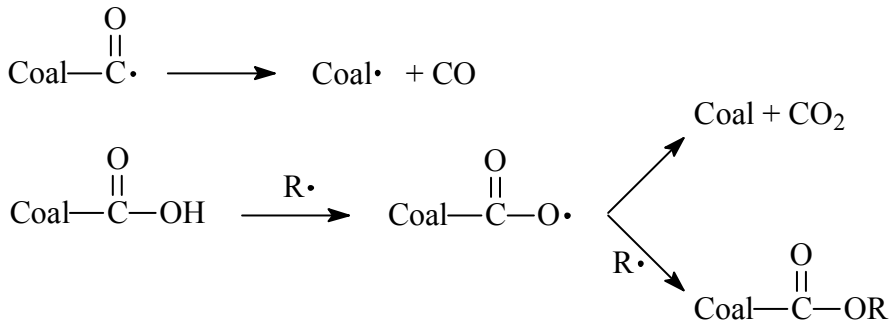


Figure 2: Schematic reaction of oxidised coal.

2.3 How humic acids work

It should be noted that humic acids are not fertilizers; they are chemically and structurally different from commercial fertilizers. Commercial fertilizers have high salt index approximately more than 1%, while humic acids have low salt index less than 1%. Salt index is an index used to measure the solubility of chemical compounds. However humic acids have properties that have confused many people to think that they are fertilizers and below are some of the properties of note:

Water penetration enabled, micronutrient transference and water sequestration and clay disaggregation all possessed by humic acids.

2.3.1 Water penetration enabled

Humic acids cause the clay particles to stand on end, allowing water penetration; it does this in two ways:

1. First, it segregates salts and removes them from the surface of the clay particle. The net negative charges resulting causes the clay particle to repel each other, loosening the soil structure.
2. Second, a carbon group on the humic acid molecule (carboxyl group) bonds with the edge of the positively charged particles. This breaks the attractive force between the positive charge at the edge of a particle and the negative charge or the flat surface of another (Figure 3).

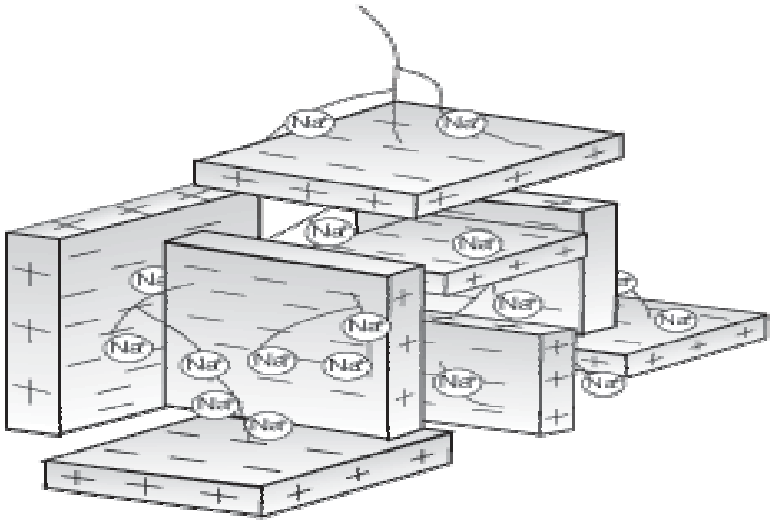


Figure 3: Humic Acids showing water penetration

As humic acids penetrate compacted clay platelets, it segregates salts (positive ions) and removes them from the clay particle surface. This restores a negative charge to the face of clay platelets, causing them to repel each other.

2.3.2 Micronutrient transference

Humic acids can acquire positive ions under one condition and release them when conditions change. It picks up ions depending on the availability of a different ion to replace the one released. Positive ions are called cations and the pickup and release property is called cation exchange capacity. Humic acids hold cations so they can be absorbed by a plant's roots, improving micronutrient exchange and transference to the plant's system (Figure 4).

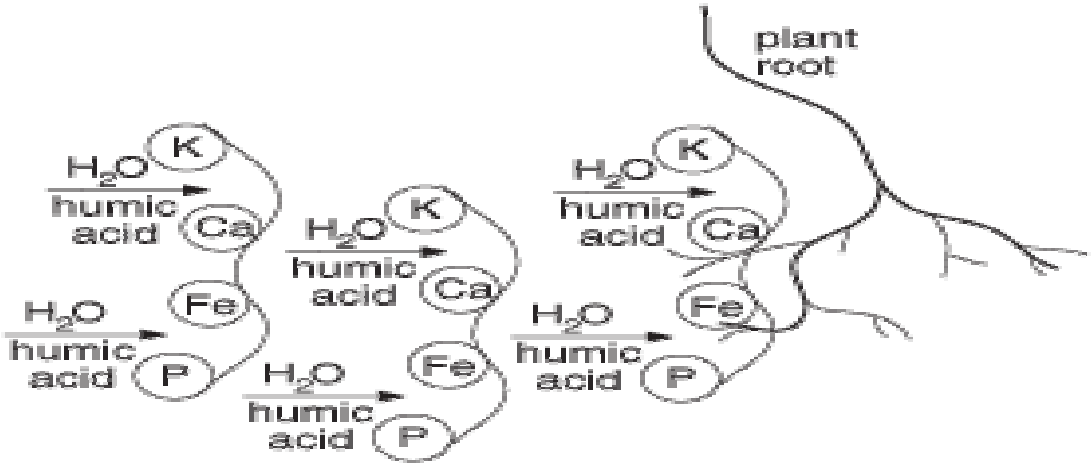


Figure 4: Micronutrient transference

2.3.3 Water sequestration

Humic acids slow down water evaporation from soil. This is important in soils where clay is not present or in a low concentration, in arid areas, and in sandy soils without the capability to hold water. In the present of water, cations absorbed by humic acids partially ionize and move a short distance away from the humic acid oxidation sites. This restores part of the bonded ion's positive attractive force. Water sequestration by humic acids is illustrated in Figure 5.

Humic acids hold cations in such a way that they can be more easily absorbed by plant's roots, improving micronutrient transference to the plant's circulation system.

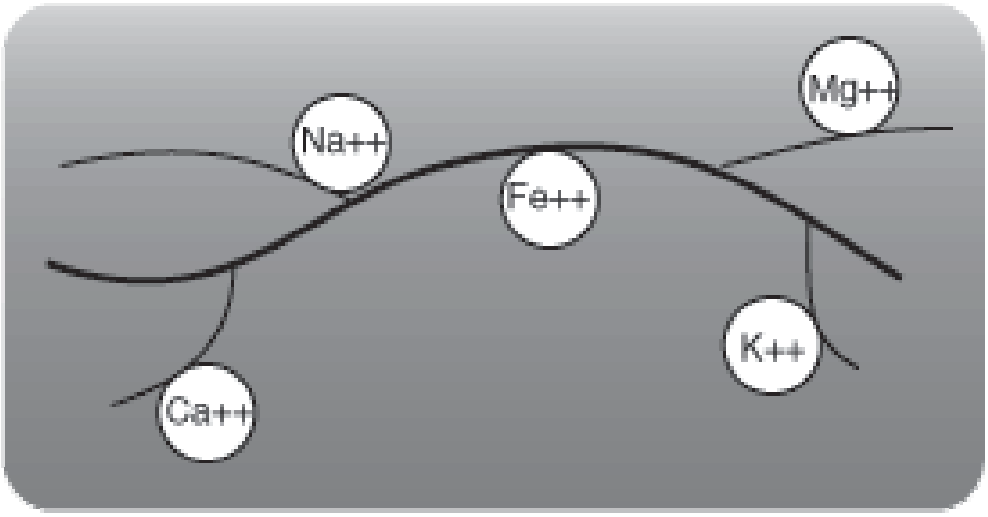


Figure 5: Positive ions found in humic acids

2.3.4 Clay disaggregation

Soils with high clay content can become so dense and compact that they may resist plant rooting. Humic acids has the ability to neutralize the negative charges found in clay and making clay platelets loose to allow water penetration.

2.4 Basic Infra-red technique

Infra-red spectroscopy is a technique for the study of a molecular structure that is based on the absorption of infra-red radiation by the vibrational modes of the bonded atoms. Essentially, there are two fundamental vibrations; stretching and bending or deformation [F. J. Stevenson, 1994].

The infra-red have provided evidence for the presence of various molecular groupings, including COOH, OH, CH, CH_2 CH_3 aromatic C=C hydrogen – bonded OH, NH and C= O [Ziechmann, 1964; Kukharenrenko et. al]. This technique will assist in the determination of molecular structures of coals that are oxidised. Table 1 below depicts a broader picture of some of functional groups found in coal and oxidised coal.

Table 1: General absorption peaks for functional groups found in coal

Vibration Frequency (cm^{-1})	**Functional groups**
~ 1438	**Aromatic, C=C, CH_3, CH_2**
~ 1380	**CH_3 (symmetrical), CH_2 (cyclic)**
~ 1607	**Undefined (Patti et al.) C=C aromatics**
~ 1300- 1000	**Ethers**
~ 2500 - 3600	**OH (alcohol, phenol, carboxyls)**
~ 1533	**NO2 (symmetric ~1350- 1300) Ass (1560- 1500) Patti et al NO2 attached to aliphatic and not aromatic**
~ 1705	**C=O**

Chapter 3

3. EXPERIMENTAL

3.1 Coal preparation

The purpose of coal preparation prior to its actual analysis is to get a general representative sample, this is due to the fact that coal composition is not homogeneous and analysis without preparation will almost always result in inconsistent (wrong) results. The method used in the preparation of coal is called the quartering and conning which is followed by crushing and sieving.

Samples of coals from Twistdraai consisting of (products, middlings and discards) and Waterberg collieries were received. The Waterberg coal was in the form of washed products.

During the preparation the coal was emptied (poured) on the ground and mixed thoroughly with a spade. This is done by taking from the sides (edges) and putting on top while moving around the coal, this is like lifting up the coal to form a cone shaped heap (conning):

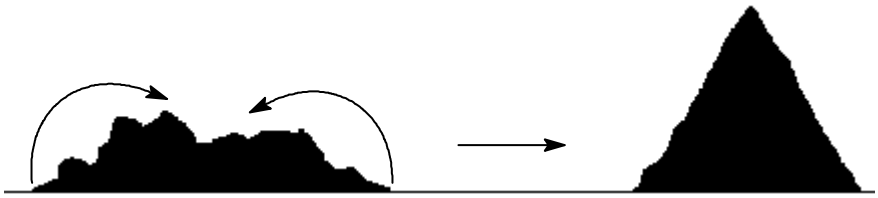


Figure 6: Shapes of the coal sample

The cone-shaped coal heap is then divided into four equal parts (quartering) with a spade, a half of which is taken for further conning and quartering following the same procedure as above; this is illustrated schematically below:

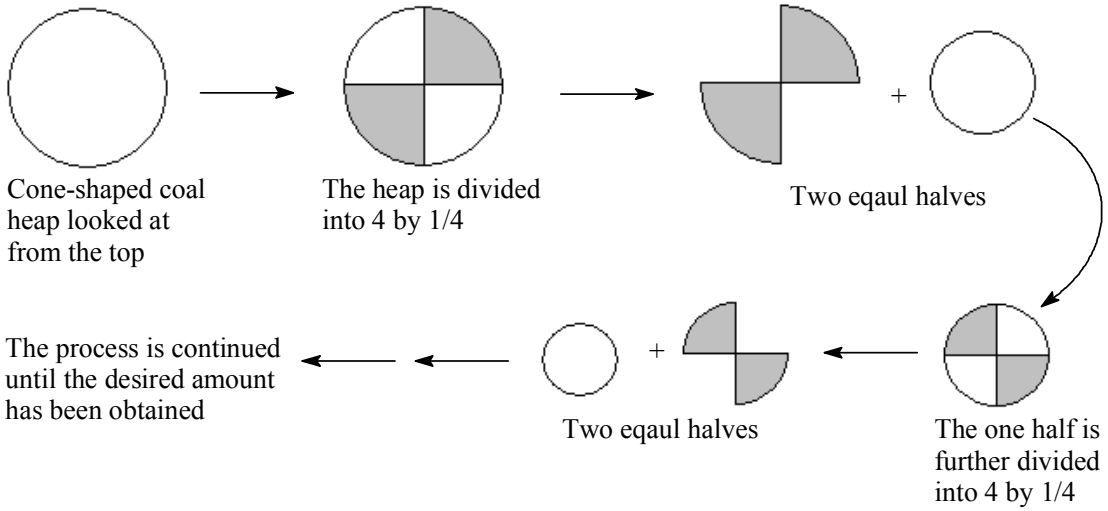


Figure 7: Quartering of the coal sample

During the process of quartering and conning the coal is milled with the milling machine for better handling. Finally a finely milled (~ 150μm, particle size) sample of a desired mass (~ 420g) as the head sample is taken for analysis; and if proper procedure is followed then the sample should be a representation of the starting bulk material. Samples were then prepared to be stored under nitrogen to reduce further oxidation taking place. Head samples were characterised through petrographic and ultimate analyses before oxidation.

3.2 Proximate analysis

This is the analysis that determines the moisture, the ash content and volatile matter content, in the analysis samples are prepared to pass 212μm. Modern instrumentation allows the analyses to be conducted semi automatically using dedicated TGA instrumentation.

3.3 Basic aspects of coal petrology

Coal petrology involves the microscopic examination of coals together with the interpretation of the analytical data and it provides valuable information regarding organic composition, maturity and the associations of the organic matter and minerals that the coals contain. Petrographic data should be used, together with the chemical and physical parameters, for full characterisation of coals necessary to gain insight into their behaviour in the technological processes.

3.3.1 Preparation of a petrographic block- Reference: ISO 7404-2:1985

A representative air dried sample of Waterberg and Twistdraai samples of which those of Twistdraai were in forms of (products, middlings and discards) were crushed to an upper size of 1mm. A 15g of each portion from the above mentioned samples was mixed with a binder and formed into particulate blocks. One face of each block were ground and polished to provide a suitable surface for the reflectance microscopy under oil immersion using reflected light.

3.3.2 Maceral analysis (% by volume) – Reference: ISO 7404-3; 1994

Macerals are the microscopically recognisable individual organic constituents of coal and they are recognised on the basis of their reflectance. A given maceral may differ significantly in composition and properties from one coal to another. Three types of macerals in coal are; Vitrinites , exinites and inertinites.

The polished surface of the prepared block is examined under oil immersion using a reflected light microscope with a total magnification of between 250 and 500. The maceral groups are distinguished by their relative reflectance, morphology, colour, and shape, size and polishing hardness.

The proportions of the individual macerals are determined by a point count technique. Transverses are made at 0.5mm intervals across the polished surface of the petrographic block. The material lying under the intersection of the cross line in the eyepiece of the microscope is identified and the point is counted. An automatic point counter is used to record 500 points on coal and to calculate the percentage of each component at the end of the analysis. The results were expressed as a percentage by volume to the nearest integer.

3.3.3 Rank determination using reflectance analysis of vitrinite macerals – Reference: ISO 7404-5; 1988

The rank of the coal is determined by means of reflectance analysis of the vitrinite macerals in the sample, according to the ISO 7404-5; 1988, 100 readings on different vitrinite particles evenly distributed over the polished surface of the petrographipic block are usually taken on the lignite sample and 250 on the bituminous and anthracite samples. The results are expressed as a mean reflectance value and also in the form of a reflectogram which shows the vitrinite–class distribution.

The reflectance distribution can provide valuable information on whether the sample is made up of a mixture or blend of two or more coals of different rank, or whether the coal contains heat affected material.

3.4 The Slurry phase oxidation of coal

The aliquots (420g) of both Waterberg and Twistdraai (products and middlings) samples were oxidised by the following procedure**:**

Coal (420g) and water (700mℓ) were slurried in a 2ℓ stirred reactor at a speed of 1100rpm. The reactor was constantly pressurised to 4 MPa with nitrogen. The autoclave was heated with external heaters of temperature profiles of 120°C, 140°C, 160°C, 180°C, and 200°C. Oxygen was allowed to flow through the slurry at a rate of 8ℓ/min. After one hour the oxygen flow was terminated, the reactor cooled down to room temperature and pressure released to atmospheric.

The slurry consisted of oxidised coal (insoluble in water and hereafter referred to as “oxicoal” and a solution of fulvic acids hereinafter referred to as “oxifulvic acids”) in water. By filtration, the oxicoal was separated from the solution of oxifulvic acid in water. The oxicoal was dried in the oven at a temperature of 105°C for a period of 18 hours (see flow diagram in Figure 8).

3.4.1 Extraction of the humic acids

The extraction procedure used was taken from the work that was carried out by Louwrens (1989). 10 g of the dried oxicoal was added into a solution of sodium hydroxide (10g) in 400cm^{3}of distilled water. The mixture was refluxed at 100°C for 5 hours. The reaction mixture was centrifuged at 2500rpm for 15 minutes and the supernatant (humic acid in solution) was collected. The residue was washed with 0.1M NaOH (2×200cm^3) followed by 400cm^3 distilled water. The filtrate was decanted to the supernatant. The residue was also washed with 200cm^3 of 10% HCl followed by 200cm^3 of distilled water.

The residue was dried at 100°C and collected for proximate and ultimate analysis for mass balance.

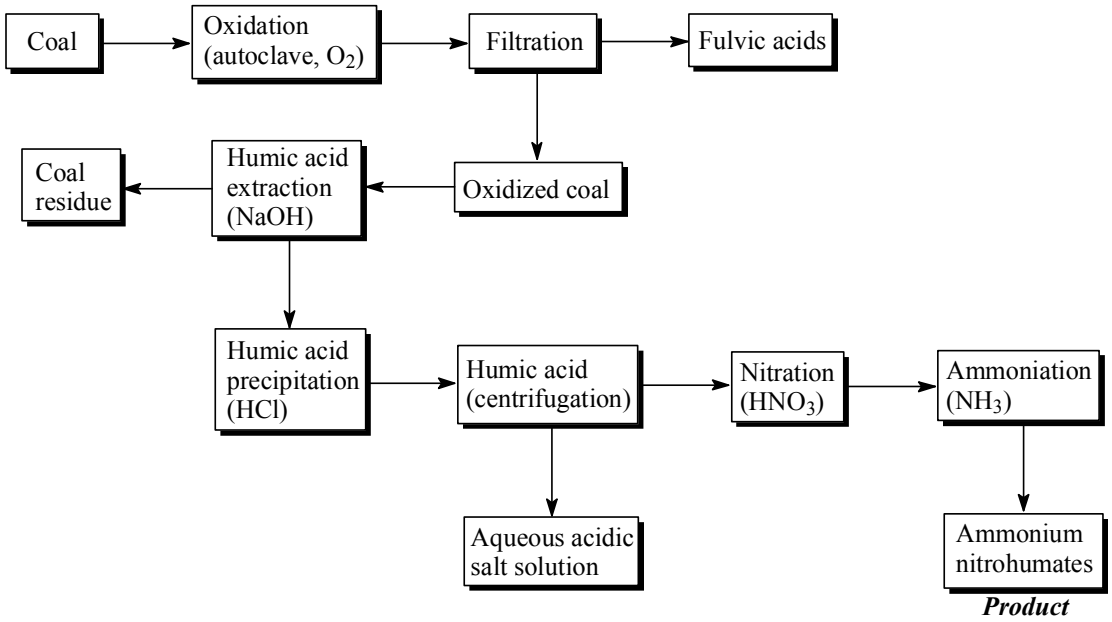


Figure 8: Flow diagram for humic acids production and insertion of Nitrogen element through nitration and ammoniation

3.4.2 Characterisation of the oxidised products

The oxicoals were characterised using Ultimate and surface dependable techniques that indicated oxidation and types of oxygen groups on the coal surface (i.e. the determination of carboxylic groups, the phenolic groups, as well as the total acids). The humic acids extracted from oxicoals were also investigated by the application of Fourier Transform Infra Red spectroscopy (FTIR).

3.4.3 Ultimate analysis

The method ASTM D5373 used for the determination of carbon, hydrogen and nitrogen while the Total sulphur was determined using ASTM D4239, and oxygen by difference. This was carried out in order to establish whether oxidation has taken place.

3.4.4 Functional groups determination

This determination was carried out to establish the manner in which oxygen binds to the coal surface. The oxygen can bind forming either the carboxylic acids groups (-COOH) or the phenolic groups (OH). The total acids were also determined as described below. The procedures were followed using the work carried out by John Bunt (1997) as reference.

Before any functional group determination, demineralisation of the oxicoal was carried out. About 10g of oxicoal was added to 500cm^3 of a 1mol/dm^3 HCl solution and stirred for a period of 24 hours in order to hydrolyse all carboxylic salts to the corresponding acids form. Excess water was removed from the sample by filtration, and acid removed from the sample by soaking in distilled water. The product was dried in a vacuum oven at 100°C for a period of 6 hours. A correction was made regarding the reduction in ash content following the removal of the carbonate minerals.

3.4.5 Carboxylic acid groups

Carboxylic acids were determined using ion exchange reactions using calcium acetate; the concentration of the acetic acid formed was determined

titrimetrically against standard sodium hydroxide. The reaction scheme for the ion exchange is as follows:

$$2RCOOH + Ca(COOCH_3)_2 \longrightarrow (RCOO)_2 Ca + 2CH_3 COOH$$

About 300mg of the dried coal was added into a beaker together with a solution of 10cm^3 of 0.5 mol/dm^3 calcium acetate and 50 cm^3 of deionised water, the beaker was sealed under nitrogen and the mixture was stirred for a period of 18 hours. After filtration, the sample was copiously washed with small quantities of deionised water and the filtrate titrated against a standard 0.02 mol/dm^3 sodium hydroxide solution using phenolphthalein as an indicator. The amount of carboxylic acids was then calculated using the formula below:

$$C.A = \frac{((Vs - Vb) \times N(NaOH))(\%C_{OXICOAL})}{Coal_{MASS} \times 100}$$

Where: C.A = Carboxylic Acids; Vs = volume of base used with the coal; Vb = volume of base for the blank

3.4.6 Phenolic groups

Phenolic groups were determined from the amounts of the total acid groups and carboxylic acid groups by taking the difference of the two. It was reported in the literature that the sum of carboxylic acid groups and the phenolic groups equals the total acid groups in coal.

3.4.7 Total acids

The method applied provides the understanding of the reaction between excess barium hydroxide and the organic group present. The reduction in barium hydroxide concentration was determined titrimetrically against a standardized hydrochloric acid solution. The reactions involved are shown in the scheme below:

1) 2 ROH +2 RCOOH + nBa $(OH)_2$ →

$(RCOO)_2Ba + 2H_2O + (RO)_2 Ba + 2H_2O(n-2) Ba(OH)_2$

2) (n-2)$Ba(OH)_2$ + 2(n-2) HCl → (n-1) $BaCl_2$ + 2(n-2)H_20

About 1g of the dried coal which was pretreated as described in section 3.4.1 was accurately weighed and added to a solution containing 2g of barium hydroxide in 40cm^3 of double deionised water. The reaction mixture was stirred for 24 hours under nitrogen atmosphere, filtered and the coal residue washed with small quantities of distilled water in order to remove all the barium hydroxide present. The filtrate was titrated against a standardized 1mol/dm^3 HCl solution using bromothymol blue as an indicator. The formula that was used to calculate the total acid groups is:

$$T.A.G = \frac{\left((Vs - Vb) \times N(HCl)\right)\left(\%C_{OXICOAL}\right)}{Coal_{MASS} \times 100}$$

Where: T.A.G = Total Acid Groups; Vs = volume of acid used with the coal; Vb = volume of the acid for the blank

3.5 Infra-red analysis

To determine the nature of the characteristics of functional groups in an unoxidised coal, oxidised coal and humic acid extracted, the instrument 1720-X infrared Fourier Transform Spectrometer FTIR (Fourier transference infra red spectrometry) with the help of Perkin Elmer IRDM software was used. 0.4 mg of the pulverised samples (0.4 mg) of Twistdraai (products and middlings) and Waterberg in unoxidised, oxidised and humic acids was palletised with the addition of potassium bromide (15mg) (KBr). The samples were inserted into the holding of the spectrometer where readings were shown on the PC at different wavelengths depicting different functional units.

3.6 Nitration of the humic acids

The nitration method was carried out following the work carried out by D Schwarzt, L Afielf and R green, 1965. The purpose was to increase the amount of nitrogen content introduced into the humic acid structure.

20g of the humic acids aliquots were mixed into slurry with distilled water (60ml) in a three- neck flask and 180 ml of nitric acid (55%) concentration. These humic acids were derived from oxidised samples of Twistdraai product and Waterberg. The mixture was heated at 65°C in a water bath for three hours after which it was suction filtered. After drying at 65 °C in an oven for two hours, total nitrogen were subsequently determined.

3.7 Ammonium nitrohumates

Dried nitrohumic acids, in 20% water slurry, were treated with a 0.5 N ammonium hydroxide until pH of 7.15 was reached. The slurry was placed in

the water bath at 65°C for three hours. The solution was dried in an oven at 110°C for 16 hours. The solids were washed and filtered and dried for 2 hours. Total nitrogen was determined after the test runs.

3.8 Determination of the Slow release fertilizers (23 February 2004, Analysis of Slow- release fertilizers, CL Wilsnach)

Since there was no standard method used to determine the release rate of nitrogen content from fertilizers, a method was developed by Agri-LASA to establish any slow release fertilizers that reaches the shores of South Africa. The method is as follows:

12.5g of Waterberg and Twistdraai product samples final products produced at 180°C were weighed into 250ml volumetric flasks and diluted to the mark with distilled water. All experimental test runs were carried out at a room temperature. The samples were stirred for 20 minutes and left to settle and filtered after the following hours: 5 hrs, 22 hrs, 8 days and 14days. The samples were analysed for NPK using the Sasol standards methods. The best and accepted time frame should be at least 12 weeks. For this purpose only 14 days was taken.

Chapter 4

RESULTS

4.1 Introduction

In this section results are presented and discussed, starting from the preparation of the coal samples from both the Twistdraai and the Waterberg. Twistdraai consisted of three types, namely: Twistdraai products, Twistdraai middlings and Twistdraai discards. Results for the Twistdraai discards only show the characterisation of the feed while most of the elaboration of the other samples of the Twistdraai was compared with the Waterberg samples. Further more results on the oxidation and extraction of humic acids and their subsequent nitration and ammoniation to produce slow-controlled release fertilizers are also given.

4.2 Coal Analysis

The results in this section indicate the characterisation of the coal feeds of both the Waterberg and the Twistdraai (products, middlings and discards) samples before oxidation. These results include the proximate, ultimate and petrographic analyses. The particle sizes of both the Waterberg and the Twistdraai (products, middlings and discards) were in the range of -150 μm.

4.2.1 Proximate analysis

From Table 2 it can be observed that the Twistdraai product and the Waterberg samples had fixed carbon content of ~ 67.4 and 58.6 % and volatile matter content ~ 32, 6 and 41.4 % respectively. The lower fixed carbon was observed in the Twistdraai discards at 15%. The volatiles of both the Twistdraai middlings and discards were at 29 and 12 % as received

respectively. The ash content of the Twistdraai discards was the highest at 71.24% followed by the Twistdraai middlings at 32.97% as compared to the Twistdraai product and the Waterberg samples each at 12.43 % and 10.30 % respectively.

Table 2: Proximate analysis of the Waterberg and the Twistdraai (product and middlings and discards samples)

	% as received			% Dry Ash Free (DAF)	
Sample	**Fixed carbon**	**Volatiles**	**Ash**	**Fixed carbon**	**Volatiles**
Waterberg	**50.8**	**35.9**	**10.30**	**58.6**	**41.4**
Twistdraai (product)	**49.0**	**35.9**	**12.43**	**67.4**	**32.6**
Twistdraai (middlings)	**30.4**	**26.80**	**32.97**	**44**	**29**
Twistdraai (discards)	**9**	**15.80**	**71.24**	**15**	**12**

4.2.2 Ultimate analysis

The summary of other ultimate analyses of the slurry phase of oxidation of Twistdraai (products and middlings) and Waterberg samples are summarised In Table 10,11,12 in the Appendixes A4, A5, A6. The ultimate analyses of the samples mentioned were reported as received. Table 3 shows the total sulphur of both Waterberg and Twistdraai middlings exceeding those of Twistdraai product sample. Carbon content of Waterberg sample registered 70.16% and was higher than those of Twistdraai (products and middlings) which each contained 69% and 48.41% respectively. There was no significant difference in the oxygen content amongst all the samples

Table 3: Ultimate analysis of the Waterberg and the Twistdraai (products, middlings) samples

Sample	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Total Sulphur (%)	Oxygen (%)
Waterberg	**70.16**	**4.63**	**1.22**	**1.02**	**10.28**
Twistdraai (products)	**69**	**4.35**	**1.87**	**0.94**	**10.05**
Twistdraai (middlings)	**48.41**	**2.72**	**1.10**	**1.42**	**9.85**

4.2.3 The Petrographic composition

4.2.3.1 Maceral and mineral analysis- proportions of organic components

From Table 4 & 5 it is apparent that the inertinites of Twistdraai middlings sample were the highest at ~ 61% MMB as compared to other inertinites such as those of Twistdraai products at ~ 49% MMB and Twistdraai discards at ~ 19% MMB while Waterberg sample was at ~ 41% MMB . The visible minerals were significantly higher in Twistdraai middlings and discards samples each counting at ~ 24 % and 71% MMB respectively ,while those of Twistdraai product and Waterberg sample were very low at ~ 5% and ~6% MMB respectively. The increase in visible minerals was also expected since the ash contents of these samples (Twistdraai middlings and discards) were extremely higher than those of Twistdraai product sample. The highest vitrinite content was observed in Waterberg sample at ~ 84% MMB while the Twistdraai sample showed ~49%MMB. The vitrinites in Twistdraai middlings and discards samples were very low each counting at ~ 12% MMB and 6% MMB respectively.

Table 4: The maceral analyses and visible minerals of the Twistdraai sample based on percentage by volume mineral matter basis

Name of sample	**Total vitrinite (%MMB)**	**Total Inertinite (%MMB)**	**Liptinite (%MMB)**	***Visible minerals* (%*MMB*)**
Twistdraai (products)	**49**	**41**	**5**	**5**
Twistdraai (middlings)	**12**	**61**	**3**	***24***
Twistdraai (discards)	***6***	***19***	***1***	***74***

Table 5: The maceral analyses and visible minerals of the Waterberg sample based on percentage by volume mineral matter basis

Name of sample	**Total vitrinite (%MMB)**	**Total Inertinite (%MMB)**	**Liptinite (%MMB)**	**Visible minerals (%MMB)**
Waterberg sample	**84**	**6**	**4**	**6**

4.2.3.2 Rank analysis

Table 6 indicated that all the samples, Waterberg and Twistdraai (products, middlings and discards) were classified as Ortho–bituminous and ranked all as medium C. Their standard deviation from the classification was < 0.1 which showed a single seam, non blend coal.

Table 6: Rank analysis of feed coal

Name of sample	Rank	ECE- UN in SEAM CLASSIFICATION	Mean Random Reflectance (%)	Standard deviation
Waterberg	**Ortho-bituminous**	**Medium rank C**	**0.65**	**0.05**
Twistdraai (products)	**Ortho-bituminous**	**Medium rank C**	**0.61**	**0.06**
Twistdraai (middlings)	**Ortho-bituminous**	**Medium rank C**	**0.61**	**0.07**
Twistdraai (discards)	**Ortho-bituminous**	**Medium rank C**	**0.61**	**0.08**

4.3 The Slurry phase oxidation of the Waterberg, Twistdraai (product and middlings) samples

The samples of Waterberg and Twistdraai (products and middlings) were oxidised using the procedure as described in section 3.5.1 in Chapter 3 (the slurry phase oxidation method). Results obtained for Waterberg sample are shown in Figure 9**.** It can be observed that mass products of the Waterberg sample decreased with an increase of the temperatures during oxidation. However, it was also observed that by-products, namely, CO and CO_2 of the process increased with the increase in temperature. The amount of these by-products was calculated as:

$$\%C_{(CO2 + CO)} = \%C \text{ coal} - \%C_{\text{oxicoal}} - \%C_{\text{fulvic acid}}$$

The % C of the by-products (CO and CO_2) ranged from 2.86 to 12.6. Increase in the yields of Humic acids is depicted in the figure 9, the highest yield was observed at 180°C and 200°C as 82 and 80 % mass respectively. The lowest yields of humic acids were observed at 120°C.

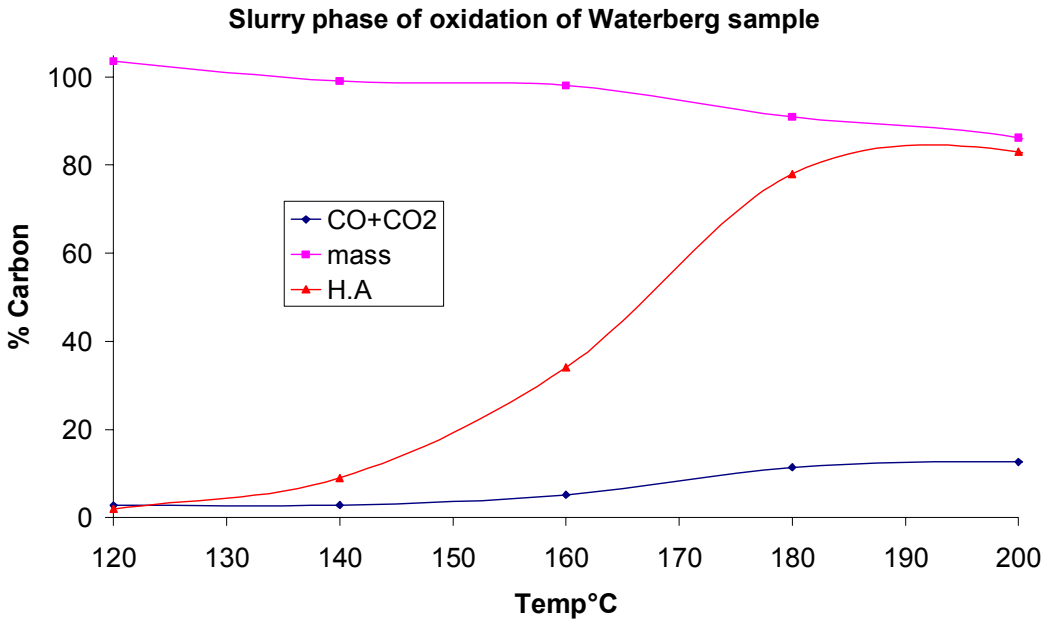


Figure 9: The slurry phase oxidation of the Waterberg sample

The slurry phase oxidation results of Twistdraai product sample are shown in Figure10. Results obtained showed a decrease in the mass of products (Twistdraai product) and an increase in the by-products, and the yields of humic acids with an increase in temperatures. The % C of the CO and CO_2 as by-products during oxidation ranged from 0.45 and 11.25 at 120 and 200 °C respectively.

No yields of Humic acids were observed in the Twistdraai product sample at 120°C while the highest yields (43 and 41% mass) were obtained at temperatures like 180°C and 200°C respectively.

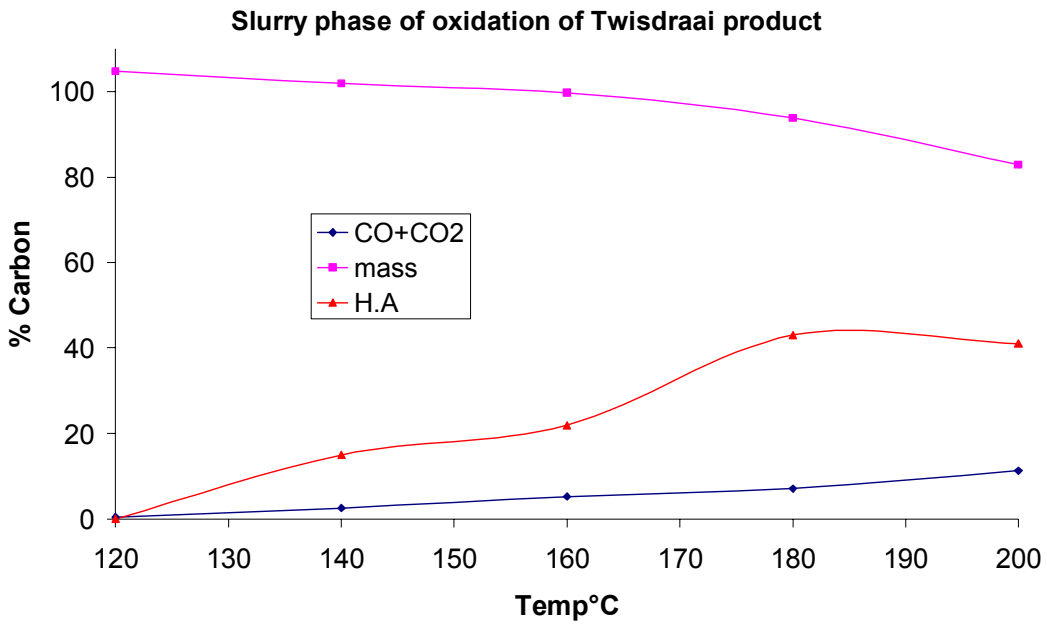


Figure 10: The slurry phase oxidation of the Twistdraai product sample

Similar trends but different amounts from the slurry phase oxidation of Twistdraai middlings are depicted in Figure 11**.** The highest humic acids yield was 20 % at 200°C while 10% was observed at 180°C. Nothing was obtained with regards to humic acids from the temperature profiles of 120 to 140°C.

4.3.1 Characterisation of the oxidised products

Oxidation was carried out on both Waterberg and Twistdraai (products and middlings) samples. Twistdraai discard sample was not oxidised due to its high ash content at 71% (Air Dry Basis) and finger printing carried out by FTIR indicated less carbonaceous materials in the sample. Therefore, the characterisation of the oxidised products was carried out on both Waterberg and Twistdraai (products and middlings) samples. The following techniques were followed:

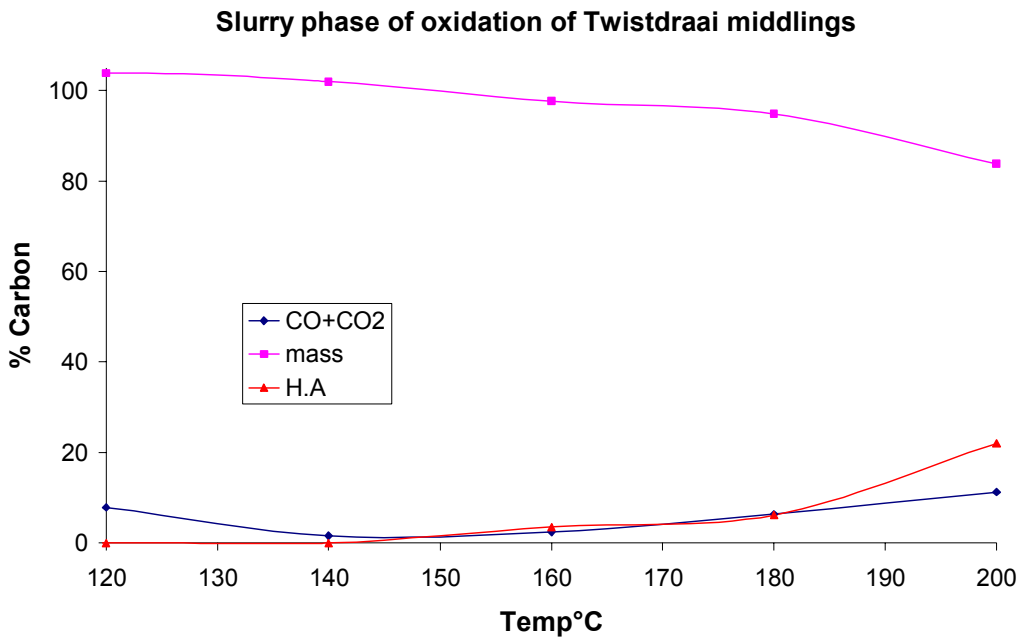


Figure 11: The slurry phase oxidation of the Twistdraai middlings sample

4.3.1.1 Ultimate analysis

Experimental test runs were carried out using the method of ASTM D5373 as described in section 3.5.1.4 of chapter 3. Results obtained are shown in Table 10, 11 and12 in the appendixes; A, B and C. It was observed that the percentage carbon and hydrogen contents of both the Waterberg and the Twistdraai samples (products, middlings) decreased with the increase in temperature. The decrease in hydrogen content may be due to the conversion of methylenes to carbonyls. There was no significant difference amongst all the samples. However the percentage mass of oxygen of all samples increased with the increase in temperature. This was an indication that oxidation did take place during the experimentation.

4.3.1.2 Carbon to oxygen ratios

The carbon to oxygen ratios of Waterberg and Twistdraai (products and middlings) are depicted in figure 12**.** The ratios did not vary significantly for all samples. They indicated a decrease with an increase in temperature showing a significant increase in oxidation as the temperature increased.

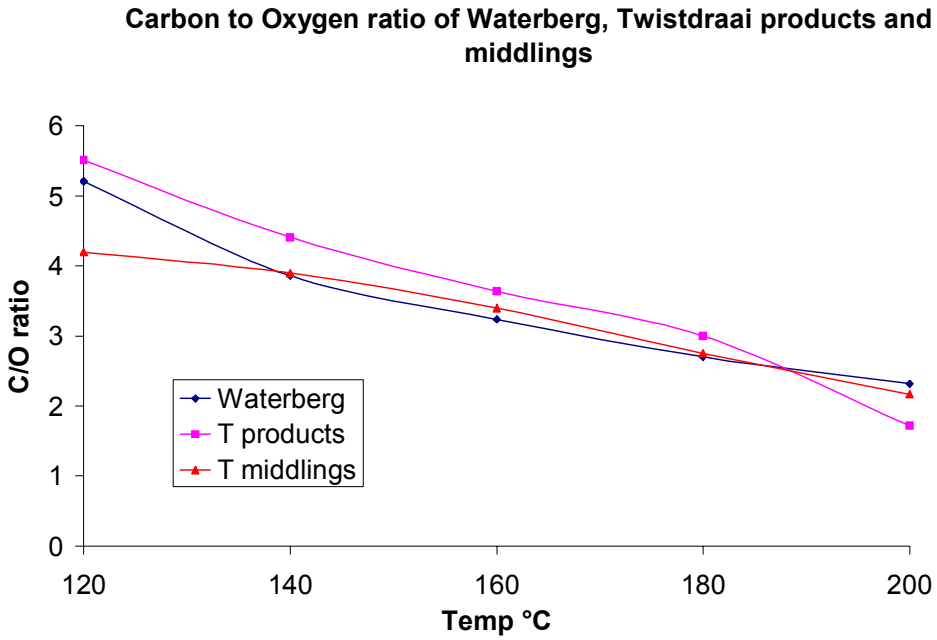


Figure 12: Carbon to oxygen ratio of Waterberg and Twistdraai (products and middlings) oxi- coal samples

4.3.1.3 Functional groups determination

Functional groups determined were carboxylic acids, phenolics and total acids. Figure 13 shows the functional groups of Waterberg sample. The carboxylic groups increased with the increase in temperature but slightly decreased after 180°C probably due to decarboxylation. The phenolics also increased with the increase in temperature.

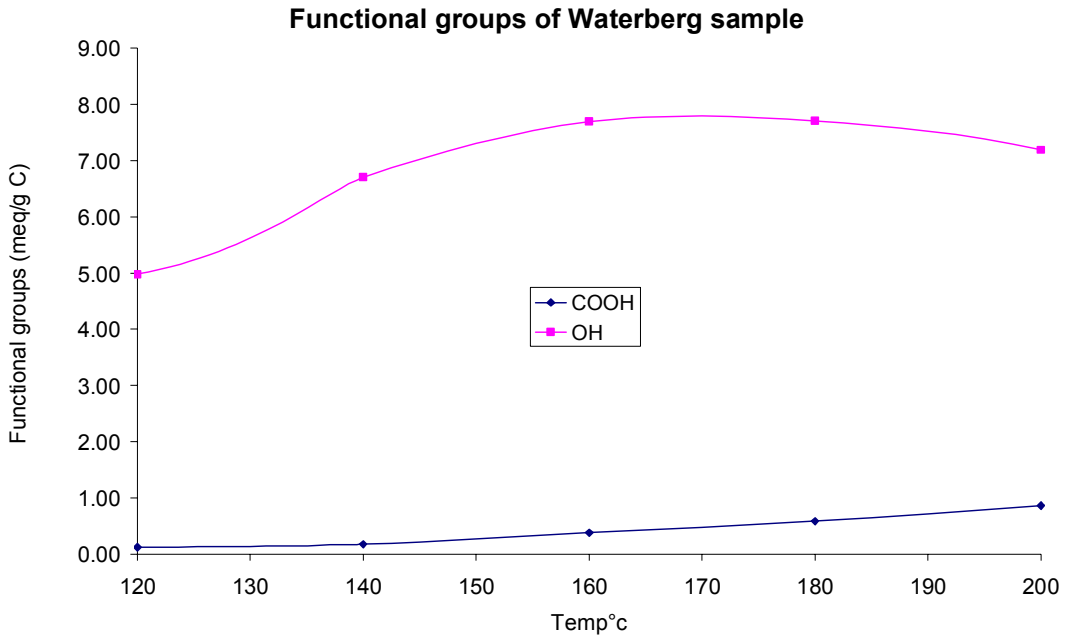


Figure 13: Functional groups of Waterberg sample

The results obtained of the functional groups of Twistdraai products and middlings are depicted in Figure 14 and 15 respectively. It can be seen from the figures that similar trends were observed in Waterberg sample but different quantities are indicated. The increase in the carboxylic and phenolic groups of Twistdraai products and middlings were also increasing with the increase in temperature as shown in the Waterberg sample. Waterberg sample had the highest phenolics from ~ 5-7 meq/gC followed by Twistdraai products from ~ 1.5–3 meq/gC and lastly the lowest was Twistdraai middlings at ~ 0.39 to 1.39 meq/gC. The carboxylics also showed that the highest amount was observed in Waterberg followed by Twistdraai products and Twistdraai middlings showed the least.

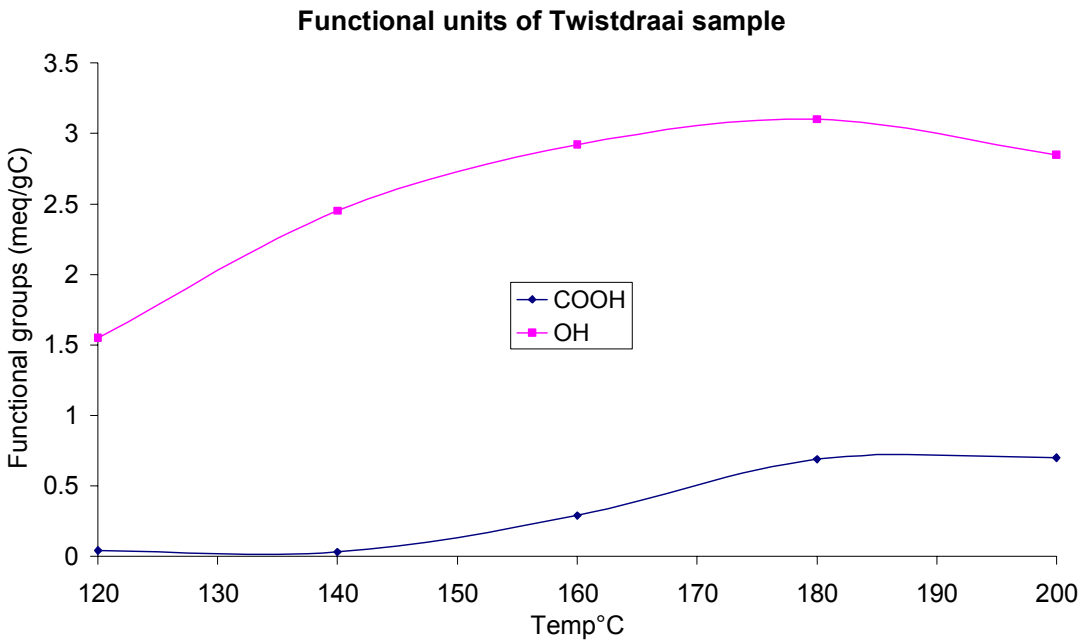


Figure 14: Functional groups of Twistdraai products sample

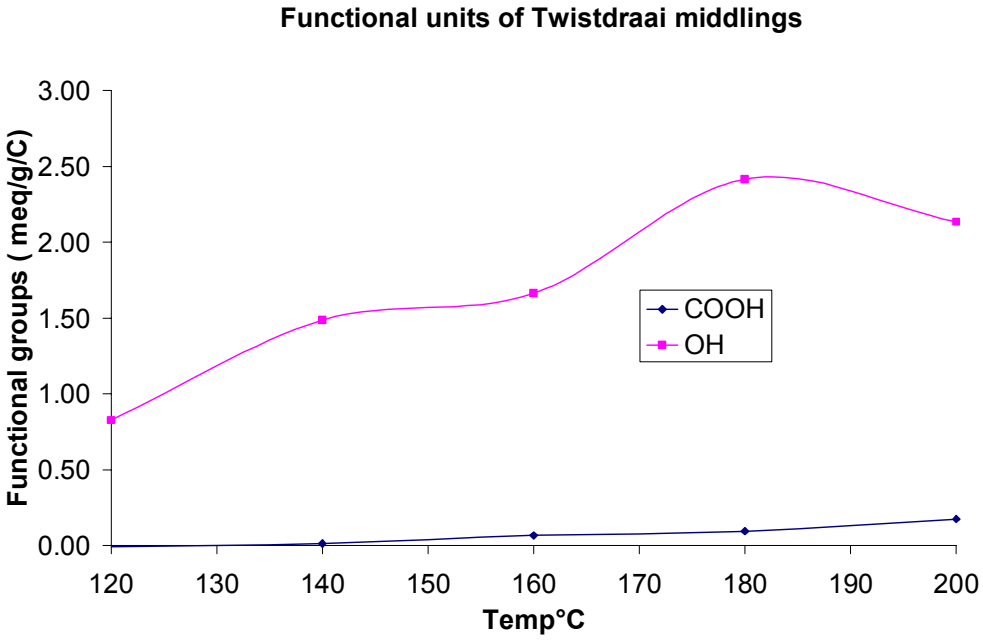


Figure 15: Functional groups of Twistdraai products sample

4.3.1.3 Infra-red analysis

The infra red analysis was carried out on an unoxidised and oxidised coal, the extracted humic acids and the final product called ammoniated nitro humic acids. The purpose is to determine the presence functional groups in addition to those detected using the wet chemistry method.

i) IR-spectra for oxidation (Waterberg and Twistdraai product and middlings)

The IR spectra graphs of Waterberg, Twistdraai products and middlings results on oxidation are depicted in Figure 16, 17 and 18 respectively. The 2900 cm^{-1} band of aliphatic C-H stretching vibrations was clearly pronounced for unoxidised and low temperature oxidised coals at 120°C of Waterberg and Twistdraai product samples. The intensity of the peaks of aliphatic C-H stretching vibrations disappeared at 180°C. However, in all Twistdraai middlings samples there were aliphatic hydrocarbon chains which contained carboxylic acid salts and a silica type of compound. The absorptions at 1032 and 1009 cm^{-1} are an indicative of the asymmetric Si-O stretching vibration of a silica type of compound and at 913 cm^{-1} the Si–N asymmetric stretching vibrations were detected. The C=O stretching vibrations of the COOH at 1720-1700 bands were detected in all highly oxidised coals, irrespective of the type of coal. O-H stretching vibrations were wider for Twistdraai product and the intensity of vibrations was deeper, indicating the higher presence of OH groups Waterberg sample.

ii) IR-spectra for the Final Products (Waterberg and Twistdraai products samples)

IR spectra for humic and the ammoniated nitro humic acids found in Waterberg and Twistdraai samples are depicted in Figure 19 and 20 respectively. Humic substances showed a broad absorption in the 3300 –

3400cm^{-1} region and this is usually attributed to O-H stretching. Absorption near 1575 and 1390 cm^{-1} may also be due to the COO^- ion. The presence of R-NH_2 stretching vibration were obtained at 3300- 3500 (approximately) and were broad in all the final products of Waterberg and Twistdraai product samples. NO_2 stretching vibrations were also observed in the two figures of Twistdraai product and Waterberg. However Twistdraai product sample seemed to be containing symmetrical NO_2 at bands of ~ 1350 – 1300 cm^{-1}, while Waterberg obtained both the asymmetric at
(1560- 1500) and the symmetric NO_2 .

Figure 16: IR-spectra of the Waterberg unoxidised and the oxidised coal @ 120°C & 180°C

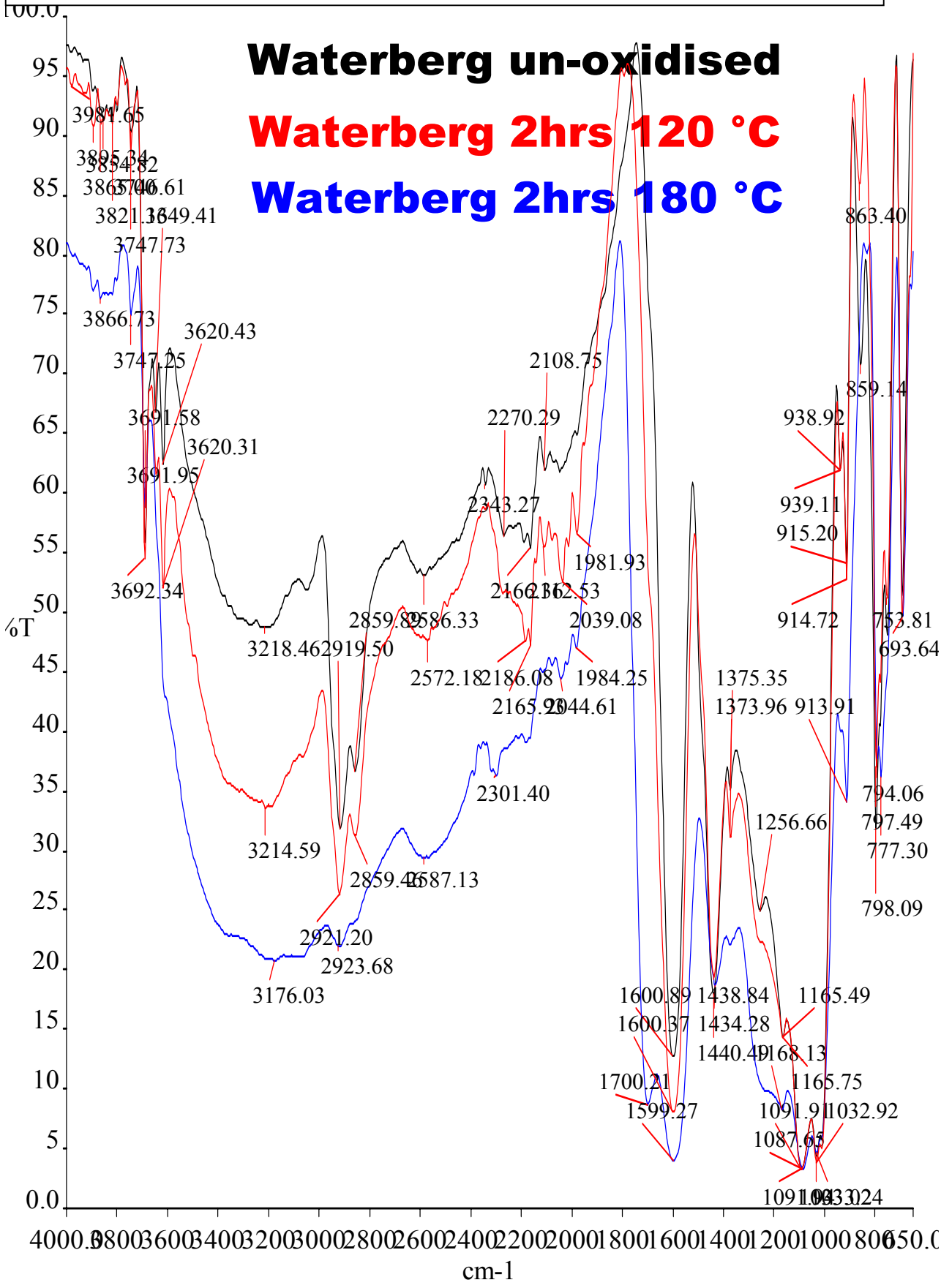


Figure 17: IR-spectra of the Twistdraai product unoxidised and the oxidised coal @ 120°C & 180°C

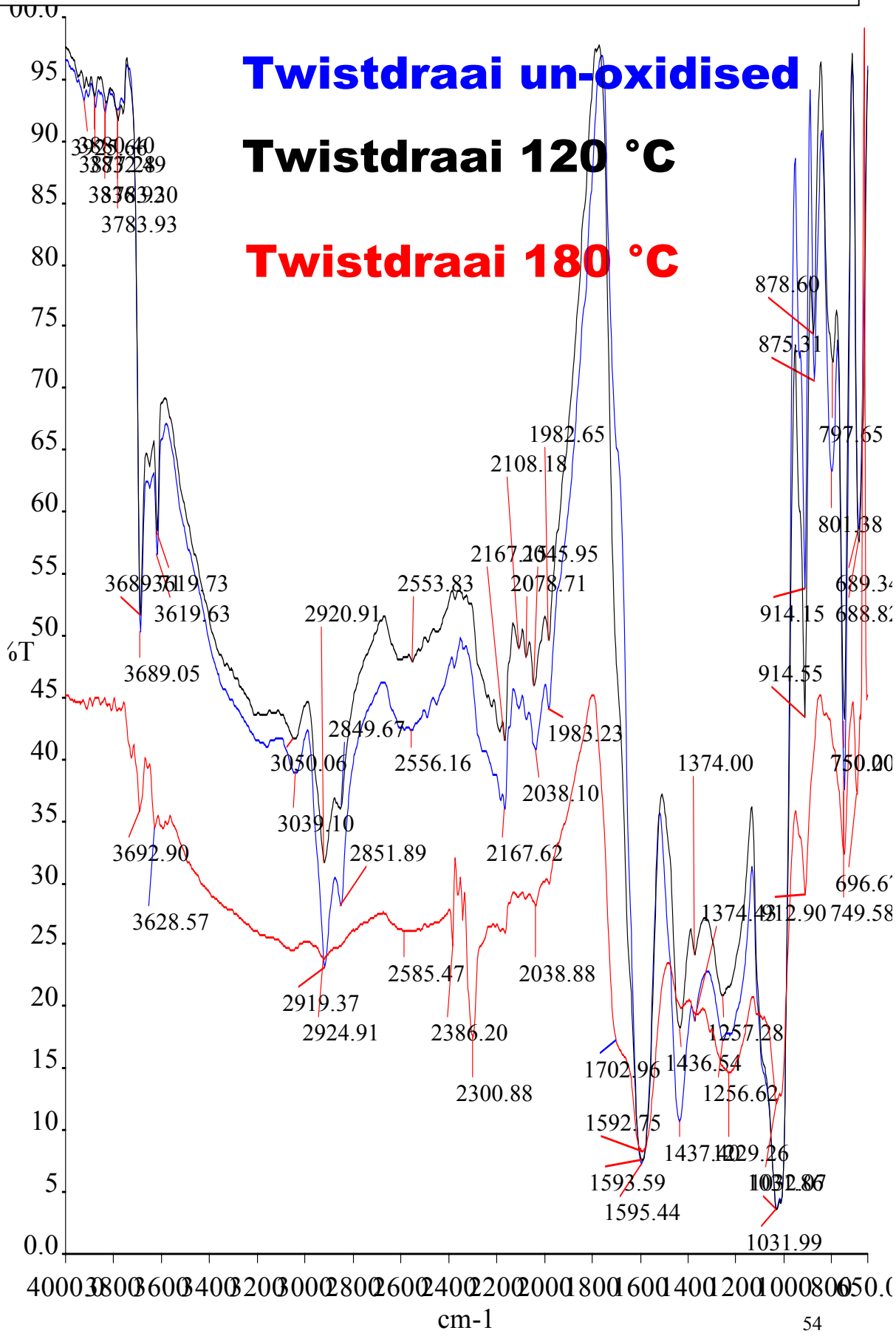


Figure 18: IR-spectra of the Twistdraai middlings unoxidised and the oxidised coal @ 120°C & 180°C

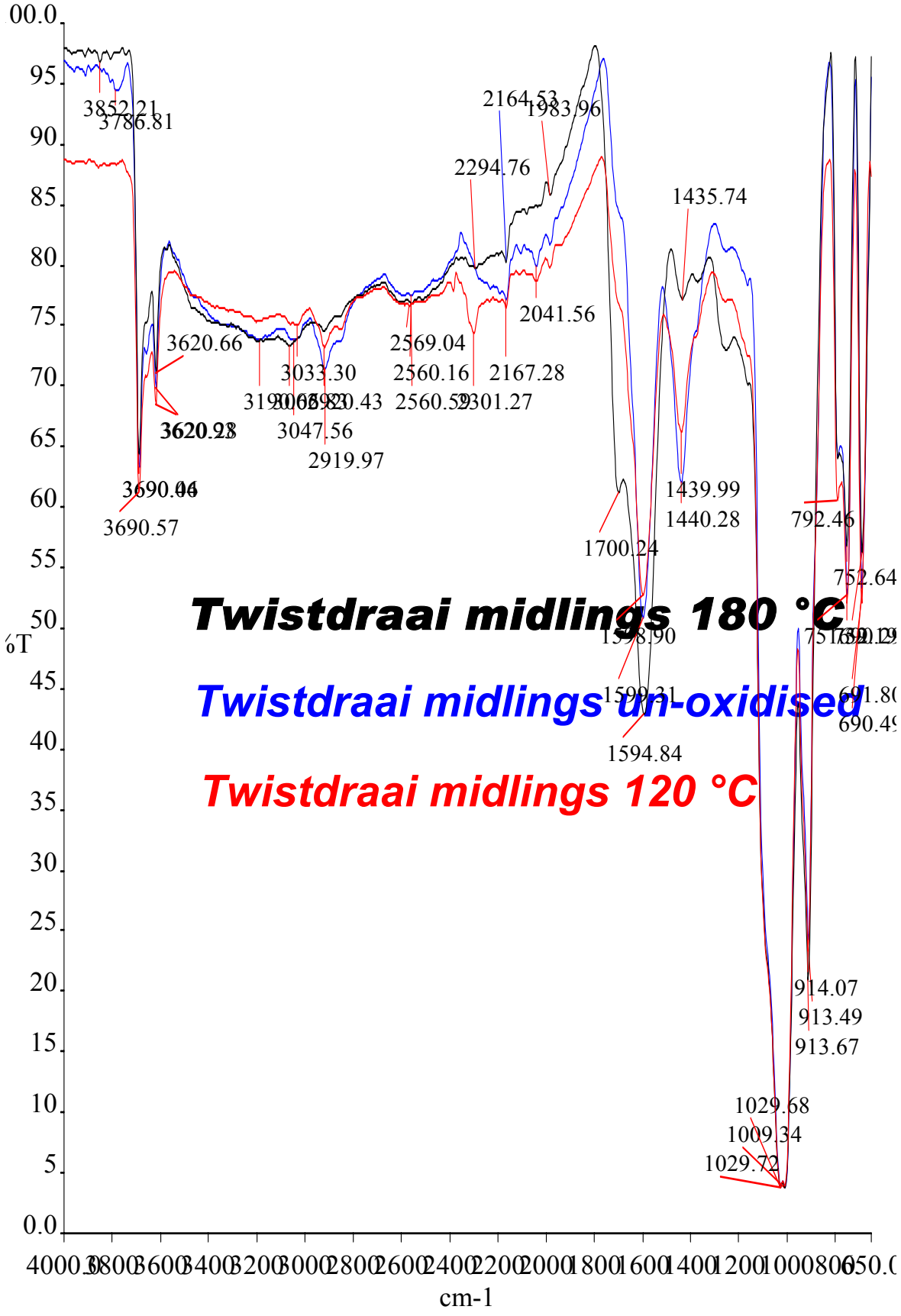


Figure 19: IR-spectra of the Waterberg humic acids and the ammoniated nitro humic acids @ 180°C

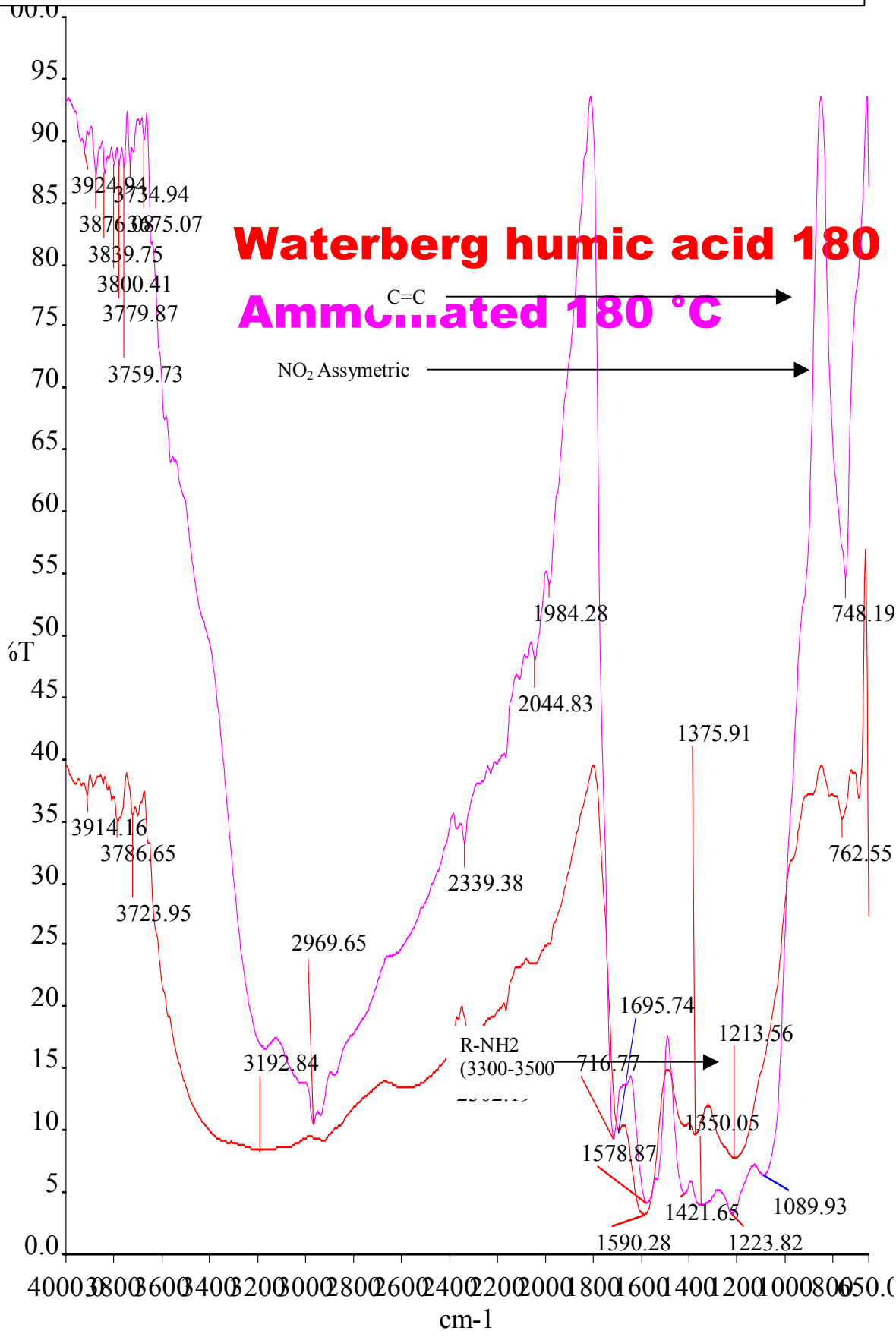
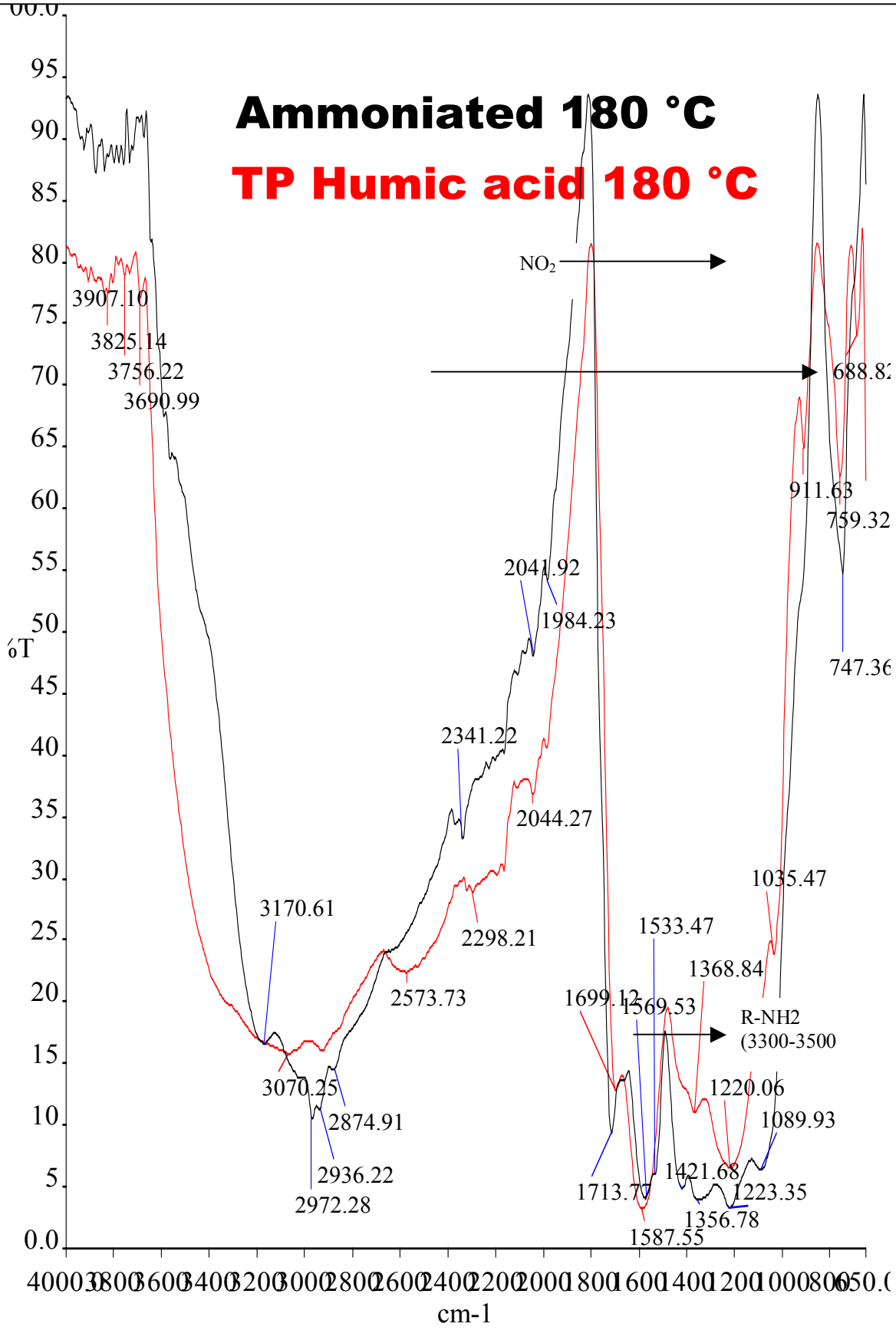


Figure 20: IR- spectra of the Twistdraai product humic acids and the ammoniated nitro humic acids @ 180°C



4.4 Nitration of the humic acids

The results obtained after nitrating extracted humic acids from oxidised coal samples of both Waterberg and Twistdraai products are shown in Table 7 below. Experimental work ammoniating humic acids was also carried out in Twistdraai products and Waterberg samples. The highest yield of humic acids was obtained at temperatures of 180°C and 200°C respectively in both samples.

Humic acids before being nitrated had 1.79 and 1.26% mass nitrogen for Waterberg and Twistdraai product samples respectively. It can be observed that the remaining % mass content of nitrogen was probably bound to the minerals.

Table 7: Nitrated results of Waterberg and Twistdraai products samples

Name of sample	Analyses	Units	Results
Waterberg @ 180°C	**TKN**	**%**	**5.3**
	Free ammonia	**%**	**1.1**
	Bonded Ammonia	**%**	**0.4**
Waterberg @ 200°C	**TKN**	**%**	**5.2**
	Free ammonia	**%**	**1.2**
	Bonded Ammonia	**%**	**0.4**
Twistdraai@ 180°C	**TKN**	**%**	**3.7**
	Free ammonia	**%**	**<1**
	Bonded Ammonia	**%**	**0.3**
Twistdraai @ 200°C	**TKN**	**%**	**3.8**
	Free ammonia	**%**	**<1**

	Bonded Ammonia	**%**	**0.3**

The nitrogen content of Waterberg sample was increased from 1.79% to a range of 5.2 – 5.3 % and Twistdraai product sample increased from 1.23 % to a range of 3.7 -3.8%.

4.5 Ammoniation of Humic acids

There was further increase in nitrogen content as both Waterberg and Twistdraai samples were ammoniated. Table 8 below indicate the variations from both Waterberg and Twistdraai samples.

Table 8: Results of the ammoniation of both Twistdraai products and Waterberg samples after nitration analyses

Name of sample	Analyses	Units	Results
Waterberg @ 180°C	**TKN**	**%**	**9.2**
	Free ammonia	**%**	**2.0**
	Bonded Ammonia	**%**	**5.9**
Waterberg @ 200°C	**TKN**	**%**	**9.7**
	Free ammonia	**%**	**1.7**
	Bonded Ammonia	**%**	**6.9**
Twistdraai@ 180°C	**TKN**	**%**	**9.3**
	Free ammonia	**%**	**1.2**
	Bonded Ammonia	**%**	**4.8**
Twistdraai @ 200°C	**TKN**	**%**	**9.03**
	Free ammonia	**%**	**2.1**

	Bonded Ammonia	**%**	**4.9**

The total nitrogen of Waterberg and Twistdraai product samples were both in the range of 9.2 - 9.3 % irrespective of the type of coal used.

Chapter 5

DISCUSSIONS

5.1 Introduction

This chapter highlights the importance of the results discussed earlier and their relevance to the current industrial application.

5.1.1 The comparison between the commercial humic acids and Waterberg humic acids sample

In an attempt to determine the chemical purity of the humic acids, Waterberg humic acids and commercial humic were used. The objective is to compare the chemical substances of these humic acids. The commercial humic acids used for this test runs is derived from the brown coal of Australia and is called The Huma- Tech Granular Humic acid ^{Tm} .The proximate and ultimate analyses results are summarised in Table 9.

Table 9: Proximate and Ultimate analysis of Waterberg and Huma- Tech Granular Humic acid ^{Tm}

Sample	C (%)	H (%)	N (%)	Total S (%)	Moisture %	Ash (%)	Volatiles (%)
Waterberg	**59.20**	**1.84**	**1.30**	**0.72**	**11.41**	**6.93**	**40**
Huma-Tech Granular humic acids)	**45.71**	**1.84**	**0.83**	**0.13**	**16.84**	**22.58**	**26.96**

From the results given in Table 9, it is clear that the ash content of Waterberg humic acids is 6.93%; lower than that of the Huma- Tech Granular humic acids ™ at 22.58%. The low ash content could be the indication that the leachability of elements present in Waterberg humic acids could be extremely higher than those in the commercial humic acids. It further projects that the life span of Waterberg humic acids could be lesser than the Huma- Tech Granular humic acids ™.

The volatile content in Waterberg humic acids is 40% while that of commercial humic acids mentioned is 26.96%. It can therefore be concluded that these two humic acids are totally different from each other based on their physical properties.

The ash composition of both Waterberg and Huma – Tech Granular humic acids ™ are also summarised in Table 10.

It can be seen from Table 10 that both Waterberg and Huma- Tech Granular ™ humic acids contains major elements such as Si , Al, Na and minor elements such as Ca, Cr and K. It can also be seen from the results given in Table 10 that elements such Al at 2.9 mass% and Na at 0.42 mass% in Waterberg humic acids sample are higher than those of Huma Tech Granular ™ humic acids. This may be due to the fact that different extraction methods may have been applied. Further more the high Al in Waterberg humic acids may be due to the crystallisation and co-precipitation of colloids, e.g. Al $(OH)_3$.

Table 10: Chemical composition of Waterberg humic acids sample

	Sample name	
Substances (mg/kg) or%	**Waterberg Humic acids(mg/kg)**	**Huma- Tech Granular humic acids ^{Tm}(mg/kg)**
Al	**2.90**	**0.68 %**
Ca	**107**	**0.10 %**
Cr	**206**	**0.17 %**
K_2O	**163**	**1.30 %**
Mg	**41.0**	**0.52 %**
Na	**0.42 %**	**<0.1 %**
P_2O_5	**89.0**	**0.03 %**
Pb	**7.00**	**0.50 %**
Si	**0.56 %**	**0.52 %**
LOI	**93.4 %**	**78.18 %**

LOI ~ Loss on ignition

The LOI (Loss on ignition) in Waterberg humic acids is at 93.4 mass % higher than the Huma – Tech granular humic acids ^{Tm} at 78.18 mass %. The high LOI in Warterberg humic acids sample may be due to the association of the hydroxyls adsorbed on the ultra fine of the carbonaceous matter of humic acids.

5.1.2 Slow release results of Waterberg and Twistdraai products samples.

Tests that would indicate whether these fertilizers have slow-release characteristics are described in section 3.8.1 of Chapter 3 and the results thereof are shown in Figure 21. The results observed indicate a decrease of the mass of nitrogen as the time increases. It can also be observed that there was a reverse reaction that took place between the two samples. Furthermore Waterberg sample was observed to be higher in nitrogen content at ~ 8.5% as compared to Twistdraai product sample at 7.1% nitrogen content. Though the method elaborated that at least twelve weeks would be the required time range to observe the trend in the rate and control of 'slow release fertilizers', there is an indication that if further time were allocated, a certain reaction would have taken place.

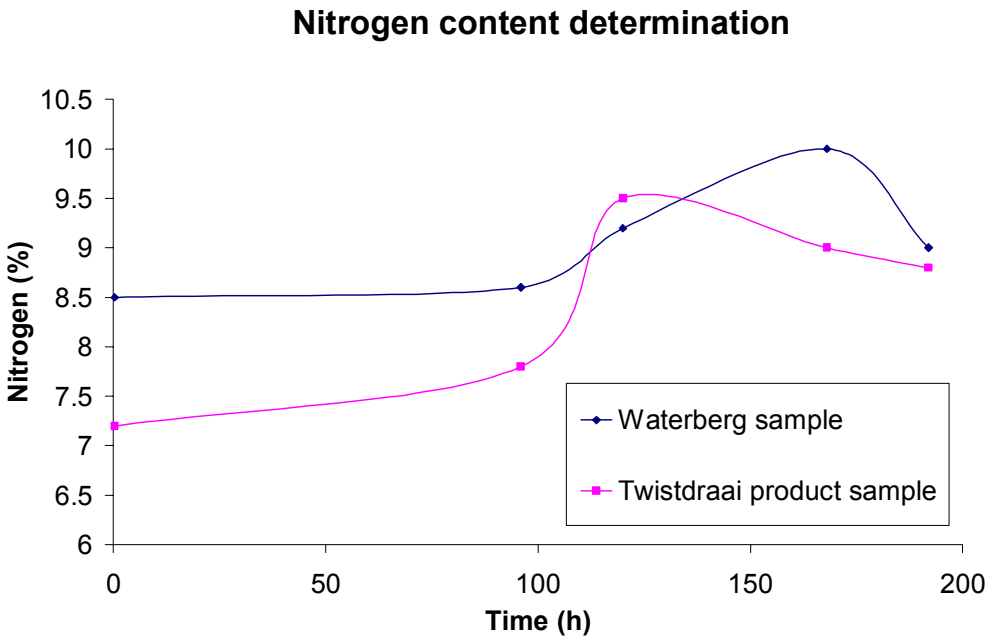


Figure 21: The determination of slow release method on Waterberg and Twistdraai product samples

5.1.3 An evaluation of the chemical purity of both Waterberg and Twistdraai (products) final products

In an attempt to evaluate the chemical purity of the ammoniated nitro humic acids, final products that are regarded as slow release fertilizers, samples were analysed using ash composition technique. The results are summarised in Table 11.

Table 11: The chemical substances of both Waterberg and Twistdraai products final products

Sample	Al mass (%)	Ca mass (%)	Na mass (%)	Pb mass (%)	Si mass (%)	LOI Mass (%)
Waterberg ammonium nitro humic acids	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**1.01**	**97.27**
Twistdraai (products) ammonium nitro humic acids	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**1.52**	**96.98**

It can be seen from Table 12 that there is a significant decrease of major elements such Al, Na, and Ca. Further more, trace elements such as Pb were not even detected. This decrease of the elements may be due to removal of the impurities which remained in the humic acids. The decrease observed may also be due to the dissolution of elements in the solution of nitric acid at a pH 2 during the precipitation of humic acids.

Chapter 6

6.1 Conclusions

The Waterberg sample was the most reactive and highly oxidised sample as compared to the other samples such as Twistdraai (products, middlings and discards), hence the high yields of humic acids. Further more the type of maceral components have a marked effect on the extent of oxidation and the production of humic acids.

The aim of the study was to produce an organic molecular substance from oxidised coal and bind Nitrogen (N) in such a way that its release can be controlled.

The organic molecular substance in the form of humic acids was obtained. nitrogen (N) element was successfully inserted into the molecules of organic “humic acids” and the release and control of the nitrogen was technically feasible.

The presence of nitriles and amides in Waterberg, Twistdraai products humic acids as well as the final products as indicated by FTIR, showed that the nitrogen was associated with the organic molecule and was immobile. This immobility of nitrogen is an indication of the property of slow release fertilizers.

The final products of Waterberg and Twistdraai products samples were tested to show if they were slow release fertilizers using the Agri-LASA method. However, the results obtained could not sufficiently provide the required conclusion. Therefore it is recommended that a quick response method should be developed to determine the efficacy of the slow release fertilizers.

Most of the hazardous elements such as Al, Na, Pb were significantly less detectable in the final products of Waterberg and Twistdraai products samples.

6.2 Recommendations

1. It is recommended that the economic evaluation of the process should be carried out before further investigation is done.
2. Optimisation of other existing parameters of the process should also be carried out.
3. The efficacy of the final products should be tested in soils and plants.

Appendix A.1: Volumetric method of Waterberg functional groups

Table 1: Carboxylic acid groups as functional units of Waterberg sample

Parameter	Temperature °C				
	120	140	160	180	200
Vs (ml)	2.87	2.55	8.78	19.71	22.14
Vb (ml)	1.91	1.91	1.91	1.91	1.91
Mass of coal (g)	0.3	0.311	0.30	0.3	0.32
COOH (meq/gC)	0.04	0.03	0.29	0.73	0.64

Table 2: Total acid groups as functional units of Waterberg sample

Parameter	Temperature °C				
	120	140	160	180	200
Vs (ml)	6.71	5.38	4.1	2.53	2.66
Vb (ml)	9.08	9.08	9.08	9.08	9.08
Mass of coal (g)	1	1	1	1	1
(Total acid) (meq/gC)	1.63	2.46	3.18	4.01	3.25

Table 3: The phenolic groups and the ratio of COOH/OH of Waterberg sample

Parameter	Temperature °C				
	120	140	160	180	200
OH (meq/gC)	1.58	2.43	2.89	3.29	2.61
COOH/OH	0.03	0.01	0.1	0.22	0.25

Appendix A 2: Volumetric method for functional groups Twistdraai product sample

Table 4: Carboxylic acid groups as functional units of Twistdraai product sample

Parameter	Temperature °C				
	120	140	160	180	200
Vs (ml)	1.75	2.71	5.4	14.05	19.26
Vb (ml)	1.91	1.91	1.91	1.91	1.91
Mass of coal (g)	0.3	0.311	0.30	0.3	0.32
COOH (meq/gC)	0.02	0.03	0.15	0.50	0.55

Table 5: Total acid groups as functional units of Twistdraai product sample

Parameter	Temperature °C				
	120	140	160	180	200
Vs (ml)	7.65	6.07	4.82	4.34	3.84
Vb (ml)	9.08	9.08	9.08	9.08	9.08
Mass of coal (g)	1	1	1	1	1
(Total acid) (meq/gC)	0.98	2.00	2.72	2.90	2.66

Table 6: The phenolic groups and the ratio of COOH/OH of Twistdraai product sample

Parameter	Temperature °C				
	120	140	160	180	200
OH (meq/gC)	0.96	1.97	2.57	2.41	2.11

COOH/OH	**0.02**	**0.02**	**0.06**	**0.21**	**0.26**

Appendix A 3: Volumetric method for functional groups Twistdraai middlings sample

Table 7: Carboxylic acid groups as functional units of Twistdraai middlings sample

Parameter	**Temperature °C**				
	120	**140**	**160**	**180**	**200**
Vs (ml)	**1.64**	**2.41**	**4.1**	**5.36**	**9.36**
Vb (ml)	**1.91**	**1.91**	**1.91**	**1.91**	**1.91**
Mass of coal (g)	**0.3**	**0.311**	**0.301**	**0.3**	**0.3**
COOH (meq/gC)	**-0.01**	**0.02**	**0.07**	**0.1**	**0.18**

Table 8: Total acid groups as functional units of Twistdraai middlings sample

Parameter	**Temperature °C**				
	120	**140**	**160**	**180**	**200**
Vs (ml)	**7.06**	**5.87**	**5.3**	**3**	**2.98**
Vb (ml)	**9.08**	**9.08**	**9.08**	**9.08**	**9.08**
Mass of coal (g)	**1**	**1**	**1**	**1**	**1**
(Total acid) (meq/gC)	**0.82**	**1.50**	**1.73**	**2.51**	**2.31**

Table 9: The phenolic groups and the ratio of COOH/OH of Twistdraai middlings sample

Parameter	Temperature °C				
	120	140	160	180	200
OH (meq/gC)	0.96	1.97	2.57	2.41	2.11
COOH/OH	-0.01	0.01	0.04	0.04	0.08

Appendix A 4: Slurry phase oxidation of Waterberg sample

Table 10: Slurry phase oxidation of Waterberg sample

Parameter	Units	temperature °C					
		0	120	140	160	180	200
C	mass %	70.16	67.1	67.03	64.55	57.74	55.23
H	mass %	4.63	4.18	3.91	3.57	2.73	2.28
N	mass %	1.22	1.21	1.22	1.21	1.17	1.28
S	mass %	1.02	0.9	0.88	0.83	0.67	0.63
Ash	mass %	9.85	9.53	9.1	9.97	9.01	10.84
Moisture	mass %	2.84	4.21	0.52	0.48	7.31	5.95
Volatile	mass %	35.04	32.47	33.52	34.69	34.59	36.96
Heat value	kJ/kg	28 945	27 377	26 569	24 959	21 134	19 389
Oxygen	mass %	10.28	12.87	17.34	19.39	21.37	23.79
Fulvic acid	g		1.39	2.9	3	10	20
Fulvic acid	% C		0.3	0.31	0.44	0.99	2.33
Product (mass)	g	420	435	416	412	382	362
CO+CO2	mass %		2.76	2.82	5.17	11.43	12.6
humic acid.	mass %	0	1.9	9	34	80	82

Appendix A5: Slurry phase oxidation of Twistdraai product sample

Table 11: Slurry phase oxidation of Twistdraai product sample

	Temperature °C						
Parameter	**Units**	**0**	**120**	**140**	**160**	**180**	**200**
C	**mass %**	**69.2**	**68.7**	**66.55**	**63.9**	**61.25**	**50.67**
H	**mass %**	**4.35**	**4.11**	**3.86**	**3.42**	**2.97**	**2.48**
N	**mass %**	**1.87**	**1.87**	**1.86**	**1.84**	**1.9**	**2.05**
S	**mass %**	**0.94**	**0.07**	**0.69**	**0.62**	**0.49**	**0.53**
Ash	**mass %**	**12.03**	**10.14**	**10.05**	**10.39**	**10.33**	**11.82**
Moisture	**mass %**	**1.61**	**1.66**	**1.91**	**2.26**	**2.69**	**2.87**
Volatile	**mass %**	**34.77**	**34.08**	**34.91**	**34.31**	**32.52**	**56.69**
Heat value	**kJ/kg**	**27604**	**26647**	**25972**	**24079**	**22233**	**20656**
Oxygen	**%**	**10.05**	**13.45**	**15.08**	**17.57**	**20.37**	**29.59**
Fulvic acids mass	**mass %**		**1.39**	**2.9**	**3**	**10**	**20**
Fulvic acids % carbon	**mass %**		**0**	**0**	**0.03**	**0.77**	**1.38**
Product (mass)	**g**	**420**	**440**	**428**	**419**	**394**	**348**
CO+CO2	**mass %**		**0.45**	**2.6**	**5.22**	**7.13**	**11.25**
humic acid.	**mass %**	**0**	**0**	**15**	**22**	**43**	**41**

Appendix A6: Slurry phase oxidation of Twistdraai middlings sample

Table 12: Slurry phase oxidation of Twistdraai middlings sample

Parameter	Temperature °C						
	Units	0	120	140	160	180	200
C	mass %	48.41	40.53	46.81	45.79	41.84	37.89
H	mass %	2.72	2.75	2.56	2.37	2.01	1.76
N	mass %	1.1	1.11	1.06	1.07	1.06	1.04
S	mass %	1.42	1.21	0.7	0.61	0.99	0.65
Ash	mass %	34.26	34.2	32.96	32.88	36.13	38.99
Moisture	mass %	2.24	1.09	3.82	3.62	2.77	2.24
Volatile	mass %	23.42	23.2	25.04	26.04	27.32	23.42
Heat value	kJ/kg	19.106	19131	18412	17455	15292	13596
Oxygen	mass %	9.85	19.11	12.09	13.66	15.2	29.59
Full-mass	mass %		0.5	0.33	2	9	10
Full-carbo	mass %		0	0	0.22	0.25	1.02
P(mass)	g	420	436	428	410	398	352
CO+CO2	mass %		7.88	1.6	2.4	6.32	11.25
Humic Acid % yield	mass %	0	0	0	3.5	6.2	22

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- Keywords leonardite, fertilizer, slow
  http://www.google.com

- Dr. Kline's research regarding Arkansas lignite and its possible use as a soil amendment that could be useful to the rice industry in Arkansas:
  http://www.atu.edu/acad/mining/people/misk/lignite.htm