CHINHOYI UNIVERSITY OF TECHNOLOGY

Characterisation and utilisation of acid tar waste from crude benzol processing for environmental sustainability

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Concilia Danha
BSc in Applied Chemistry (Hons)(NUST) and MSc in Water Resources Engineering Management (UZ)

Registration number: C1112205Q

DECLARATION

I, Concilia Danha do hereby declare that this thesis is a result of my own investigation and findings, with the exception indicated in the acknowledgements, references and by comments included in the body of the report. This thesis has not been submitted in part or in full to other universities for any other degree.

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Student's Signature Date

Abstract

Acid tar waste is produced from the purification of benzene, toluene and xylene using concentrated sulphuric acid or oleum. The acid tar waste increases sulphate ion concentration in ground-water if stored in ponds as is the current practice. In view of this, the study will investigate the use of acid tar waste for pavement binding. The acid tar waste studied was obtained from two process streams namely the benzene purification labelled benzene effluent stream acid tar and the toluene and xylene purification labelled toluene and xylene effluent stream acid tar.

The acid tar wastes were characterised separately. The parameters were: viscosity, organic compound identification using Gas Chromatography-Mass Spectroscopy (GC-MS) and Fourier Transform Infrared (FTIR), sulphuric acid composition determined by titration, metal and anion content using Inductively Coupled Plasma/ Atomic Emission Spectroscopy (ICP/AES). The acid tar waste was rheologically characterised using the method developed by Frolov et al (1981) and later refined by Stanciu (2014). The acid tar waste was neutralised with calcium hydroxide and calcium oxide with the objective of determining the best agent in terms of producing a more insoluble product with less gas emissions during neutralisation. The acid tar waste was modified to produce a material with high flow resistance that could be used in pavement construction. Rubber from tyres, calcium oxide and used engine oil were used to modify acid tar to produce material that is suitable for use as pavement binders. There were five materials produced from the two acid tars. The modified acid tar waste was compared with standard 60/70 bitumen grade material in terms of viscoelastic, stiffness and the rutting resistance parameter.

Benzene effluent stream acid tar viscosity measured average value of 28.6mPa.s while that of toluene and xylene effluent stream acid tar determined as 183.0mPa.s. The toluene and xylene effluent stream acid tar contained pyrrole, carboxylic acid, ketone and phenol while benzene effluent stream acid tar contained quinoline, ketone and phenol which are some of the functional groups found in asphalt used for pavement binders. The sulphuric acid percentage concentration (wt) was found to be 24.2 and 23.7 for the benzene effluent stream acid tar and toluene and xylene effluent stream acid tar, respectively. Calcium oxide salt for both acid tar waste materials had lower solubility (10.3%) after heating as compared to calcium hydroxide salt for both acid tar wastes which was approximately 20%. The benzene effluent stream acid tar behaved as a Herschel-Bulkely fluid while the toluene and xylene effluent stream acid tar displayed a flow characteristic resembling a Bingham fluid. Of the five modified materials produced from the two acid tar wastes, two of the products behaved like bitumen grade 60/70 and other asphalt binders found in literature. The two were designated Benzene effluent stream acid tar with Rubber and Calcium oxide (BRC) and Toluene and xylene effluent stream acid tar with Calcium oxide (TC).

The two acid tar waste streams were different in the physical and chemical characteristics, thus the two acid tar wastes have to be treated differently. Calcium oxide was the best neutralising agent and is recommended to be used in neutralising the acid tar waste before further modification. The inference drawn is that fewer chemicals will be leached to the environment if calcium oxide is used to neutralise the acid tar waste. The modified acid tar waste products need further adjustment in the viscoelastic behavior by adding bitumen 60/70 grade.

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ZIMCHEM refineries for providing acid tar waste material and the picture of the lagoon in Figure 1.1. National tyres services of Zimbabwe for providing ground tyres used in modifying the acid tar.

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Nomenclature

cm	centimeter
r^2	correlation coefficient
^{o}C	degrees Celsius
eV	electronvolt
m/z	mass per charge number
mm	millimeter
mins	minutes
mPa.s	milipascals multiplied by seconds
mol/l	moles per litre
rad/s	radian per second

CHAPTER ONE

INTRODUCTION

Waste has to be managed from the source if production processes are to be environmentally sustainable. The characterisation of the waste is a necessary first step in order to determine its composition thereby providing indicators for possible end use. This also enables one to determine whether to use the waste without modification or to modify before use. Acid tar is waste produced from purification of benzene, toluene and xylene (BTX) process that use sulphuric acid. The BTX components are obtained from the processing of benzol which is a byproduct of coal carbonisation. Benzene finds wide application as it is the main raw material in the production of plastics, synthetic rubber, detergents and dyes (Vagner and Tryasunov, 2012). Its separation from other hydrocarbons, namely: thiophene and cyclohexane using physical methods is rather difficult because their respective boiling points are close (Vagner and Tryasunov, 2012). The use of chemical method to achieve separation is perhaps the best but unfortunate solution that leads to the production of a large amount of acidic tarry waste material due to the excessive use of sulphuric acid.

Acid tar wastes are derived from three main processes, namely:

a) The re-refining of spent lubricating oils,
b) The refining of petroleum fractions,
c) Crude benzol refining (Nancarrow et al., 2001).

Crude benzol refining involves washing with concentrated sulphuric acid which sulphonates the more undesirable compounds to allow easier separation and recovery of 98% pure benzene, toluene and xylene fractions.

The acidic tarry waste material generated is regarded industrially as a product of low commercial value and as such is disposed in purpose built landfill sites or ponds. It has been suggested in recent years that, acid tar wastes from crude benzol can be used as feedstock in the synthesis of many valuable hydrocarbon based products (Kolmakov et al., 2007). The focus in European, American and Asian countries, for example, is on the remediation of acid tar waste ponds created at former gas works sites, processing involving benzol refining, refining of crude oil into petroleum diesel and heavy fraction oil (Banks et al., 1998 and Nancarrow et al., 2001). The remediation activities are mainly centered on reclaiming the land, combustion in waste heat steam boilers and utilisation as tar in road construction and maintenance operations (Nancarrow et al., 2001, Druzina and Perc, 2010).

In Africa and Zimbabwe in particular, there is no information that relates to the valorisation of acid tar waste as road surfacing material. Acid tar waste that is generated from crude benzol processing at ZIMCHEM Refineries (PVT) LTD situated at Zimbabwe Iron and Steel Company (ZISCO) in Redcliff, Zimbabwe has been stored in purpose built dumpsites referred to as waste acid tar lagoons. The plant at ZIMCHEM Refineries has the capacity to process crude benzol from Hwange Colliery in Hwange, Zimbabwe and ZISCO coal carbonisation operations and these operations lead to acid tar waste accumulation. The acid tar waste from crude benzol processing is either black or brown in color, very acidic and tarry. At ZISCO Redcliff works, the waste is contained in lagoons that are lined with sealing tar and is generally exposed to air and rain. The acid tar waste is liquid when initially disposed in the lagoons but solidifies with time. Fig 1.1 shows the acid tar waste in one of the ZIMCHEM Refineries lagoons.

Figure 1.1: Acid tar waste in a lagoon at ZIMCHEM Refineries landfill site, Redcliff, Zimbabwe.

There are two production processes that generate acid tar waste at ZIMCHEM Refineries, namely:

a) The benzene purification process, which uses oleum,

b) The toluene and xylene purification which uses 98% sulphuric acid.

Under normal production, the company disposes off about 40 tonnes of acid tar waste per month into the lagoons. Regrettably, the landfill site is situated close to Kwekwe River, a major source of water for the residents of Redcliff town, Torwood and Rutendo townships. The river also provides all the process water requirements for the ZISCO Redcliff works. The Kwekwe River is a major tributary of the Sebakwe River and therefore part of the Zibagwe catchment area.

The acid tar waste is currently being disposed into lagoons and at the rate of 40 tonnes a month, more land will be required resulting in a further increase in the area polluted in addition to an increase in human and animal exposure. This study will investigate the composition of the fresh acid tar waste and the rheological behaviour of modified acid tar waste material, and the latter will be compared with pavement asphalt as a road construction material.

1.1The problem statement

The chemical composition of acid tar waste that ZIMCHEM Refineries is disposing into the environment in large quantities is unknown and the current disposal method is environmentally unsustainable. It has been established however, that as a product of benzol refining, the acid tar waste contains polycyclic aromatic hydrocarbons (PAHs) which:

i) irritate the eyes and respiratory system,
ii) Causes cancer and is very toxic to aquatic organisms,
iii) Pollutes the atmosphere, soil, ground and surface water (Ševčĭková et al., 2015).

In this respect any remedial solution will require a detailed understanding of chemical composition and material rheological behaviour as this will provide valuable indicators of likely co-products and ultimate disposal routes.

1.2 Main objective

To characterise and utilise acid tar waste generated from the purifying benzene, toluene and xylene products at ZIMCHEM Refineries for environmental sustainability.

1.3Specific objectives

(i) To characterise fresh acid tar waste using physical, organic and inorganic properties;

(ii) To characterise the neutralised acid tar waste using solubility, organic and inorganic properties;

(iii) To determine the most effective environmentally sustainable base (calcium hydroxide and calcium oxide) to use in the neutralisation of acid tar waste;

(iv) To determine the viability of producing asphalt material for road pavement application from neutralisation of acid tar waste.

1.4 Research questions

(i) What is the composition of fresh acid tar waste material?

(ii) What is the composition of the neutralised acid tar waste material?

(iii) What is the most effective environmentally sustainable base to use in the neutralisation of acid tar waste?

(iv) What is the best composition of fresh acid tar waste, base and rubber for production of pavement binder?

1.5Justification

In view of the shortage of petroleum asphalt for paving streets and roads in Zimbabwe's urban and rural areas it is necessary to search for new sources of raw materials to produce asphalt. One possible source is the acid tar that is formed as a waste material at the Zimbabwe Iron and Steel Company (ZISCO). The acid tar waste forms after toluene, xylene and benzene are washed with concentrated sulphuric acid or oleum. Normally, acid tar waste does not contain asphaltenes, resins and paraffins in the recommended ratios necessary to produce high quality asphalt. It is therefore necessary to investigate suitable blends to bring these ratios into the recommended range and to improve the quality indices of the final product. One of the most important quality indicators is (1) the rheology of the acid tar waste derived asphalt, which is a good indicator of the performance of roads derived from these asphalts. Other asphalt quality indices of importance are (2) the softening point, (3) adhesion to mineral materials, (4) ductility and (5) the content of water soluble compounds in the asphalt. The rheology of the acid tar waste derived asphalt was investigated with a view to ascertaining whether the acid tar waste derived asphalt was meeting the primary requirement for road service. The use of acid tar waste to produce asphalt is an environmentally friendly and economically viable solution to a key technical problem in the iron and steel industry.

The research is significant because the current disposal method of acid tar waste material leads to environmental degradation in the long-term and yet the utilisation of co-products formations to give useful products that result in major pollution reduction. The composition of acid tar waste has been determined before in countries like Russia, Poland and United Kingdom but it was found that no two samples from different crude benzol processing plants had the same chemical composition (Frolov et al., 1985, Chojnacki et al., 2005, Kolmakov et al., 2007, Leonard et al., 2010). There is thus the need to characterise acid tar waste from ZIMCHEM Refineries since the source of crude benzol and its processing and purification to produce benzene, toluene and xylene is different from that reported in studies carried out elsewhere. This will result in utilisation of this specific acid tar waste.

There is a need to develop process pathways for the utilisation of acid tar waste from a specific acid tar waste producer since the composition varies from place to place, from process to process and differ based on raw materials used in the original coal carbonisation process. In Zimbabwe, Chihobo et al. (2016) considered pyrolysis of acid tar waste from the lagoons of ZIMCHEM Refineries as one approach to clean the area occupied by the waste. Different from Chihobo's study, this study will be based on developing a method for preventing the waste from getting to the lagoons by finding a way to utilize the fresh acid tar waste as a road construction material.

1.6 Structure of research

Chapter One contains the background of acid tar waste, its generation and disposal. This also includes the objective of the study and the justification. Chapter Two presents the review of related literature on the problems associated with the disposal of acid tar waste materials in lagoons, characterisation methods, composition of different acid tar wastes and utilisation processes for acid tar wastes. This Chapter also includes the models used to classify liquids, the properties of asphalt and methods of analysis. Chapter Three provides experimental details of the methods used to:

a) Characterise acid tar waste,
b) Neutralise acid tar waste,
c) Modify acid tar waste,
d) Characterise the modified acid tar waste.

Chapter Four is a presentation of results and discussion of the:

i) Physical and chemical characterisation of acid tar waste
ii) Inorganic and organic characterisation of neutralised acid tar waste,
iii) Viscoelastic behavior of modified acid tar waste.

In Chapter Five conclusions based on the results presented and discussed in Chapter Four are drawn and recommendation for further work proposed.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

The processing of crude benzol in a bid to recover firstly valuable materials and secondly to reduce waste products from carbonisation of coal leads to the production of waste known as acid tar waste. This Chapter will review literature relevant to the generation, characterisation and the utilisation of acid tar waste in the past three decades worldwide. Much focus will be placed on the approaches that have been developed or devised for the disposal and possible utilisation of acid tar waste being generated at ZIMCHEM Refineries in Zimbabwe. The comportment of acid tar waste during handling and storage will also be studied. Rheological characteristics will be reviewed as an approach for the characterisation of acid tar waste for utilisation in pavement application. An attempt will be made to provide the rationale for adoption of certain technologies that will render processed fresh acid tar waste a useful road construction material.

2.2 Acid tar waste generation

Acid tar waste materials are normally defined as tars of high sulphuric acid content and are produced from the refining of oils by the addition of sulphuric acid (Nancarrow et al., 2001). There are three major processes that produce acid tar waste:

a) Crude benzol refining which involves washing of liquid residues from coal carbonisation processes with concentrated sulphuric acid to remove impurities,

b) White oil production process which uses oleum to remove unsaturated and aromatic hydrocarbons with sulphur from heavy lubricant fractions,

c) Oil re-refining process where metals such as lead and zinc are removed from the spent lubricating oils using concentrated sulphuric acid (Nancarrow et al., 2001).

Frolov et al. (1985) defined acid tar waste as a thick, viscous liquid with acidic odour and is highly corrosive toward metal and is unstable. Generally, the acid tar waste solidifies when exposed to air for prolonged periods of time. The acid tar waste that Frolov et al. (1985) defined was straight from the treatment of distillate lube and falls under the white oil production category. More recently, Pensaert and De Puydt, (2010) described pond acid tar waste as waste produced in the refining of benzol and white oil production processes. The definition included that heavy sulphonated hydrocarbon compounds with high residual levels of sulphuric acid waste part of the pond acid tar waste. The nature of acid tar waste was said to vary from low viscous oily substances to hard brittle glassy carbon rich materials. In this regard, it may be very difficult to separate the acid tar waste produced in crude benzol refining from that produced in white oil processing since both contain hydrocarbons.

2.3 Disposal of acid tar waste and environmental impact

Acid tar waste has been disposed into unlined ponds or lagoons worldwide despite the fact that it is highly corrosive and unstable (Catney et al., 2005; Pensaert and De Puydt, 2010). Storing acid tar waste material in ponds often leads to leaching of the acid component into ground water. For example, acidification of groundwater was observed and high levels of sulphates identified in areas close to the Pesniski Dvor dumping site (Zilic-Fiser and Dvorsak, 2010). Pensaert and De Puydt (2010) have recently reported high levels of sulphate concentration in shallow and deep groundwater sources near three ponds of acid tar waste material in Belgium. In another research carried out in South Derbyshire, United Kingdom, sulphate ions and total organic compounds were found in groundwater associated with acid tar waste material amounting to 183000mg/l and 2960mg/l, respectively (Banks et al., 1998).

During storage in holding ponds, the chemical composition of the acid tar waste changes as a result of leaching of acid from the tar into the ground that is caused by rainfall. The evolution of sulphur dioxide and condensation of the substances present in the acid tar waste may occur concurrently leading to an inconsistent chemical composition of the acid tar waste (Frolov et al., 1980 and Burtanaya et al., 2007). The use of quick lime to neutralise acid tar waste in ponds has been practiced and found to be environmentally unacceptable since it produces sulphur dioxide (Pensaert and De Puydt, 2010), which lead to environmental problems such as acid rain (Catney et al., 2005). Manahan (2009) has shown how the presence or release of sulphur dioxide (SO_2) in the air can cause acid rain (equation 2.1).

$$SO_{2(g)} + H_2O_{(aq)} \rightarrow H_2SO_{3(aq)} \qquad (2.1)$$

The SO_2 reacts with water (H_2O) to form sulphorous acid (H_2SO_3). It means, therefore, that the disposing of acid tar waste in ponds or other situations where it interacts with the environment is not sustainable. Statutory instrument 10 of 2007 (Environmental management (Hazardous waste)) is used to regulate such waste as acid tar.

2.4 Techniques for characterising acid tar waste

Characterisation of waste material is usually guided by the purpose. This includes the determination of environmental effect of the waste, monitoring of the waste in the environment and possible utilisation of the waste. The purpose then has to direct the selection of parameters to be used to characterise the waste material. Table 2.1 describes a number of parameters for the characterisation of acid tar waste, resulting from the work of several researchers working independently in the last three decades.

Table 2. 1: Parameters used to characterise acid tar waste with respect to source and purpose.

Researchers	Source of acid tar waste	Parameters analysed	Purpose of characterisation	Country
Frolov et al. (1981)	Fresh and Pond	Viscosity, temperature dependence of viscosity	Comparison with asphalt produced	Russia
Frolov et al. (1985)	Fresh and pond	Sulphuric acid content and with time of storage	Utilisation (pavement production)	Russia
Puring et al. (1990)	Fresh and pond	Viscosity, sulphuric acid, sulpho acid content, carboxylic acid and sulphur dioxide	Storage and transportation	Russia
Chojnacki et al. (2005)	Fresh	Organic and inorganic composition	Utilisation (phosphoric acid production)	Poland
Kolmakov et al. (2006(b))	Pond	Asphaltenes, carbenes, carboids, resins, hydrocarbon	Utilisation and development of procedure to study composition of heavy petroleum products	Russia
Leonard et al. (2010)	Unknown	Asphaltenes, resins, organic content, inorganic content, pH, density and thermal characteristics	Risk assessment and utilisation	United Kingdom
Chihobo, (2016)	Fresh and pond	Ultimate, proximate analysis and organic composition	Determination of combustion profile	Zimbabwe
Musademba, (2016)	Fresh and pond	Ultimate and proximate analyses	Design of a fluid bed incinerator	Zimbabwe

In Table 2.1, a summary is presented in which both fresh and pond acid tar waste materials were extensively studied. Leonard et al. (2010) worked with an acid tar waste from an unknown source that at best was described as resinous and grainy. The bulk density of the sample indicated that the material was solid and that it was similar to that described earlier by Kolmakov et al. (2006(b)) who worked with pond acid tar waste. The material had to be heated to approximately 100^0C to transform it to a liquid. Puring et al. (1990) confirmed that sample materials from ponds were usually solid, hence the need for the acid tar waste to be made liquid by heating to facilitate experimental work. Frolov et al. (1985) observed that in the course of storage, hardening of acid tar waste at the surface occurs with exposure to air and water. The solidification is associated with chemical reactions between the organic compounds in the tar as suggested by Vagner and Tryasunov, (2012) and these are represented by equations (2.2) and (2.3).

$$R\text{-}SO_3\text{-}H + C_4H_4S \rightarrow C_4H_5S\text{-}SO_3\text{-}R \qquad (2.2)$$

$$C_4H_4S + C_4H_4S \rightarrow SC_4H_4\text{-}C_4H_4S,$$

$$SC_4H_4 + C_4H_4CH_2 \rightarrow SC_4H_4 = C_4H_4CH_2 \qquad (2.3)$$

$R\text{-}SO_3\text{-}H$ is the sulphonated organic compound from the reaction of sulphuric acid and organic matter present in acid tar waste. Thiophene (C_4H_4S) is one of the organic compounds found in acid tar waste. Reactions 2.2 and 2.3 are catalyzed by sulphuric acid in the presence of water to form large organic molecules that are described as resinous or solid acid tar waste.

The pond acid tar waste is said to contain caustic waste (derived from neutralisation treatment), refining waste, used technical motor and industrial oil with sulphuric and sulphonated mineral oils (Druzina and Perc, 2010). Nichol, (2000) identified the major components of Hoole bank acid tar waste pond in Cheshire, United Kingdom as comprising sulphuric acid, tar like hydrocarbons and spent bentonite. In an earlier study, Aminov et al. (1989) noted that the pond acid tar waste varied in composition and properties, depending on the type of the petroleum stock treated, storage time and the depth of the pond. Thus, pond acid tar waste cannot be compared to fresh acid tar waste since it will have other components that may not be present following the purification of crude benzol to give benzene, toluene and xylene.

The fresh acid tar waste used by Frolov et al. (1985) was obtained from petroleum oils treated with sulphuric acid and this might be similar to acid tar waste material that was investigated by Chojnacki et al. (2005) who used acid tar waste from crude benzol acidic refining petrochemical plant that produced ethyl benzene. Frolov et al. (1981; 1985); Chojnacki et al. (2005); Kolmakov et al. (2006(b)); and Leonard et al. (2010) defined the parameters for characterising the acid tar waste particularly as they relate to possible industrial application, as tarry materials.

Leonard et al. (2010) considered chemical (organic and sulphuric acid content) and physical (density and moisture content) property determination to characterise the acid tar waste. Frolov et al. (1981) explored the use of the acid tar waste as pavement binders hence the need to determine the temperature dependence of viscosity of the acid tar waste. Kolmakov et al. (2006(b)) later wanted to produce binders but with emphasis on the soluble characteristic of the acid tar waste. In recent investigations, Leonard et al. (2010) worked toward establishing the energy potential of the acid tar waste and thus concentration on determining thermal behaviour of acid tar waste. These relate to both combustion and the furnace construction material properties (Chihobo, 2016 and Musademba, 2016). Puring et al. (1990), however, characterised the acid tar waste with respect to flow ability for ease of transport and storage.

Organic, inorganic and sulphuric acid content, pH, density, viscosity, colour and solubility were some of the parameters used to characterise acid tar waste in most investigations that have been carried out in the past three decades (Frolov et al., 1985; Puring et al., 1990 Chojnacki et al., 2005; Kolmakov et al., 2006(b) and Leonard et al., 2010). It is important, therefore, to consider further the determination of these parameters and their importance in characterising acid tar waste currently being investigated. Such an approach enables the investigator to select the most appropriate technique leading to results that better reflect the acid tar waste under consideration and will provide good indication of possible uses and limitations.

The proper utilisation of acid tar waste in any application requires an in depth understanding of the chemical composition of acid tar waste. The acid tar waste has both inorganic and organic chemical constituents that include sulphuric acid which is inorganic and the extracted organic compounds. Thus, characterisation techniques should identify and quantify both inorganic and organic entities that make-up the acid tar waste.

Sulphuric acid is the major inorganic component found in acid tar waste where it remains as a residue after processing and purifying organic reagents of interest. The sulphuric acid content in the acid tar waste is important in determining the material potential use in other applications. For example, if there is high acid concentration, effort is be made to recover the sulphuric acid. At the same time knowledge of presence and concentration of sulphuric acid helps in the design and the selection of handling materials in order to minimise corrosion effects.

Sulphuric acid content is estimated by titration with potassium hydroxide (Frolov et al., 1985; Aminov et al., 1989; Puring et al., 1990) and the potentiometer used to determine the end point. Frolov et al. (1985) and Aminov et al. (1989) have applied the same method in which the acid tar waste dissolved in a 1:1 alcohol and toluene solution and then titrated with potassium hydroxide dissolved in alcohol. The reason for dissolving the acid tar waste in alcohol and toluene solution is that the pond acid tar waste is not soluble in water. Years later Puring et al. (1990) dissolved the acid tar waste in acetone and followed by titration with 0.1 N spirit solution of di-ethanol-amide and potassium hydroxide. The results showed that the titration with potassium hydroxide gave a more pronounced curve. Chojnacki et al. (2005) used sodium hydroxide to determine the sulphuric acid content of fresh acid tar waste an approach that has been rated as being more accurate than those previously described.

Inductively coupled plasma/atomic emission spectroscopy has been used to determine the inorganic components in acid tar waste (Chojnacki et al., 2005; Leonard et al., 2010). Samples do not need elaborate treatment before being introduced to the machine or equipment where inorganic compounds to determine metal (ion) concentration.

Methods for determining the chemical organic composition of acid tar waste have been developed as reported by Chojnacki et al. (2005); Kolmakov et al. (2006(b)), and Leonard et al. 2010. Kolmakov et al. (2006(b)) developed a method referred to as group analysis. The sample is first transformed from solid to liquid at approximately 100^0C before cleaning with distilled water to remove sulphuric acid. A soxhlet extractor with hexane is then used to separate asphaltenes, carbenes and carboids from hydrocarbons and resins. Asphaltenes are later separated from the carbenes and carboids, then hydrocarbons from the resins. After solvent removal, the products are weighed. The process takes about 24 hours to complete and involves considerable handling, ultimately leading to inconsistencies. It is not uncommon for final estimates to be either under or over stated. The process assumes that what is obtained are hydrocarbons, asphaltenes, carbenes, carboids and resins without providing the individual chemical identification, in itself a major limitation.

Chojnacki et al. (2005) neutralised the acid tar waste using 2.5mol/dm^3 sodium hydroxide and then extracted the sample with diethyl ether. A gas chromatography with a flame ionization detector was then used to analyse and identify the constituents of the treated sample. Leonard et al. (2010), however, used Gas chromatography with a mass spectrometer as a detector (GC-MS) to determine organic content of acid tar waste after the sample had been treated following the procedure proposed and developed by Kolmakov et al. (2006(b)). Mass spectra of the compounds in the sample are used to identify the constituent components by comparing with literature mass spectra in the machine library (Jiang et al., 2007 and Machado et al., 2011). The mass spectrometric approach simplifies the analysis by eliminating the need for standards in the identification of the organic groups. Fourier transform infrared (FTIR) is then used to further confirm the presence of organic functional groups such as –C=C-, that will have been detected by GC-MS (Leonard et al., 2010).

Infrared spectroscopy uses vibrational group frequencies to provide information specific to a functional group and interaction of the functional group with other parts of the molecule (Coates, 2000). For example when –C=C- is attached to methyl compound, it will give a vibration frequency that is different from that obtained when it is attached to a benzene ring. Thus, the frequencies give the indication that the organic matter being investigated is either an alkane or an alkene, or an indication that it is attached to an aromatic compound or a sulphur element.

GC is used to separate the organic components at oven temperatures adapted to each mixture (alkanes, branched alkanes, cycloalkanes and aromatics). The temperature range selected is often in the range 28 to 270^{0}C using a column that is 30 meters long packed with substances that assist in adsorption and desorption of the organic matter thus aiding in the separation process (Chojnacki et al., 2005). The use of a long column and an appropriate temperature variation regime removes the need to use the method developed by Kolmakov et al. (2006(b)). The column separates the organic compounds according to their ability to adsorb on the column and desorbs from the column and this depends on the chemical elements that make up the organic compounds and the molecular mass. Temperature further aids the separation since the different compounds have different molecular masses that evaporate at different temperatures. The different intermolecular forces between different compounds are influenced differently as the temperature is varied. Ultimately the compounds are separated and eluted at different times from the column. They give different residence times on the column and these are unique to the different organic compounds.

Rincon et al. (2005), Semenova and Patrakov (2007), Hu et al. (2012) and Semenova et al. (2012) demonstrated that the determination of organic compounds can be accomplished using FTIR and conclusions drawn based on knowledge associated with functional groups.

2.5 Viscosity determination and fluid rheology

Viscosity is a measure of resistance offered by a fluid to flow (Esteban et al., 2012). Yet Schramm, (2000) states that viscosity describes the physical property of liquids as resistance to shear induced by flow. In this regard viscosity of a material depends on the interplay of several parameters: physical, chemical nature, temperature, pressure, shear rate, electrical and time. Viscosity is a complex phenomenon, deserving a thorough understanding.

The ease of application particularly when spreading the tarry material on designated surface is affected by its internal flow resistance. Puring et al. (1990) measured viscosity for the reason that they were looking for ways to transport and store the acid tar waste, but did not give an account of the methods used. The viscosity of the acid tar waste depends on temperature and generally increases with decreasing temperature (Frolov et al., 1985; Puring et al., 1990). The viscosity of the fresh acid tar waste as reported was found to be less than that of the pond acid tar waste. Since the temperature, pressure, shear rate, electrical field and time were constant, the only reasons for the variation in the measured viscosity values may be attributed to the physical or chemical nature of the material. In general the pond acid tar waste contained higher molecular mass compounds caused by chemical reactions induced by the presence of air, water, and prolonged periods of exposure to ultra violet light.

2.5.1 Temperature effect

Viscosity is affected by temperature and different liquids behave differently to the changes in temperature. The viscosity of Newtonian liquids decreases with an increase in temperature according to the Arrhenius relationship (Barnes et al., 1993).

$$\eta = Ae^{B/T} \qquad (2.4)$$

Where η is viscosity, A is frequency factor, B is the activated energy divided by gas constant and T is the temperature. The greater the viscosity, the stronger is the temperature dependence (Barnes et al., 1993). In non Newtonian fluids, variations of viscosity with temperature show a variety of trends (Tadros, 2010). Frolov et al. (1985) observed that the viscosity of acid tar waste material decreased with the increase in temperature (range 20-80°C). On the bases of these observations the flow of the acid tar waste was Newtonian. This conclusion was, however, drawn in the absence of other parameters such as shear rate effect.

2.5.2 Shear rate effect

Viscosity is affected by the rate at which the material is deformed (shear rate). Furthermore, it is very difficult to classify material as solid or fluid. Models have been developed to assist in describing the behavior of material after it has been stressed at different shear rates. It then becomes common practice to describe a material according to the model that best describes its behaviour. However, real materials usually tend to exhibit a combination of two or more effects, but the dominant characteristic is used to identify the material. Newtonian fluids, for example, have constant viscosity independent of applied shear rate (Chhabra et al., 1999, Tadros, 2010). Examples include simple liquids and very dilute dispersions such as water. Asphalt behaves as Newtonian fluid when the suspended colloids are low in concentration (Little and Petersen, 2005).

Newtonian model is described by the relationship:

$$\tau = \eta \dot{y} \qquad (2.5)$$

τ is the shear stress, η is the viscosity and $\dot{y}$ is the shear rate.

Power law fluid has no yield value. This is for pseudo plastic material (shear thinning if $n<1$ and shear thickening if $n>1$) (Tadros, 2010). The n value indicates the departure from

Newtonian behavior. An example is that it is often used to describe such materials as lubricating grease with n = 0.1 (Chhabra et al., 1999).

Power law model:

$$\tau = \eta \dot{y}^n \tag{2.6}$$

Bingham, Herschel-Bulkley and Casson models have been used to explain the behaviour of a non-Newtonian fluid in which material under consideration is said to be visco-plastic in nature (Chhabra et al., 1999). The materials that are often described by these models are polymer solution, clay solution and ink. The three models (Bingham, Herschel-Bulkley and Casson) exhibits a yield stress, a limiting stress below which a sample behaves as a solid and beyond which it exhibits liquid like behavior (Al-Sabagh et al., 2013; Liu et al., 2014). The material will deform elastically when the externally applied stress is smaller than the yield stress (Chhabra et al., 1999). Non-Newtonian behaviour of asphalt, however, is largely because of elasticity as well as viscosity (Huang et al., 2011). This means that if material behaves as described by the three models it has properties that can contribute to pavement asphalt. A liquid thus need modification to be in solid form before it can be used as pavement binder. The visco-plastic material also displays an apparent viscosity which decreases with increase in shear rate thus it is possible to regard the material as possessing a particular class of shear thinning behavior (Chhabra et al., 1999). The general equation is given as (Liao and Chen, 2011):

$$\tau = \tau_c + K\dot{y}^n \tag{2.7}$$

τ is the shear stress, τ_c is the yield stress or zero shear viscosity, K is the fluid consistency parameter, n is the flow behavior index and $\dot{y}$ is the shear rate. The nature of the fluid is pseudo plastic (shear thinning) if n<1 and dilatants (shear thickening if n>1 (Swami et al., 2013).

The viscosity and shear rate plot is known as the flow curve. If it is in log-log plot, this helps differentiate the Newtonian, Shear thinning, shear thinning with yield stress and shear thickening (Khan et al., 1997). Newtonian (since the viscosity is constant) gives a horizontal line at the value of the viscosity of that particular material. Shear thinning shows a Newtonian behaviour at the low shear rate values and at high shear rate values exhibit decrease in viscosity as shear rate increases. In shear thinning with yield stress, the material shows a decrease in viscosity with increase in shear rate at values above yield stress and at low shear rate there is a characteristic slope of -1 when log viscosity is plotted against log shear rate. Materials that show this behaviour are visco-plastics. Shear thickening is where the viscosity increases over a range of shear rate; this is not that common but it is found in concentrated colloidal dispersions and some polymer solutions.

2.6 Composition of acid tar waste

Hydrocarbon constituents in acid tar waste depend primarily on the original crude benzol organic composition (Puring et al., 1990) and associated impurities that include thiophene. Semenova and Patrakov (2007) obtained the benzene, toluene and xylene fraction percentage of approximately 83% while the other organic impurities fraction was 17%. In another study Vanger and Tryasunov, (2012) obtained the benzene, toluene and xylene fraction to be 96% while the organic impurities fraction was 4%. From the analysis for the two crude benzol materials, it can be deduced that the organic composition of the acid tar waste will not be the same after purification with sulphuric acid. This is a contributing factor to the differences in the organic composition that has been reported for the different acid tar waste materials studied.

It is also possible that some of the compounds detected in the samples examined were products of chemical reactions occurring between the various components of acid tar waste during the treatment process. For example, sulphonic acids are the outcome of aromatic compounds reacting with sulphuric acid (Leonard et al., 2010) during storage and exposure to air. The difference in results amoung the investigators (Frolov et al., (1981; 1985); Chojnacki et al., 2005; Leonard et al., 2010) may be as a result to the different compositions of the original crude benzol oils used, since the organic content is found to range from 80.5 to 6.9% as shown in Table 2.2. Thus, the crude benzol origin and process route followed to extract benzene, toluene and xylene, and ultimately mode of storage of the acid tar waste will ultimately determine the tarry material composition.

Generally the results obtained from the investigations reported indicate that the percentages of organic oils in the pond acid tar waste materials are higher than corresponding organic compounds present in the fresh samples (Frolov et al., 1981; Kolmakov et al., 2006(a); Leonard et al., 2010). It must also be acknowledged as previously noted that most of the pond acid tar waste materials cannot be said to be from one process and source. Used oils have also been disposed into the same ponds with fresh acid tar waste material. The highest percentage (63.8%) of sulphuric acid was observed by Chojnacki et al. (2005) in fresh acid tar waste as compared to the pond acid tar waste (0.01%) reported by Kolmakov et al. (2006(a)). The differences in the percentages of the sulphuric acid may be explained by the fact that the acid is either being consumed by chemical reactions with double bonded organic substances (Chechulin, 2008), water and air whilst in the lagoon or it is evaporating into the air on account of high temperatures which result from chemical reactions that favor the release of sulphur dioxide form of sulphuric acid. Semenova and Patrakov (2007) was able to demonstrate that the main impurities of crude benzol were sulphur containing, unsaturated and saturated hydrocarbons. There is thus, a possibility of these chemicals reacting with sulphuric acid when exposed to air and water resulting in low sulphuric acid concentration in lagoon acid tar waste.

Table 2. 2: Sulphuric acid and organic content in pond and fresh acid tar waste

Researchers	Year	Source of acid tar waste	Sulphuric acid %	Organic content %
Frolov et al.	1981	Fresh	45	41.25
Frolov et al.	1981	Pond (top layer)	0.026	80.5
Frolov et al.	1981	Pond (bottom layer)	12.3	42
Frolov et al.	1985	Fresh	48.2	49.5
Frolov et al.	1985	Pond	35.5	48.3
Kolmakov et al.	2006(b)	Pond	0.01	96.29
Chojnacki et al.	2005	Fresh	63.8	6.9

Table 2.2 shows that there is a difference in sulphuric acid and organic contents of the acid tar waste samples analysed by Frolov et al. (1985) and that by Kolmakov et al. (2006(b)) despite the fact that they were all pond acid tar wastes. There is, however, a close fit between Frolov et al. (1981) top layer pond sample and Kolmakov et al. (2006(b)) sample analyses. There is, no mention of the position from which Kolmakov et al. (2006(b)) collected their sample, a situation that renders the comparison meaningless. Furthermore, these are considerable time lapse between the analyses, both samples could

have collected from the top layer, but the information is not given. There being 20 years difference, the concentration of sulphuric acid could have been affected by the following:

- Chemical reaction,
- Ultra violet light and heat from the sun,
- Dilution by rain and melting ice,
- Heat generated from chemical reactions.

The examination of the bottom layer in relation to the top layer, shows that the sulphuric acid at the top vaporises into the air whilst that in the bottom layer is probably leached into the ground. Both events are time and temperature dependent. For fresh acid tar waste Frolov et al. (1981) and Frolov et al. (1985) had the sulphuric acid and organic composition both close to 50% and yet for Chojnacki et al. (2005) the sulphuric acid content was approximately ten times the organic content as shown in Table 2.2. This shows that Frolov et al. (1981) and Frolov et al. (1985) worked with acid tar waste that was from the same plant while Chojnacki et al. (2005) was from a different country. The sulphuric acid content ranged from 29.5 to 41.1% for the acid tar waste from various oil treatments (Puring et al., 1990). Fresh acid tar waste sulphuric acid composition is due to the amount of sulphuric acid used in the purification process, whereas the organic composition depends on the organic composition of the coal or petroleum used to produce the crude benzol.

The pH of acid tar waste is variable and depends on the process by which the acid tar waste is generated as well as the amount and strength of the sulphuric acid initially used in the process (Frolov et al., 1985). Pre-treatment prior to disposal for lagoon acid tar waste is also important since it affects the pH and the state of the acid tar waste (solid or liquid) (Frolov et al., 1985). In the characterisation of acid tar waste materials, two acid groups are observed and these are indicated by the two plateaus on an acid base titration curve, suggesting the presence of both weak and strong acids in the acid tar waste material (Frolov et al., 1985, Aminov et al., 1989 and Puring et al., 1990). The investigators have acknowledged that the first sharp pH change is due to neutralisation of sulphuric acid while the second is due to that of the weak organic acids. Leonard et al. (2010) was able to identify the following organic acids: methyl phenyl benzoic, naphthalenyl propenoic, phthalic, naphthalene acetic and phenanthrene carboxylic in the acid tar waste materials.

A study of the Hoole Bank Lagoon in United Kingdom showed that particles settled at the bottom of the lagoon, and that the density of acid tar waste ranged from 1.2 to 1.4 g/ml. The viscosity was observed to vary with temperature (Nichol, 2000). In a similar research at the D.I. Mendelev Yaroslav in Russia, a high ash content of approximately 6.5% for the bottom layer of acid tar waste materials was reported (Tumanovskii et al., 2004). The high viscosity at the bottom layer of the pond material could be related to the presence of the ash in the acid tar waste on account of subsequent chemical reactions that might occur. This ash can also settle at the bottom because of gravity. Puring et al. (1990) made similar observations when they reported increased density and viscosity with depth of the pond. All this leads to the conclusion that the acid tar waste contains particles which are heavy and are likely to settle to the bottom of the pond. The particles could influence the modification of acid tar waste to produce pavement binders by improving the resistance to shear of the binder material.

Frolov et al. (1981) observed viscosity differences from top to bottom in the pond samples suggesting exposure or gross particle segregation in the acid tar waste during settling. These observations are in agreement with Puring et al. (1990) who investigated acid tar waste which had been stored in a pond for over 18 years.

2.7 Neutralisation technique

In many previous acid tar waste disposal options, neutralisation has been extensively used. Because of the exothermic nature of the process, neutralisation is usually carried out under controlled temperature conditions. When the temperature exceeds 100^0C, it leads to sulphuric acid evaporation and this appears as a mist, and is accompanied by the volatisation of the lighter fractions of mineral oil present and polycyclic aromatic hydrocarbons (Druzina and Perc, 2010). Pensaert and De Puydt (2010) recently confirmed that neutralisation of acid tar waste is exothermic with temperature increases in the range 70 -100^0C being achieved.

Pensaert and De Puydt (2010) reported the use of calcium hydroxide to neutralise the acid tar waste. Sodium hydroxide may also be added to adsorb the sulphur dioxide and sulphur trioxide that is released during the neutralising process. The heat energy produced (to account for the observed temperature change) depended on the neutralising chemical (Druzina and Perc, 2010) and is true for the neutralisation of the same acid tar waste with different bases. If the acid tar waste materials are different, other factors may be considered, and these include the strength and the concentration of the acid in the acid tar waste and the amounts of organic compounds present that are capable of absorbing heat energy. The neutralising chemicals commonly used in practice include calcium oxide, calcium hydroxide and calcium carbonate. Frolov et al. (1980) experimented with calcium oxide to neutralise acid tar waste and the resulting temperatures reported were in the range 90 -100^0C.

Comparing the results of Frolov et al. (1980) obtained using calcium oxide with those due to Persaert and Puydt, (2010) using calcium hydroxide, it is clear that calcium hydroxide gives the lowest temperature. It should, however, be noted that the neutralisation effect of calcium oxide Frolov et al. (1980) used is easily influenced by moisture. Water reacts with calcium oxide to produce calcium hydroxide as shown in equation (2.8).

$$CaO + H_2O \rightarrow Ca(OH)_2 + \Delta H \text{ (heat energy)} \qquad (2.8)$$

Sulphuric acid reacts with calcium hydroxide to produce calcium sulphate dihydrate ($CaSO_4 .2H_2O$) (Deng et al. 2013). Calcium sulphate dihydrate then transforms to the calcium sulphate hemihydrate ($CaSO_4 .0.5H_2O$) when heated above 98^0C. If however, the reaction is given sufficient time to progress, the end product is calcium sulphate anhydrate ($CaSO_4$). Tlili et al. (2008) highlighted that the formation of calcium sulphate dihydrate occurs at temperatures up to 100^0C. Thus the calcium sulphate anhydrate will require higher temperatures. Calcium sulphate is generally used in agriculture as fertilizer (gypsum) and in building as filler material in ceilings and walls. It may be concluded that the sulphuric acid component of acid tar waste if present in sufficient quantities can be used to produce gypsum as a co-product following neutralisation process.

2.8 Processing and utilisation of acid tar waste

The processing of fresh acid tar waste to produce pavement binders was said to be more difficult than that of acid tar waste from lagoon due to the high percentages of sulphuric acid (Frolov et al., 1981). The pond acid tar waste on the other hand is easy to handle since it will have been stabilised by chemical reactions such as desulphurisation, condensation and polymerisation that occur during the long period of storage (Frolov et al., 1985). However, most of the lagoons are composite disposal sites thus contain different materials (Nancarrow et al., 2001). Under closed system sulphuric acid mixed with organics does not react with the organic part of the mixture (Chechulin et al., 2008). However, Yablokov et al. (2010) observed that the sulphuric acid does react with acid tar waste organic molecules when heated. In this respect, it may prove difficult to deal with freshly produced acid tar waste. It is probably this latter observation that led to failed attempt in the United Kingdom in the 1970s to make polymers and inorganic cement from acid tar waste materials. Researchers at that time concluded that the processes leading to co-products manufacturing were more expensive than the neutralisation and landfill dumping of acid tar waste material (Nancarrow et al., 2001).

Frolov et al. (1980) developed a method for the production of paving asphalt from acid tar waste using a three stage process which involved:

i. Neutralisation of the acid tar waste with technical calcium oxide at temperatures between 90 and 100^{0}C;

ii. Evaporation of water from the reaction mass at 100 to 130^{0}C;

iii. Oxidation of the neutralised mass with air at 160 to 190^{0}C in a thermostatic metal reactor with a stirrer.

Asphalt that was produced from acid tar waste met the requirements of the Russian standards for bitumen grade 60/90 paving asphalt material with respect to penetration, softening point, breaking point, flash point and adhesion to marbles but had low ductility of 3.9cm at 25^{0}C instead of the expected 61cm (Frolov et al., 1980). The acid tar waste used was from a storage pond described as having excess paraffinic oils and benzene resins. While the process description does not include gaseous emission containment, it is possible that sustainable environmental concerns had at the time not been viewed with the seriousness that is applied today. Of major interest was the need to create or recover organics that had potential use as materials for pavement binder construction.

Kolmakov et al. (2006(a)) developed a method that converted acid tar waste to asphalt using the thermal cracking approach. The resulting product using this technique was found to be process temperature sensitive. For example, the penetration was observed to decrease with time for materials processed at high temperatures ranging from 460 to 480^0C. Furthermore, exposure of acid tar waste to high temperatures for more than 10 minutes caused the formation of coke, instead of asphaltenes and resins. The latter are responsible for the viscosity characteristics that are derivable in asphalt. This type of processing also requires the control of emissions as only low temperatures (400 to 420^0C) are used. Thin film cracking of two samples of acid tar waste at 350 and 400^0C (Zorin et al., 2012) results for sample 1 were:

i) Asphaltene material (65-70%),

ii) Liquid hydrocarbons (20-25%),

iii) Gas (5-10%).

In this process the hydrocarbons were made up of polyalkylnaphthenes, polyalkylbenzenes, alkylnaphthalenes, fluorenes, phenantrenes, anthracenes and other aromatic hydrocarbons.

A technology for processing acid tar waste with the aim of obtaining solid fuel, resins and general use medium oils was proposed and developed by Burtanaya et al. (2007). The technology is based on membrane use to separate hydrocarbons and comprises the following steps:

a) Heating and filtration to remove acid water and particulate contaminants;

b) Neutralisation of the filtered acid tar waste with an alkali solution;

c) Two stage de-asphalting and subsequent series separation of oil and resin in membrane units.

The auxiliary stages of the process involved neutralisation and treatment of the acid waters generated and the recovery of the solvents used. The process yields ~60% solid fuel, ~12.5% resin and ~26% mineral oils.

Lyaklevich and Rudkovskii, (1979) patented a process for the manufacture of boiler fuel from solid and high viscosity acid tar waste mixed with a straight run petroleum fraction. The resultant boiler fuel yield was found to be 92-97.4 wt %. In an earlier study, an enriched organic matter solid fuel was derived from acid tar waste using an organic admixture (Antonishin et al., 1974 and Kondakov et al., 1976-Patent). The admixture was pulverized and simultaneously heated to 200 – 300^{0}C. It was observed that the organic matter of the acid tar waste when heated to 200-300^{0}C behaved as a reducing medium for sulphuric acid.

More recently, Chojnacki et al. (2005) developed a process that utilises acid tar waste to produce phosphoric acid. In this study, fresh acid tar waste referred to as polluted sulphuric acid or spent petrochemical sulphuric acid was used. It was concluded that there was no significant difference between the use of pure sulphuric and polluted sulphuric acid in the production of phosphoric acid but that the solubility of calcium sulphate manufactured during the process was increased. An adjustment to the calcium sulphate production process was made when 10 % of the polluted sulphuric acid made up with pure sulphuric acid.

The solidification process which involved neutralisation of acid tar waste with calcium oxide, calcium hydroxide and calcium carbonate was also carried out. The solid product was used as an energy source in a thermal power plant (Druzina and Perc, 2010).However, the neutralisation process which releases gases (sulphur dioxide and sulphur trioxide) up to a maximum of 3000 to 5000 cubic meter per hour has to be wet scrubbed with sodium hydroxide.

The method selected for processing acid tar waste should incorporate material variation in composition and properties (Aminov et al., 1989). Because of the difference in mineralogical composition of the original material and subsequent heat treatment and extraction process followed, the acid tar waste will behave differently. There is need therefore to develop independent methods that may be specific for a particular acid tar waste. For example, the acid tar waste that Frolov et al. (1985) worked with was fresh and had 48.2 % sulphuric acid and 49.5% organic matter. Chojnacki et al. (2005), on the other hand, processed acid tar waste with 63% sulphuric acid and only 6.9% organic matter. Burtanaya et al. (2007) was thus able to conclude that the failure to apply the process method appropriate for materials from different plants due to the difference in their chemical and physical properties of the acid tar wastes would naturally result in different out comes. The most important process that most utilisation processes incorporated is neutralisation.

The development of pavement binder from acid tar waste material normally follows the neutralisation process. For an in-depth review, pavement binder development is considered in section 2.9.

2.9 Pavement binder (asphalt)

Bitumen is a product obtained at the end of a hydrocarbon refining chain (Voitovich, 2010) and has been used as a binder on its own or with various fillers and polymer composite additions. Asphalt is a complex mixture of organic molecules that vary in chemical and molecular weight (Airey et al., 2002). It is also said to be a thermoplastic, viscoelastic liquid that behaves as a glass-like elastic solid at low temperatures and as a viscous fluid at high temperatures (Airey, 2004). The term bitumen is also used to describe the mixture of hydrocarbons (Lu et al., 2005). Asphalt is also developed from the residue material which is obtained during the distillation of crude oils. This material is generally referred to as bitumen (Soleimani, 2009). It means therefore that the terms bitumen and asphalt are used interchangeably to refer to the same material. Branthaver et al. (1993) reported the major functional groups found in asphalt as carboxylic acid, ketones, pyrroles, quinolones, phenols and sulfoxides.

From a physical perspective the following are used to describe the desired performance attributes of asphalt: softening point, penetration, morphology and rheological properties (Mortazavi et al., 2010). Penetration, softening point and viscosity are conventional asphalt tests. The viscosity is an important measure since a more viscous binder has high softening point. This reduces the deformation, bleeding and increases pavement stability at high temperatures (Tuntiworawit et al., 2005). Generally, asphalt binders have been graded using penetration and viscosity. However, modification techniques applied on the asphalt requires that the effect of the modifier be determined by not just the use of viscosity and penetration parameters (Zhao and Hesp, 2006). This viewpoint is also supported by Kumar and Garg, (2011) who stated that conventional tests were not satisfactory in testing the response of the material to stress. In this respect other approaches such as rheological characterisation of the material must be explored.

2.9.1 Modification of asphalt

Bituminous binders have various limitations when it comes to overloading and severe climatic conditions in as far as they relate to stress problems (Kumar and Garg, 2011). Modification of the asphalt is thus needed to increase the resistance of the asphalt to permanent deformation at high service temperature without affecting its properties at other temperatures (Airey, 2004). The increase in the elastic component of the asphalt, thereby reducing the viscous component will improve the flexibility of the asphalt. Fillers such as lime can be used as modifiers in order to improve the stiffness of the asphalt (Airey, 2004).

Latex is one of the materials used to improve binding properties of bitumen such as penetration. However, high concentrations result in reduced homogeneity of the mixture (Tuntiworawit et al., 2005). For example, the use of more than 7% latex concentration resulted in heterogeneous appearance which was observed as the physical separation of rubber particles from the binder. In this report, the addition of latex has optimum levels that are generally of low concentration.

Golalipour, (2013) investigated the use of different types of oil in asphalt modification. The oil reduced the stiffness and the rutting resistance of the asphalt meaning oil had negative effects on high temperature properties, but it improved the low temperature performance of the asphalt.

Styrene-butadiene-styrene (SBS) has been accepted as an asphalt modifier for many road projects because of its good performance in both high and low temperature applications (Wang et al., 2010). SBS polymer modification of asphalt also improves rheological properties such as the stiffness, elasticity and the rutting resistant parameters (Airey, 2004). Lu et al. (2014) noted that polymer modified binders particularly with SBS retain better rheological properties and in addition demonstrate good ageing resistance. The use of SBS is, however, limited by the high cost of the material.

The use of tyre rubber powder to modify asphalt shows enhanced physical and rheological properties (Zhu et al., 2009). Addition of crumb rubber into the asphalt improved the complex modulus and the rutting resistance parameter at each loading temperature (Wang et al., 2012). Ghavibozoo and Abdelrahman, (2013) reported similar results and concluded that crumb rubber has the ability to enhance the physical properties of bitumen and in the process reduce volumes of scrap tyres in the environment. Costa et al. (2013) observed significant improvement in the resilience or elastic recovery after penetration in the material. The asphalt rutting resistance parameter was increased by incorporating crumb rubber (Yu et al. 2016). When 18% of crumb rubber from tyres was added 60/70 grade bitumen, there was an increase in the failure temperature from 75 to 95^0C and that the phase angle was lowered to the more balanced viscoelastic behaviour. This is because scrap rubber tyres consist of four main components (Ghavibozoo and Abdelrahman, 2013):

i) Oil,

ii) Natural rubber (poly isoperene),

iii) Synthetic (rubber like) styrene-butadiene rubber and

iv) Fillers.

Tyres also contain the expensive SBS component that is generally acknowledged as a good asphalt modifier. In this respect, scrap tyre provides more than one modifier. The use of tyres thus dual: helps reduce pollution from acid tar wasteas well as from spent tyres.

2.9.2 Rheological behavior

Rheology is the study of deformation and flow of matter (Blair, 1969). Malkin and Isayev (2006) recently explained that rheology is not about deformation and flow only but about properties of matter in determining its behavior in relation to deformation and flow. Behavior is the relationship between external action (force applied to body) and internal reaction (changes of a body shape) (Malkin et al., 2006). Rheology is based upon measurement of the external forces acting tangentially per unit area on deformed body (that is shear stress, τ (Pa)), the angle of deformation (strain, y) and the rate at which deformation takes place (shear rate, ý (s^{-1})) (Williams, 1992). Rheology can be used to assess long term storage stability of dispersion, understand the properties of the mixture and help in finding ways to formulate the product to optimise processing methods (Williams, 1992). It is connected to material chemistry through existing experimental evidences of direct correlation between chemical parameters (molecular mass and molecular mass distribution, chemical structure, intermolecular interactions) and rheological properties which makes it possible to synthesise materials with desirable properties (Malkin and Isayev, 2006). Thus material of the same chemical composition should behave the same when deformed.

There are four types of rheological behaviour (Tadros, 2010). These are:

1. Inelastic solids - they exhibit no strain recovery,
2. Elastic liquid - have partial strain recovery,
3. Ideally elastic material - deformation is followed by an instantaneous recovery
4. Viscoelastic material - have slow stain recovery.

Of interest to this research is viscoelastic behaviour of a material since asphalts by their nature are considered to be viscoelastic (Tuntiworawit et al., 2005).

Viscoelastic material exhibits both elastic and viscous behaviours. Asphalt at low temperature is more elastic and at high temperature it is viscous with Newtonian viscous flow properties (Airey, 2004). Non–Newtonian behaviour of asphalt, however, is largely because of elasticity as well as viscosity (Huang et al., 2011). This is all because the response of asphalt to stress is dependent on both temperature and time. In this respect, that fresh asphalt will behave differently to stress when compared with old asphalt.

2.9.3 Dynamic shear rheometer analysis

There are three experiments that are used to determine viscoelasticity: strain relaxation after the sudden application of stress (creep), stress relaxation after the sudden application of strain and dynamic (oscillatory) technique (Tadros, 2010). The most common and popularly used technique for asphalt viscoelastic determination is the dynamic shear technique (Airey, 2004; Tuntiworawit et al., 2005; Hafeez et al., 2009; Kumar et al., 2009; Geng et al., 2014). In this method, a sample is constrained in between two plates with oscillating strain at a given frequency as shown in Figure 2.1. Sinusoidal varying deformation (strain) is applied to the sample (Khan et al., 1997) represented by:

$\gamma = \gamma_0 \sin(\omega t)$ (2.9)

Where γ_0 is strain amplitude, ω is the frequency and t is the time. Stress develops in response to the applied strain. This gives the phase angle (δ) which is the angle that the stress curve will have shifted from the strain curve (Blair, 1969). The shear generated by the oscillatory shear will again be sinusoidal but will be shifted by a phase angle (δ) with respect to the strain waveform as follows:

$\tau = \tau_0 \sin(\omega t+\delta)$ (2.10)

τ_0 is shear amplitude. The frequency of 10 rad/s is related to a traffic speed of about 100km/h and 1rad/s is appropriated for standing traffic (Kumar et al., 2009).

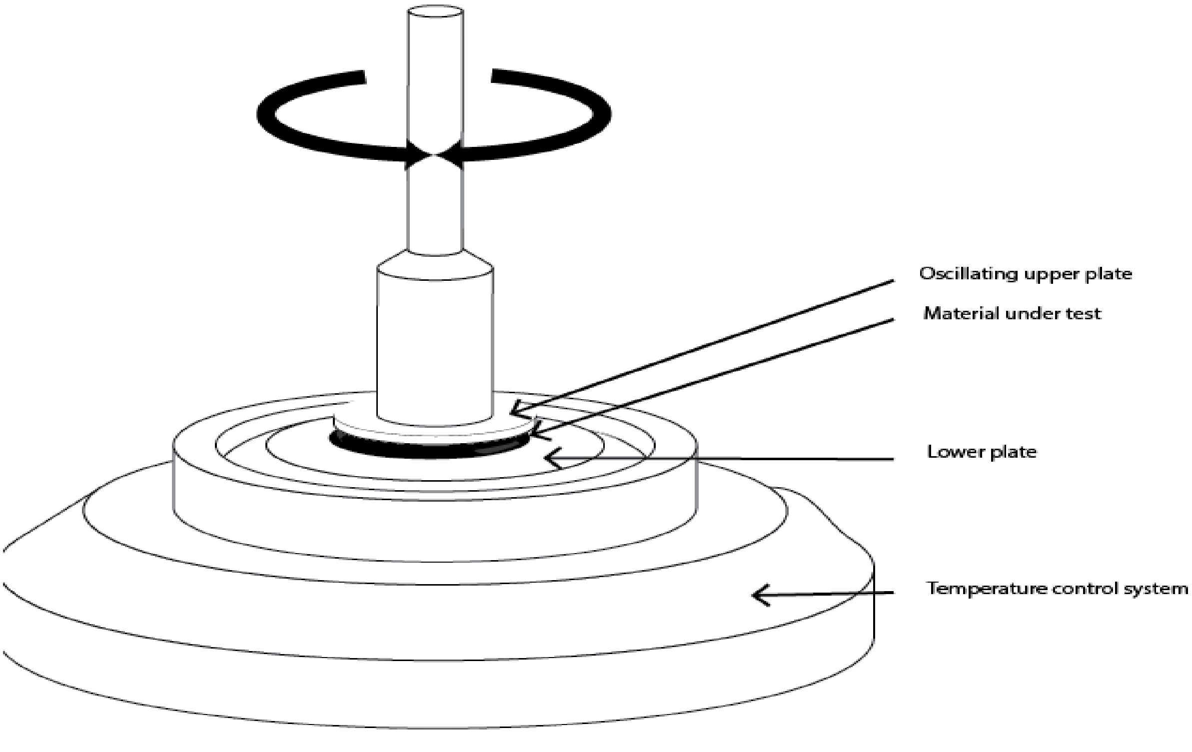


Figure 2. 1: Dynamic shear rheometer schematic diagram

Thus phase angle refers to the material behavior: elastic, viscous and viscoelastic responses can be deduced.

- Elastic response: there is no time shift between the stress and strain sine waves (phase angle is zero).

- Viscous response: there is maximum energy dissipation, the strain and stress sine waves are shifted by $\pi/2$ (phase angle is 90^0). Thus reduction in phase angle enhances the elastic properties of asphalt binder (Javid, 2016).

- Viscoelastic response: has the shift between 0 and 90^0. Viscoelastic material will exhibit viscous flow under constant stress, but a portion of mechanical energy is conserved and recovered after stress is released (Hackley and Ferraris, 2001).

The ratio of the maximum stress to the maximum strain is the complex modulus (G*) where G* refers to stiffness of the material (Tuntiworawit et al., 2005). A binder should have high values of G* at high temperatures for a good deformation resistance (Kumar et al., 2009). G* contains elastic (recoverable) and viscous (non-recoverable) components, and the ratio of these two is defined as the phase angle (Wang et al., 2012). The increase in G* can be considered as a hardening process in other words primary aging of the binder (Navarro et al., 2007).

G* divided by sin of phase angle ($G^*/\sin\delta$) is known as the rutting resistance parameter (Pareek et al., 2012). “Rutting is the main distress encountered in asphalt pavements, especially when temperatures are high” (Al-Khateeb et al., 2011). Rutting in asphalt manifests itself as depressions which are formed in the pavements wheel path due to repeated traffic loading (Huang et al., 2011). High values show rutting resistance which is high. In order to maximize the rutting resistance parameter a high value of G* and a low value of δ is required (Hafeez and Kamal, 2009). This means that the material has to be stiff and more elastic since high values of G* shows that the material is resisting shearing and low values of δ are leading toward zero which gives a more elastic behavior. The rutting resistance should be more than 1.0 kPa (Ghuzlan et al., 2013; Joshi et al., 2013). Rutting occurs during early to midlife of the pavement (Ghuzlan et al., 2013). This is the main reason for testing rutting resistance.

There is also the complex viscosity which is the frequency dependent viscosity function determined during forced harmonic oscillation of shear stress (Hackley and Ferraris, 2001). This help in determining the effect of frequency and temperature on the viscous nature of the material.

Airey, (2004) stated that it is important that strain sweeps are carried out to ensure that the dynamic tests are conducted in linear viscoelastic range so that the material functions such as complex modulus and viscosity are independent of the applied strain levels.

Most researchers who have examined 60/70 grade bitumen for modification tests (Airey, 2004; Kumar and Garg, 2011; Babalghaith et al., 2016; Yu et al., 2016). Kumar and Garg, (2011) concluded that 60/70 grade bitumen is the ideal pavement material for heavy traffic and high temperatures.

2.10 Summary

There are three different processes that generate acid tar waste:

1. Crude benzol refining;
2. White oil production;
3. Petroleum oil refining.

The crude benzol refining, in which purification of residue from coal carbonisation process is considered of interest in the current study. The literature review presented has shown that very few studies have been carried out on characterisation of acid tar waste from crude benzol refining from coal carbonisation processes. It was also found necessary to review corresponding information from the other two processes: crude petroleum refining and re-refining of spent lubricating oils.

Ground water pollution was observed near three acid tar waste dumping sites. The reason was leaching of the acid tar waste into the ground water. This leads to the conclusion that disposing of acid tar waste in lagoons is not environmentally sustainable as originally thought, thus the need to come up with a method to utilize acid tar waste in co-product manufacturing as is envisaged with respect to ZIMCHEM Refineries of Zimbabwe.

Characterisation of acid tar waste as currently reported has been done mainly for possible utilisation though the methods are varied and many. Because of the difference in the intended use, the properties used to characterise the acid tar waste have differed from one investigator to the other. Chemical properties that have been used to characterise acid tar waste include the determination of sulphuric acid, inorganic and organic matter content. Sulphuric acid content determination relies on use of titration with a metal base, and in most recent studies, sodium hydroxide has been the base of choice.

In determination of organic matter composition, several methods have been developed. Group analysis, a laborious technique that requires a lot of solvent evaporation leads to considerable losses of some organic matter during handling to increase scatter in final results. The other method uses gas chromatography with different detectors one of which is the mass spectroscopy with a reference library available that identifies the organic compounds. Sample preparation technique is fairly simple and easy to handle. Another is the FTIR method which uses absorption spectroscopy to identify functional groups. While the FTIR may be used alone, often it is used in conjunction with GC-MS to support the identification of functional groups.

In the literature available, the composition of acid tar waste varied from study to study, a situation that has led to differences in utilisation of the characterised materials:

i) Pavement binders;

ii) Phosphoric acid production;

iii) Production of fuels and energy being some of the ways.

The acid tar waste from ponds was predominantly been used for binder production as compared with fresh acid tar waste. The production process required neutralisation of the acid tar waste before use. Fresh acid tar waste is said to be difficult to process and very acidic and thus, not used for the production of pavement binders, instead, the co-production of gypsum is suggested following which the residue remaining maybe considered for asphalt production.

The production of calcium sulphate using fresh acid tar waste results in a product that is more soluble than the one produced using pure sulphuric acid. Excess sulphuric acid in acid tar waste can also be used to produce phosphoric acid.

As was alluded to by Kolmakov et al. (2007), the utilisation of acid tar waste is guided by the demand for a particular product. In Zimbabwe, there is greater need for pavement binder, hence the need to focus this study on modification of fresh acid tar waste to produce a pavement binder. This is in line with the fact that of the three utilisation methods that have been explored pavement binder production draws its raw materials from locally available wastes and that the demand for asphalt products is relatively high in Zimbabwe and the region. In addition to addressing a major environmental pollution problem, the technique to be developed offers Zimbabwe an opportunity to exploit sustainably its abundant coal resources.

The rheological viscoelastic characterisation of neutralised and modified acid tar waste is an area which has received limited attention in the available literature. In this regard, an attempt will be made to provide information that scholars may use to develop appropriate technologies that not only protect the environment, but may lead to the manufacture of co-products that are useful and of economic value.

Bitumen or asphalt has been used as a pavement binder though it manifests problems of being affected by temperature and heavy loading which necessitates its modification. Most researchers used rubber from tyres as a substitute for styrene butadiene rubber to modify bitumen. This resulted in improved bitumen in terms of its viscoelastic behavior and the rutting resistance which has been cited as a problem when pure bitumen is used.

This research will concentrate on rheology since it reveals the response of the material to deformation. This is important since materials such as bitumen have a complex chemical structure.

CHAPTER THREE

MATERIALS AND EXPERIMENTAL PROCEDURES

3.1 Introduction

The Chapter discusses the methods used to physically and chemically characterise the acid tar waste so as to understand material properties with respect to its acidity, viscous nature and chemical composition. The acid tar waste neutralisation and modification processes are described in detail. The methods for the determination of viscosity and its dependence on temperature and shear rate are included. The analysis of the modified acid tar waste material using rheology is also given in detail.

3.2 Materials

The fresh acid tar waste samples used in this study were supplied by ZIMCHEM Refineries from its benzol processing plant in Redcliff, Zimbabwe. The samples were collected from two outlets as shown in Figure 3.1. One litre amber glass bottles were used for collection and storage of the samples. Five litres of each effluent waste was collected from each outlet. Once collected, the samples were taken to the Chinhoyi University of Technology, Fuels and Energy laboratory for storage in a cool place for the duration of the research. The assumption made was that the acid tar waste does not change much with time in closed amber bottles. Chemicals of analytical grade were used and these are: calcium oxide, calcium hydroxide, sodium hydroxide and sulphuric acid. Organic solvents used were High Pressure Liquid Chromatography (HPLC) grade and these are: Hexane, pentane, methanol, dichloromethane and toluene. Ground tyres were provided by National Tyres Services of Zimbabwe, used engine oil, and bitumen grade 60/70 were supplied by Engen Petroleum (Limited), South Africa.

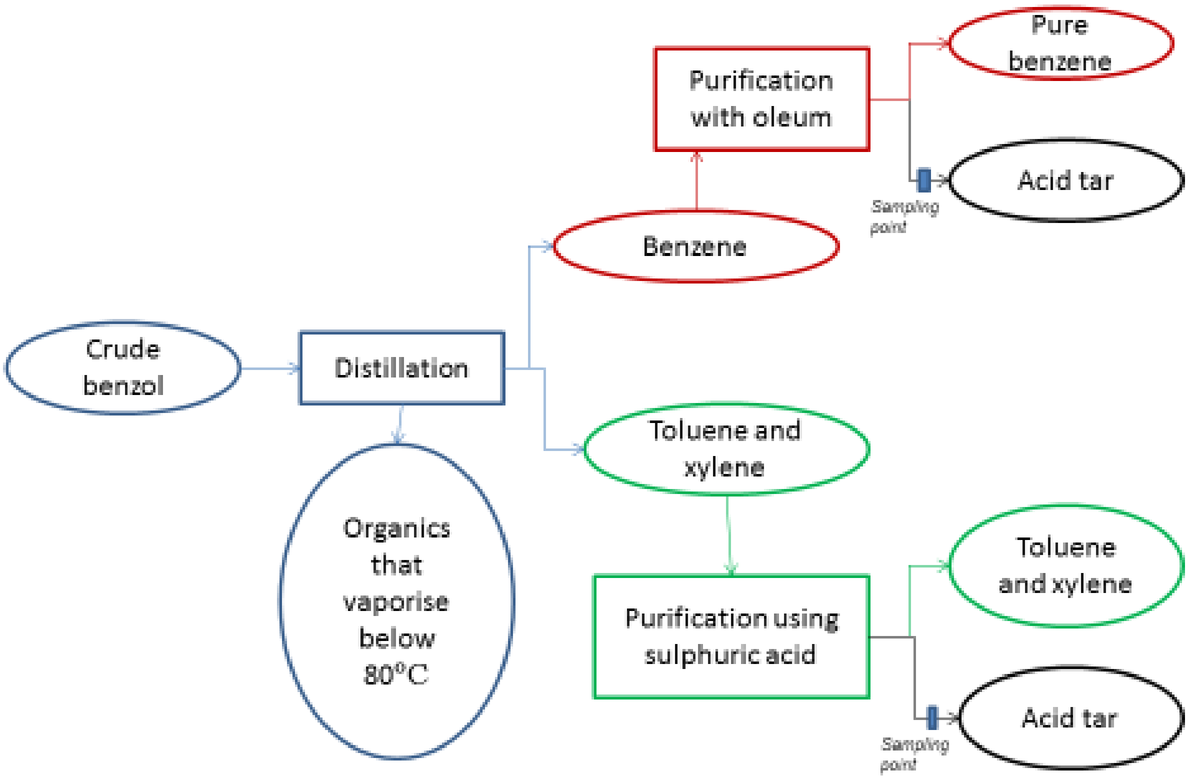


Figure 3. 1: The flow chart of the benzol process highlighting the acid tar waste sampling points

3.3 Acid tar waste samples

The two different acid tar waste samples from crude benzol processing were (Figure 3.1):

a) Toluene and xylene effluent stream acid tar obtained after purification with 98% sulphuric acid. This was a brown and viscous liquid.

b) Benzene effluent stream acid tar obtained after purification with oleum. This was black and less viscous than that from the toluene and xylene effluent stream.

The two acid tar wastes were highly acidic with pH values of 1.41 and 1.69, for the toluene and xylene effluent stream acid tar and the benzene effluent stream acid tar, respectively. The density of toluene and xylene effluent stream acid tar (1.55g/ml) was more than that of benzene effluent stream acid tar (1.52g/ml).

3.4Experimental procedures

The methods used to determine the chemical and physical characteristics of the acid tar waste are described in this section.

3.4.1Determination of Chemical Properties

The chemical properties determined include the organic and inorganic properties.

3.4.1.1 Gas Chromatography – Mass Spectroscopy (GC-MS) analysis

Acid tar waste was washed with distilled water to clean the acid tar waste of any residual sulfuric acid as proposed by (Kolmakov et al., 2006(a)). The water soluble organics were extracted using pentane and hexane. The solid part was dissolved in methanol, dichloromethane and in toluene. A 10g sample was refluxed with toluene before analysis using GCMS-QP2010 Ultra Shimadzu. The GC was operated in split mode ratio 2:1, 2µl sample with helium at 47.1cm/sec as the carrier gas. The capillary, a 30m x 0.25mm column was programmed initially to operate at 60^{o}C for 5 minutes before the temperature was increased to 300^{o}C at 10^{o}C/minute, and held at 300^{o}C for 2 minutes, to obtain a 31 minutes total run time. The MS scanning was between 35 and 500m/z with an inlet line temperature of 250^{o}C, ion source temperature of 200^{o}C and electron ionization mode of 70eV. All this was done to identify the organic compounds present in the acid tar waste. The above conditions were adopted from Leonard et al. (2010) with adjustment made for the initial temperature, final temperature and analysis time to suit the samples.

3.4.1.2 Fourier transform infrared spectroscopy (FTIR)

Samples were filtered and neutralised with calcium oxide and later analysed with the Agilent 600 FTIR. A 1g sample was analysed in solid form. The results were interpreted using the method developed by Coates, (2000) and refined by Semenova et al. (2012).

3.4.1.3 Inorganic cations and anions analysis

The cation and anion analysis were carried out using inductively coupled plasma/ atomic emission spectroscopy. The samples had to be digested with nitric acid to remove any trace of organic matter before being introduced into the machine (Leonard et al., 2010).

3.4.1.4 Acid concentration determination in acid tar waste

About 1g of acid tar waste was placed into 100ml volumetric flask and diluted with distilled water to 100mls, and 20 mls aliquots withdrawn for titration with 0.1M sodium hydroxide. A Lasany L1-702 pH meter calibrated using buffers at two pH: 4 and 7, was used to measure pH after every 2mls of base addition. Plots of volume of base added versus pH were made from which the volume at pH 7 was obtained. The concentration of the acid was then calculated.

3.4.2 Viscosity measurements

The viscosity of each of the two acid tar wastes was measured using NDJ-85 viscometer. The instrument is basically a rotational viscometer. Benzene effluent stream acid tar waste required the use of spindle 1 while the toluene and xylene effluent stream acid tar waste required spindle 2 at 25^0C using a water bath. A rotational speed of 60 rounds per minute was chosen since it gave the highest % torque. Three readings for each sample were made from which the mean or average was calculated.

3.4.2.1 Viscosity temperature dependence

The viscosity was determined in the temperature range 293K - 333K at 10K intervals using a heating mantle with temperature control probe (Frolov et al., 1981). The sample was held for ten minutes at each set temperature before recording viscosity. Value of r^2 were obtained using the Origin 2015 software by fitting the data to exponential equations with the value of r^2 closest to 1 picked to represent the relationship of viscosity and temperature.

3.4.2.2 Shear stress shear rate dependence

The shear stress in percentage torque was measured against shear rate from 0.3 to 60 revolutions per minute (rpm) at 298K following the method proposed by Stanciu, (2014). The data was then fitted into the five models described in section 2.5.2. The model that best described the acid tar waste behaviour was determined using correlation coefficient. The value of correlation coefficient closest to 1 gave the best fit. The correlation coefficient was obtained using Origin 2015 software. The models used in the software were Newtonian, Power law, Bingham, Herschel-Bulkley and Casson, and these have been discussed in detail in Chapter Two.

3.4.2.3 Viscosity shear rate dependence

Viscosity was measured against shear rate ranging from 0.3 to 60 rpm in order to determine the behavior of the acid tar waste using the flow curve on a log-log plot at

298K. The results were then used to characterise the material as either: Newtonian, shear thinning, shear thinning with yield stress or shear thickening.

3.4.3 Neutralisation

Approximately 10 grams of acid tar waste was placed in a beaker and neutralised using calcium hydroxide (3.51g and 3.89g for the benzene and toluene and xylene effluent stream respectively) and calcium oxide (2.67g for the benzene effluent stream and 2.94g for the toluene and xylene effluent stream). The amount of calcium hydroxide and calcium oxide used was calculated using the results from the acid concentration determinations. Equations 3.1 and 3.2 were used to calculate the number of moles of the bases which was then used to calculate the mass of the base.

$$2H^+ + Ca(OH)_2 \rightarrow 2H_2O + Ca^{2+} \qquad (3.1)$$

$$2H^+ + CaO \rightarrow H_2O + Ca^{2+} \qquad (3.2)$$

The initial and maximum temperatures attained were recorded. The gas emission levels were checked using the E4500-S gas analyser. The solubility of the products in water was determined using 1g sample in 100mls water. The composition of the product was determined using methods described in sections 3.4.1.2 and 3.4.1.3. The neutralised acid tar waste salt was heated for 20mins at 150^0C in an attempt to produce a less soluble material from the acid tar waste. The procedure was adopted from a study by Zhernovaya and Onishchuk, (2005) where a mineralogical slime waste was heated to produce gypsum.

3.4.4 Modification of acid tar waste

The acid tar waste was mixed with calcium oxide and the viscoelastic behavior determined as described in section 3.4.5. Mixtures were made of neutralised acid tar waste, ground tyres of mesh size 20 and used engine oil as shown in Table 3.1. The mixtures were subjected to 100^0C for two hours and were stirred continuously.

Table 3. 1: Modified acid tar waste

Sample	BROC	BRC	BC	TROC	TC
Benzene effluent stream acid tar (wt%)	44	84	80	-	-
Toluene and xylene effluent stream acid tar (wt%)	-	-	-	52	80
Used engine oil (wt%)	44	-	-	34	-
Ground rubber (wt%)	1	4	-	1	-
Calcium oxide (wt%)	11	12	20	13	20

Where B – Benzene effluent stream acid tar, T – Toluene and xylene effluent stream acid tar, R – Rubber (tyres), O – Oil (used engine oil) and C – Calcium oxide. The calcium oxide was used to neutralise the mixture to a pH around 7. The used oil was first reacted with the acid tar waste to determine the weight ratio requirement using the viscosity of the mixtures. The amount of rubber used was determined by the consistency of the material, where high concentration produced inconsistency in the mixture.

The mixtures were compared with bitumen grade 60/70 and the BRC material was mixed with the 60/70 at a ratio of 1: 1.

3.4.5 Dynamic mechanical analysis

The analysis was performed using a dynamic shear rheometer (Anton Paar Physica MCR 51 model). The AASHTO-T315-10 procedure which is the standard method of test for determining rheological properties for asphalts using a dynamic shear rheometer was followed. Parallel plates of 25mm with a gap of 1mm were used.

The strain sweep was conducted to determine the strain percentage in order to ensure that the analysis was conducted in the linear viscoelastic region. The frequency sweep was performed at constant temperature (45^{0}C) and constant strain in the viscoelastic region of each sample from 0.1 to 100 rad/s. The temperature sweep was conducted at constant frequency of 10 rad/s and constant strain in the range 45 - 85^{0}C. Complex modulus, phase angle and complex viscosity were measured and master curves were constructed. The rutting resistance parameter was also calculated.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

The differences and similarities of toluene and xylene and benzene effluent stream acid tar waste is shown in various physical and chemical characteristic results. The characterisation results that include the organic composition, sulphuric acid content and inorganic content have a bearing on the utilisation of the acid tar waste as a raw material for pavement binder production. The link between the FTIR and the GC-MS results will be presented and explained. The results of organic composition are related to the viscosity and the gas emissions during neutralisation. The choice of best base to use for neutralisation according to solubility of the product and the emission of gases during neutralisation is shown. The results of the behaviour of the acid tar waste materials to temperature and stress also has an effect on its ability to be utilised in the pavement production. The results of the behaviour of modified acid tar waste in comparison with the bitumen grade 60/70 will be discussed and conclusions drawn used to make appropiate recommentations on how acid tar waste may be applied as a pavement binder.

4.2 Acid tar waste characterisation

The section gives the results and discussions of the chemical and physical properties of acid tar waste.

4.2.1 Organic characterisation

The results of organic characterisation are from the GC-MS and the FTIR.

4.2.1.1 Gas Chromatography – Mass Spectroscopy

In this area the organic compounds are identified and functional groups derived from the compound structures. Figures 4.1 and 4.2 show the chromatograph of the two acid tar waste from the purification of benzene, toluene and xylene dissolved in toluene. The chromatographs were used to estimate the difference in the amount of organic chemicals soluble in toluene present in the two acid tar wastes. Benzene effluent stream acid tar has less organic materials as compared to toluene and xylene effluent stream acid tar.

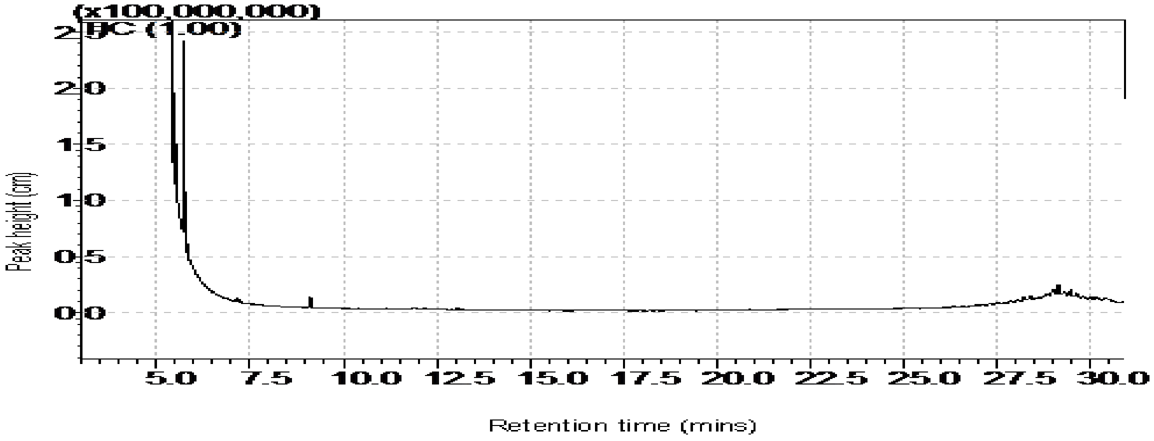


Figure 4. 1: Benzene effluent stream acid tar chromatography

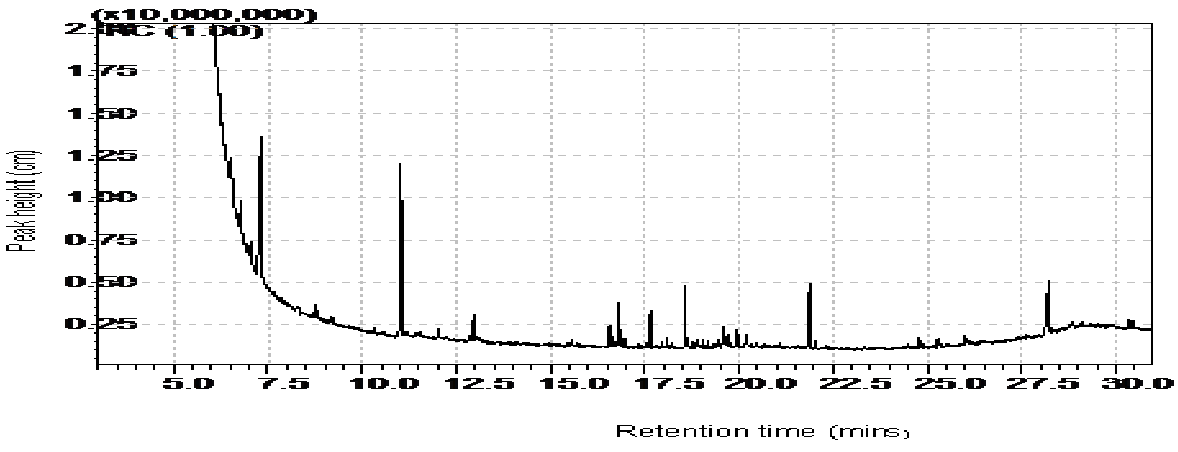


Figure 4. 2: Toluene and xylene effluent stream acid tar chromatography

Table 4.1 shows the organic compounds identified by GC-MS for benzene effluent stream. Benzene effluent stream acid tar contains phenol, alkynes, carbonyl, ethers, cyclo, quinoline, nitro compounds, amines and alkenes while toluene and xylene effluent stream acid tar contains amines, amides, alkenes, pyrrole, carboxylic acids, sulphur compounds, ketones, thiophene, indene and ethers (Table 4.2).

Table 4. 1: Organic compounds identified in benzene effluent stream acid tar by GC-MS

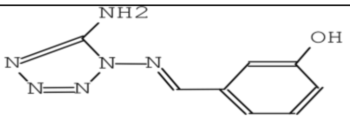
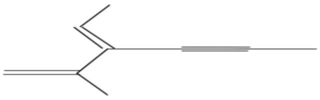
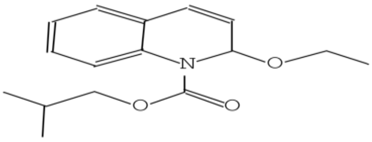
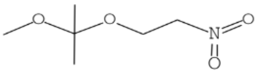
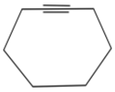
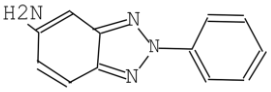
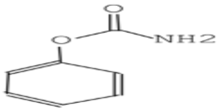
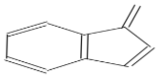
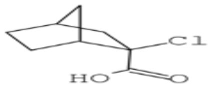
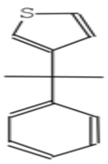
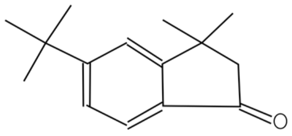
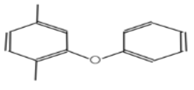
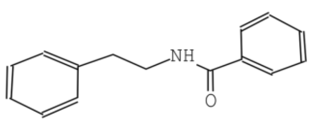
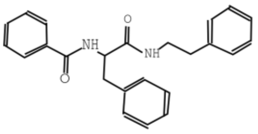
Retention time (mins)	Chemical name	Molecular formula	Chemical structure
6.735	3-[(5-Amino-tetrazol-1-ylimino)-methyl]-phenol	$C_8H_8N_6O$	
8.890	3-Ethylidene-2-methyl-1-hexen-4-yne	C_9H_{12}	
10.995	Isobutyl 2-ethoxy-1(2H)-quinoline carboxylate	$C_{16}H_{21}NO_3$	
11.800	2-Methoxy-2-(2-nitroethoxy) propane	$C_6H_{13}NO_4$	
12.045	Cyclooctyne	C_8H_{12}	
13.035	E-1,5,9 Decatriene	$C_{10}H_{16}$	

Table 4. 2: Organic compounds identified in toluene and xylene effluent stream acid tar by GC-MS

Retention time (mins)	Chemical name	Molecular formula	Chemical structure
5.300	2-Phenyl-2H-1,2,3-benzotrial-5-amine	$C_{12}H_{10}N_4$	
7.310	Phenyl carbamate	$C_7H_7NO_2$	
11.045	1-Methylene-1H-indene	$C_{10}H_8$	
12.965	2-Chloro-2-norbornanecarboxylic acid	$C_8H_{11}ClO_2$	
16.800	3-(1-Methyl-1-phenylethyl)-thiophene	$C_{13}H_{14}S$	
17.645	5-(1,1-Dimethylethyl)-2,3-dihydro-3,3-dimethyl-1H-inden-1-one	$C_{15}H_{20}O$	
18.585	1,4-Dimethyl-2-phenoxybenzene	$C_{14}H_{14}O$	
21.875	N-(2-Phenylethyl)-benzamide	$C_{15}H_{15}NO$	
28.220	2-Benzoylamino-3-phenyl-N-(2-phenylethyl) propanamide	$C_{24}H_{24}N_2O_2$	

The difference is the presence of phenol, quinoline and alkynes in the benzene effluent stream acid tar and the presence of carboxylic acids, pyrrole and sulphur compounds in toluene and xylene effluent stream acid tar, with the rest of the functional groups being present in both acid tars. Toluene and xylene effluent stream acid tar contains pyrrole, carboxylic acid and ketone functional groups found in bitumen used for pavement binders (Branthaver et al., 1993), while benzene effluent stream acid tar have quinoline, ketone and phenol. Thus both acid tar wastes have the potential to produce pavement binders. The presence of amides and carboxylic acid will lead to formation of larger molecule compounds, which will increase the resistance to flow of the fluid. The toluene and xylene effluent stream acid tar has more polar organic compounds as compared to benzene effluent acid tar. This can lead to toluene and xylene effluent stream acid tar having a higher potential of producing a better binder.

4.2.1.2Fourier transform infrared spectroscopy results

The identification of functional groups from the spectra in this section has been done using the interpretation provided by Coates (2000). The FTIR has then been used to confirm the functional groups obtained in the GC-MS section.

Figure 4.3 shows the spectrum of benzene effluent stream acid tar. At 3402.33cm^{-1}wavenumber, the organic group represented is phenol and primary amine which were also observed by GC-MS. The band at 1682.07cm^{-1} is for alkene and quinoline that have also been identified in the GC-MS, and that at 1618.64cm^{-1} is for aliphatic nitro compounds while those at 1545.57 and 869.02cm^{-1} are for aromatic compounds.

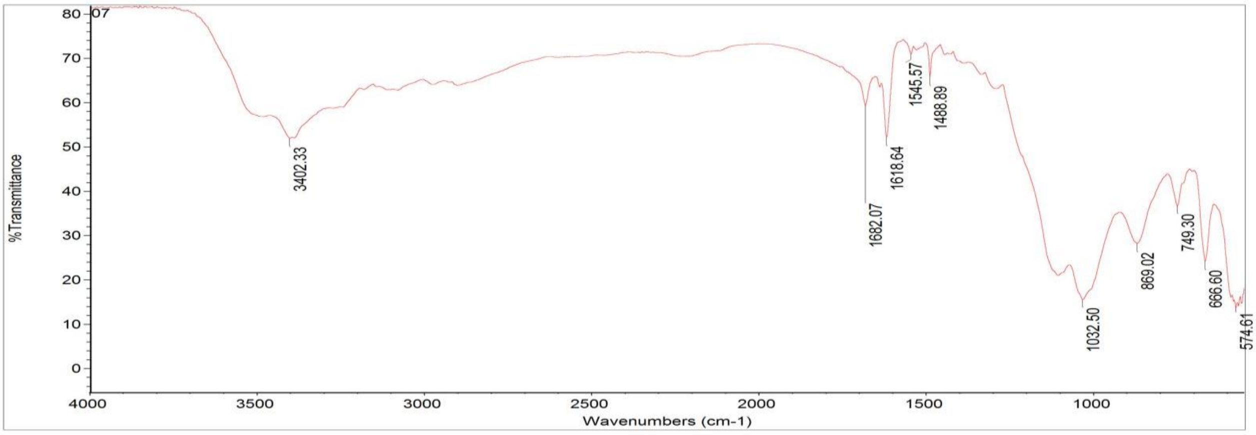


Figure 4. 3: Benzene effluent stream acid tar FTIR spectrum

Of the six compounds identified by GC-MS there are only two compounds with aromatic group, these are 3-[(5-Amino-tetrazol-1-ylimino)-methyl]-phenol and isobutyl-2-ethoxy1 (2H)-quinoline. The spectrum at 1032.50cm^{-1} is for cyclo compound and GC-MS obtained a cyclooctyne. The following bands1488.89 and 747.61cm^{-1}are for alkane mostly methyl attached to a benzene ring and the other methyl attached to an alkyne, is at 666.60cm^{-1} for alkyne. There is a general agreement between FTIR and GC-MS results except where the GC-MS identified an ether compound that was not picked by the FTIR. This could be due to overlaying of bands since there were so many compounds which would then produce vibrational energies in the same range and at the same time.

Figure 4.4 shows a spectrum of benzene effluent stream acid tar washed with water. In this regard water soluble organic compounds are not expected to be in the spectrum.

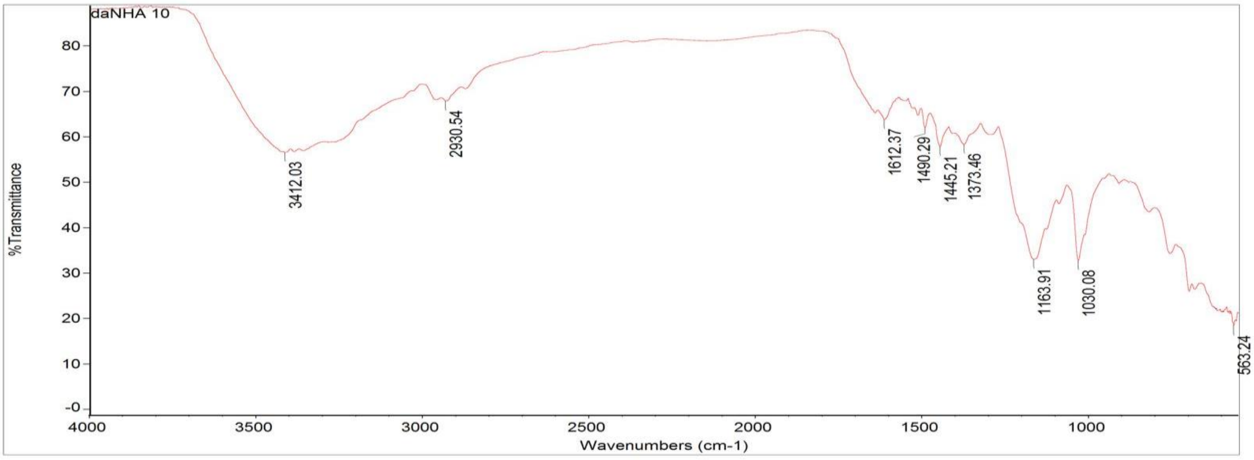


Figure 4. 4: Benzene effluent stream acid tar washed with distilled water FTIR spectrum

The spectra then show that the compounds which exhibited the following functional groups in the benzene effluent stream acid tar are soluble in water or the functional groups that react in the presence of water: aromatic nitro compound, quinoline, phenyl, alkyne bend and aromatic 1,4 substitution.

Figure 4.5 shows the FTIR spectrum of toluene and xylene effluent stream acid tar sample. The bands at 2901.31, 1488.50 and 676.28cm^{-1} are for alkanes and these are largely the ethyl and methyl groups. The 1616.40cm^{-1} band is associated with aliphatic nitro compounds and has an intensity that is less than that produced by the benzene effluent stream acid tar. There are more nitro compounds in benzene effluent stream acid tar than in toluene and xylene effluent stream acid tar. The bands 1543.74 and 864.14cm^{-1} are for aromatic compounds, and are similar to those found in the benzene effluent stream acid tar. The intensity is almost the same and the results from the GC-MS are complimentary in both acid tar wastes and most of the compounds are aromatic compounds. The band found at 1148.49cm^{-1}is for ether while that at 1025.51cm^{-1} is for amine and both are in conformity with the GC-MS results presented for amines as well as amides. The spectrum, for toluene and xylene effluent acid tar shows that all the bands found are associated with functional groups that have been identified by the GC-MS. The GC-MS has however, identified two functional groups that the FTIR spectrum failed to pick-up namely: the ketone and carboxyl groups. This may be attributed to the fact that, there are too many organic compounds whose vibrational frequencies are in the same range resulting in overlaps.

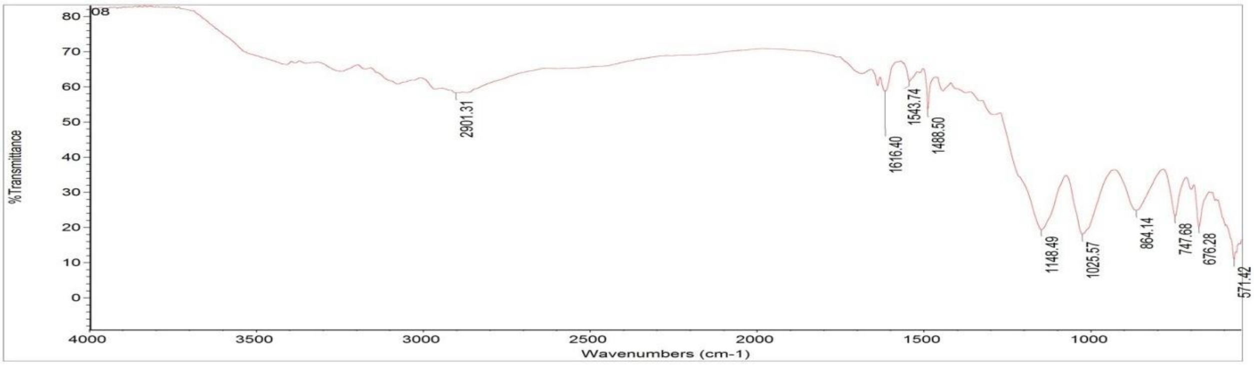


Figure 4. 5: Toluene and xylene effluent stream acid tar FTIR spectrum

Figure 4.6 shows the spectrum of distilled water washed toluene and xylene effluent acid tar. The two spectra show that the aromatic nitro compound (1543.74cm^{-1}) might have dissolved in water or reacted to produce an additional peak at (3256.83cm^{-1}) which is amino group.

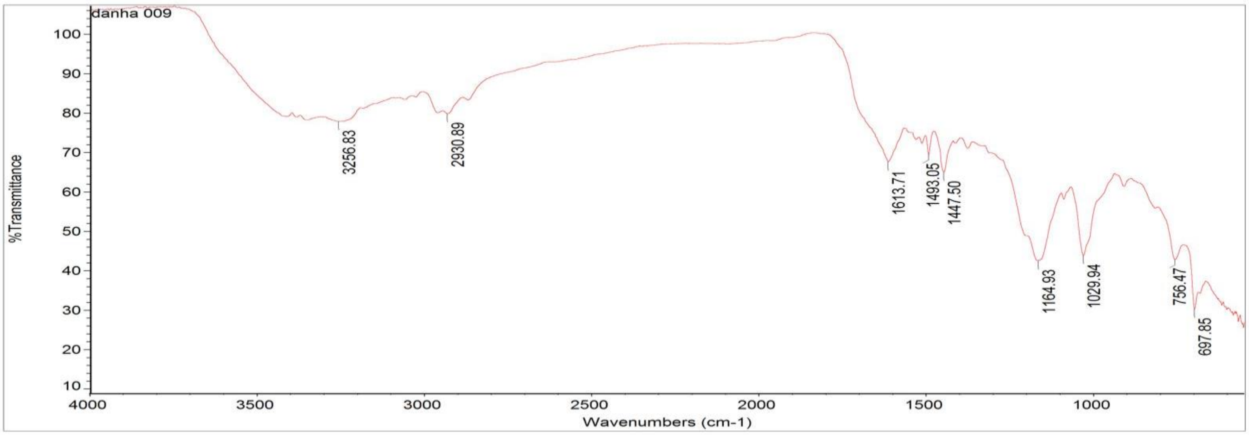


Figure 4. 6: Toluene and xylene effluent stream acid tar washed with distilled water FTIR spectrum

Toluene and xylene effluent stream acid tar spectrum was least affected by the washing as compared to the benzene effluent stream acid tar. The toluene and xylene effluent stream acid tar may thus be described as less reactive to negatively influence the modification processes. The agglomeration of organic particles will produce non-coherent product due to weak bonding between micro-structural units and this will affect the flow (Little and Petersen, 2005).

4.2.2 Inorganic characterisation

The main high light of the inorganic characterisation is the results of the sulphuric acid concentration.

4.2.2.1 Cations and anions

The ion characteristic of acid tar waste is described in this section. Table 4.3 shows the percentage amounts of metal ions and anions present in benzene, toluene and xylene effluent stream acid tars. The results show that there are very low concentrations of metal ions that are accompanied by a very high sulphate ion concentration.

Table 4. 3: Results of metal ions and anions

Acid tar	Benzene effluent	Benzene effluent washed with water	Toluene and xylene effluent	Toluene and xylene washed with water
Sulphate ion (wt %)	36	1.76	15	4.42
Chloride ion (wt %)	-	0.26	-	0.43
Nitrate ion (wt %)	-	-	-	0.33

Sodium (wt %)	0.07	0.0045	0.0064	0.0061
Iron (wt %)	0.053	0.0047	0.012	0.0031
Calcium (wt %)	-	-	0.064	0.0014
Potassium (wt %)	0.016	-	0.0031	0.0015

The sulphate ion content in the samples washed with water show that most of the sulphate ions originated from sulphuric acid and is water soluble. The low concentration of metal ions is due to the fact that prior to purification of benzene, toluene and xylene is distillation to leave behind most of the heavy metal ionic species as solid residue. This remaining residue had components whose boiling points were difficult to differentiate using temperature changes. The difference in content of sulphate ions between benzene and toluene and xylene acid tar effluent stream is on account of the difference in composition of organic compounds present with the benzene effluent stream acid tar comprising a high sulphate ion content (36%) compared with the toluene and xylene effluent stream acid tar (15%).

4.2.2.2 Acid composition

The acidic character of the acid tar waste is shown in Figure 4.7.

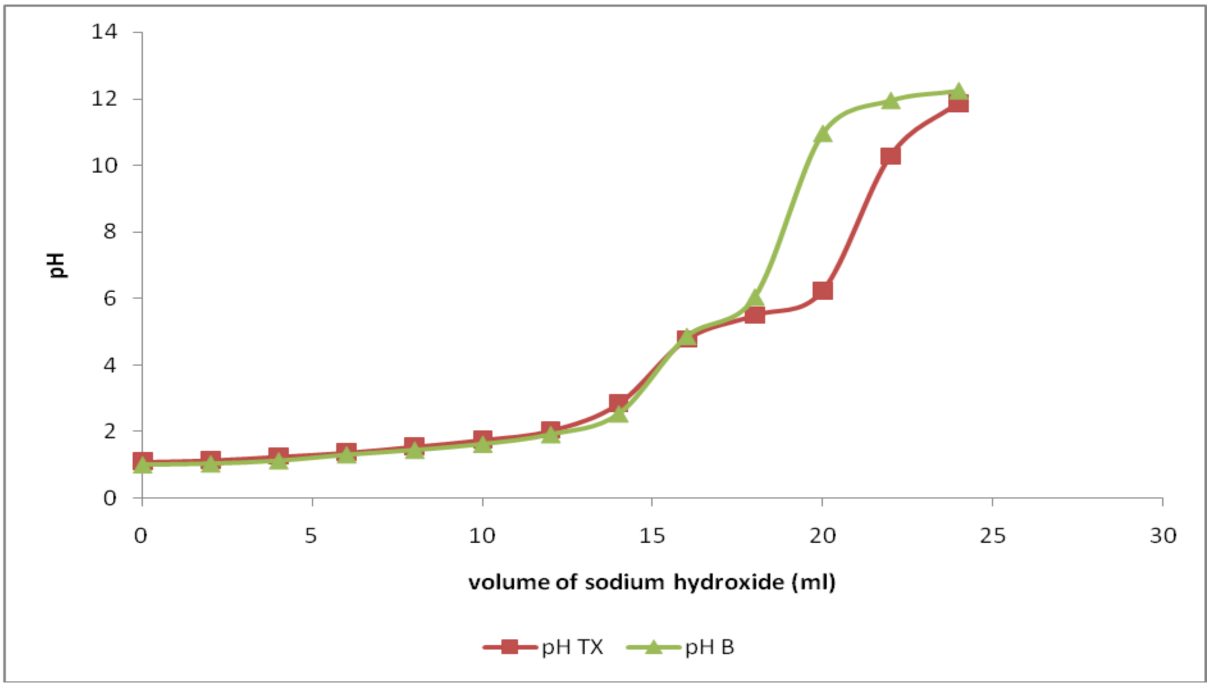


Figure 4. 7: Acid tar waste titration with sodium hydroxide.

Despite the difference in organic content between the two effluent streams the acid content appears to be the same (Figure 4.7). The amount of sodium hydroxide required to achieve approximately pH 7 differs marginally with two pH jumps. This corroborates the results obtained by Leonard et al. (2010). There is, however, a strong possibility that both organic (weak) acids and inorganic (strong) acids are present in both effluent streams. These acids behave differently with partial and complete dissociation of the weak (organic) and the strong (inorganic) acids respectively. The first sharp rise at pH of 4 is as a result of complete neutralisation of the strong acid (sulphuric acid). The second sharp raise at pH 6-7 is due to the weak organic acids and these takes time to dissociate resulting in a drag before equilibrium between the acid and the dissociated ions is achieved. The drag towards equilibrium is different for the two effluent streams with the toluene and xylene effluent stream having the longer drag compared with that of benzene effluent stream acid tar. This observation is in agreement with the results in Table 4.4

which shows that toluene and xylene effluent stream acid tar has more organic acid components than benzene effluent stream acid tar.

$$RCOOH + NaOH \rightarrow RCOONa + H_2O \quad (4.1)$$

$$RCOONH_2 + NaOH \rightarrow RCOONa + NH_2OH \quad (4.2)$$

Equation (4.1) and (4.2) present the reaction of 2-Chloro-2-norbomanecarboxylic acid and phenyl carbamate with sodium hydroxide, these two compounds are part of the organic acids found in toluene and xylene effluent stream acid tar. Benzene effluent stream acid tar has isobutyl-2-ethoxy-1(2H)-quinoline carboxylate represented by equation (4.3).

$$RCOOR_1 + NaOH \rightarrow RCOONa + R_1OH \quad (4.3)$$

Where R is the quinolone section and $R_1$is the isobutyl-2-ethoxy part.

Table 4. 4: Acidic concentration of acid tar waste

Acid tar waste	Acid concentration (mol/l)	Sulphuric acid concentration(mol/l)	% of sulphuric acid in sample	Organic acid concentration (mol/l)
Benzene effluent	9.5	7.5	24.2	2
Toluene and xylene effluent	10.5	7.5	23.7	3

As has been alluded to by Chechulin et al. (2008) the sulphuric acid does not react with the organics in the absence of air and water. It is, therefore, suggested in the current study that the organic acid compounds associated with the toluene and xylene acid tar effluent stream is from organic compounds extracted from crude benzol during purification.

4.2.3 Viscosity

This section describes how acid tar waste behaves when it is forced to move. Table 4.5 shows the viscosity of the acid tar waste. The toluene and xylene effluent stream acid tar is more viscous than benzene effluent stream acid tar. This has a bearing on the behavior of the acid tar waste as they are exposed to heat and stress.

Table 4. 5: Viscosity of acid tar waste.

Acid tars	Viscosity (mPa.s)
Benzene effluent stream	28.6
Toluene and xylene effluent stream	183

4.2.3.1 Temperature effect

In order to investigate the temperature effect, the Arrhenius relationship was applied. The two acid tar waste materials points for temperature dependency did not fit the Arrhenius equation, indicating that the acid tar waste materials do not behave like Newtonian fluids when considering their viscosity temperature dependence. The two acid tar waste have different equations that explain the viscosity-temperature relationship (Figures 4.8 and 4.9).

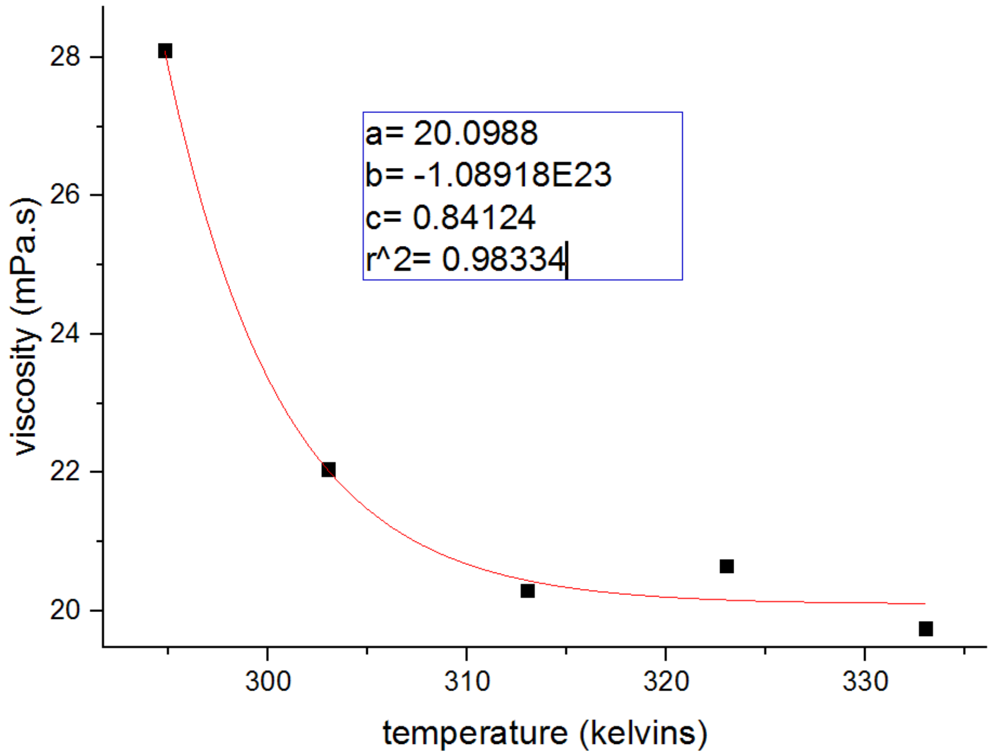


Figure 4. 8: Effect of temperature on viscosity of benzene effluent stream acid tar

Figure 4.8 shows that benzene effluent stream acid tar viscosity decreases exponentially with an increase in temperature even though it did not fit in the Arrhenius equation. The equation for the relationship with a correlation coefficient of 0.98334 is:

$$\eta = 20.0988 + 1.08918 \text{ x } 10^{23}(0.84124)^{T} \qquad (4.4)$$

Benzene effluent stream acid tar will attain a zero viscosity at 562.63K.

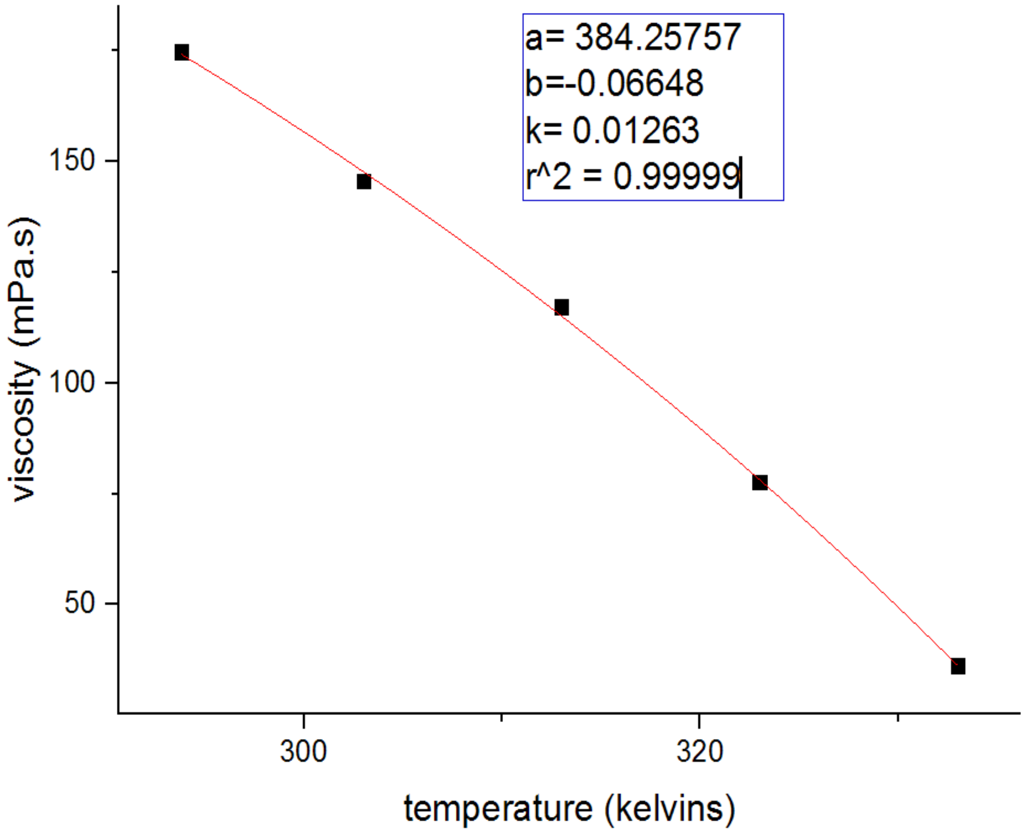


Figure 4. 9: Effect of temperature on viscosity of toluene and xylene effluent stream acid tar

Figure 4. 9 shows that the viscosity of toluene and xylene effluent stream acid tar decreases with temperature but do not obey the Newtonian fluid viscosity versus temperature relationship. The following equation had a correlation coefficient of 0.99999:

$$\eta = 384.25757 - 0.6648e^{(T\ -1/0.01263)} \qquad (4.5)$$

Using the equation the temperature at which viscosity is zero can be obtained by substituting for viscosity with zero. The acid tar waste has a zero viscosity at 360.988K. The value is much less than that of benzene effluent stream acid tar (562.63K) which has viscosity lower than that for the toluene and xylene effluent stream acid tar at 298K. This value is the temperature at which the fluid no longer has resistance to flow. The reduction in viscosity with an increase in temperature is then at a much faster rate in toluene and xylene effluent stream acid tar which has higher organic composition than in benzene effluent stream acid tar. Organic compounds are affected by heat resulting in increased thinning due to melting of the solid organic compounds. This affects their ability to produce a binder that resists high temperatures, thus the need for modification. Both acid tar waste materials did not behave as Newtonian fluids but in ways best described by equations (4.4) and (4.5) from which the zero viscosity temperature could be estimated by extrapolation.

4.2.3.2Shear rate effect

The behaviour of the two acid tar waste when sheared is reported and the acid tar waste classified.

4.2.3.2.1 Benzene effluent stream acid tar

Table 4.6 shows the correlation values of the models fitted to the shear stress, rate of benzene effluent stream acid tar.

Table 4. 6: Models, the correlation coefficient and chi square of benzene effluent stream acid tar

Model	Correlation coefficient
Newtonian	0.98000
Power law	0.97200
Bingham	0.99440
Herschel-Bulkley	0.99787
Casson model	0.97546

The correlation coefficients in Table 4.7 show that all models can fit the values of benzene effluent stream acid tar very closely since the values are all close to one. This could be the reason why Frolov et al. (1981) concluded that the acid tar waste they worked with was Newtonian fluid. This then shows that acid tar waste can be described by many different models. The results in the Table 4.7, however, show that Herschel-Bulkley model has the best fit to the experimental data. The correlation coefficient of 0.99787 is closest to one than the other four. The Bingham model can also be considered since the two models describe the behavior of polymer substances in suspension. This is suitable for asphalts thus leading to the conclusion that the material can with other additions be modified to produce a pavement binder since it is viscous in nature as alluded to by Huang et al. (2011). What remains therefore, is the elasticity to produce viscoelastic asphalt.

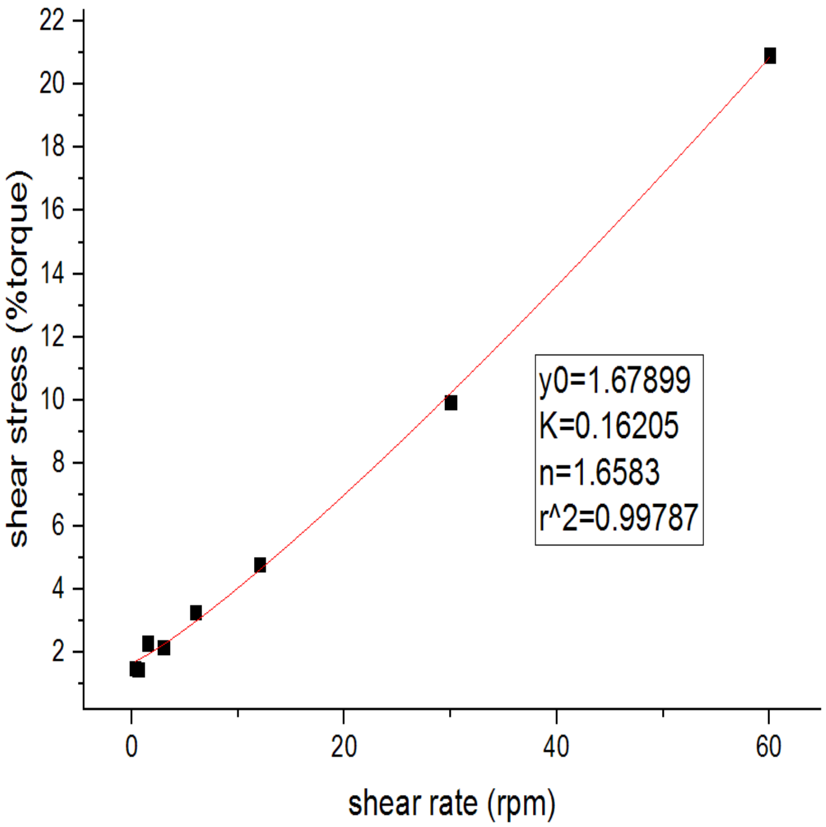


Figure 4. 10: Herschel-Bulkley model for benzene effluent stream acid tar

The relationship as shown in Figure 4.10 is:

$$\tau = 1.67899 + 0.16205\grave{y}^{1.6583} \tag{4.6}$$

The value of n is greater than one meaning that the benzene effluent stream acid tar exhibit shear thickening qualities (Swami et al., 2013). This then explains why the benzene effluent stream acid tar takes longer to reach zero viscosity as compared to toluene and xylene effluent stream acid tar despite the fact that it has lower viscosity than toluene and xylene effluent stream acid tar. The plastic viscosity is 0.162, which is very low suggesting less organic giant molecules are present. The rheogram has a curvature showing that the Herschel-Bulkley model is the best for benzene effluent stream acid tar.

4.2.3.2.2 Toluene and xylene effluent stream acid tar

Table 4. 7 shows the correlation coefficient and chi square values for the five models fitted to the data of toluene and xylene effluent stream acid tar.

Table 4. 7: Models, correlation coefficient and chi square for toluene and xylene effluent stream acid tar

Model	Correlation coefficient
Newtonian	0.98800
Power law	0.99690
Bingham	0.99975
Herschel-Bulkley	0.99971
Casson model	0.99453

The correlation coefficient values also show that the experimental values of toluene and xylene effluent stream acid tar can fit the five model thus these models can be used to explain the behavior of toluene and xylene effluent stream acid tar just as it can be used for benzene effluent stream acid tar. The Bingham model, however, has the best fit since the correlation coefficient is the one closest to one and the chi square value is the smallest as compared to the other four. The relationship as shown by Figure 4.11 is:

$$\tau = 1.44563 + 0.43535\dot{y} \qquad (4.7)$$

The plastic viscosity of toluene and xylene effluent stream acid tar is 0.435 which is greater than that of benzene effluent stream acid tar which is 0.162. This might be because toluene and xylene effluent stream acid tar has more polymeric substance than benzene effluent stream acid tar since the increase in polymer concentration also increases the value of consistency index (plastic viscosity) (Gomez – Diaz et al., 2008).

The rheogram shows no curvature and is a typical Bingham model as shown in Figure 4.11. The Herschel-Bulkley model is also a perfect fit. The two acid tar waste can be said to be similar in behavior when considering their viscosity shear rate dependence.

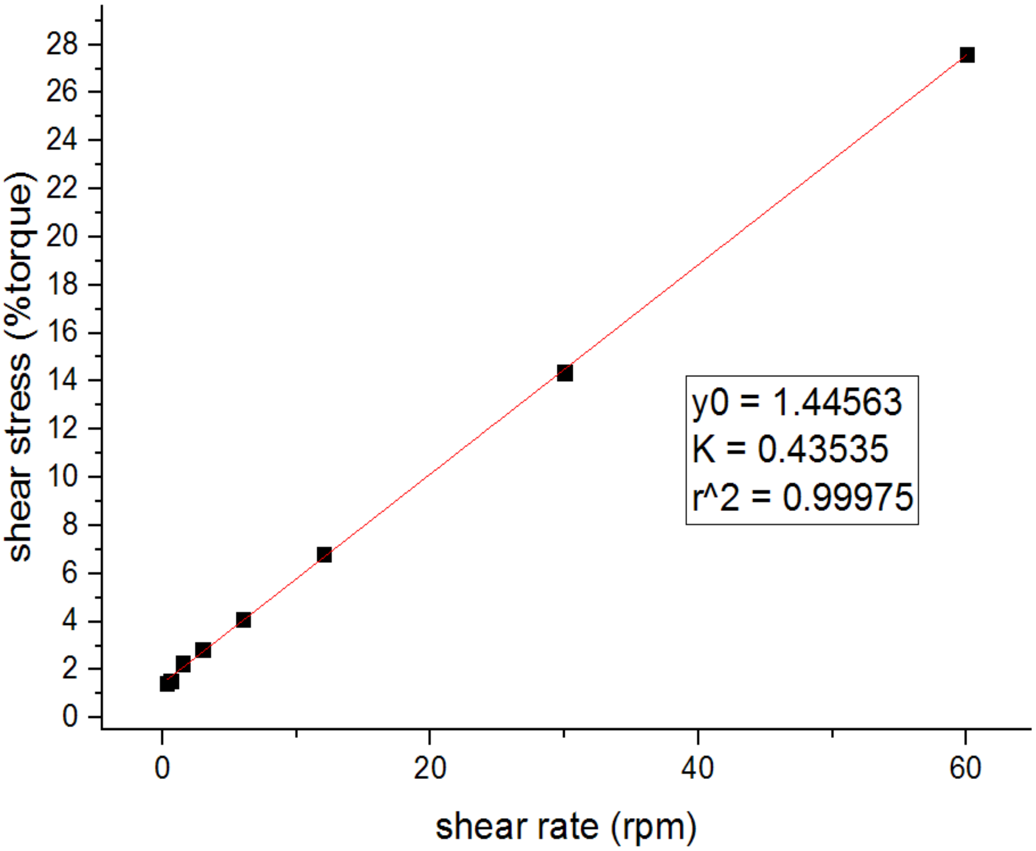


Figure 4. 11: Bingham model graph for toluene and xylene effluent stream acid tar

4.2.3.3 Viscosity shear rate relationship

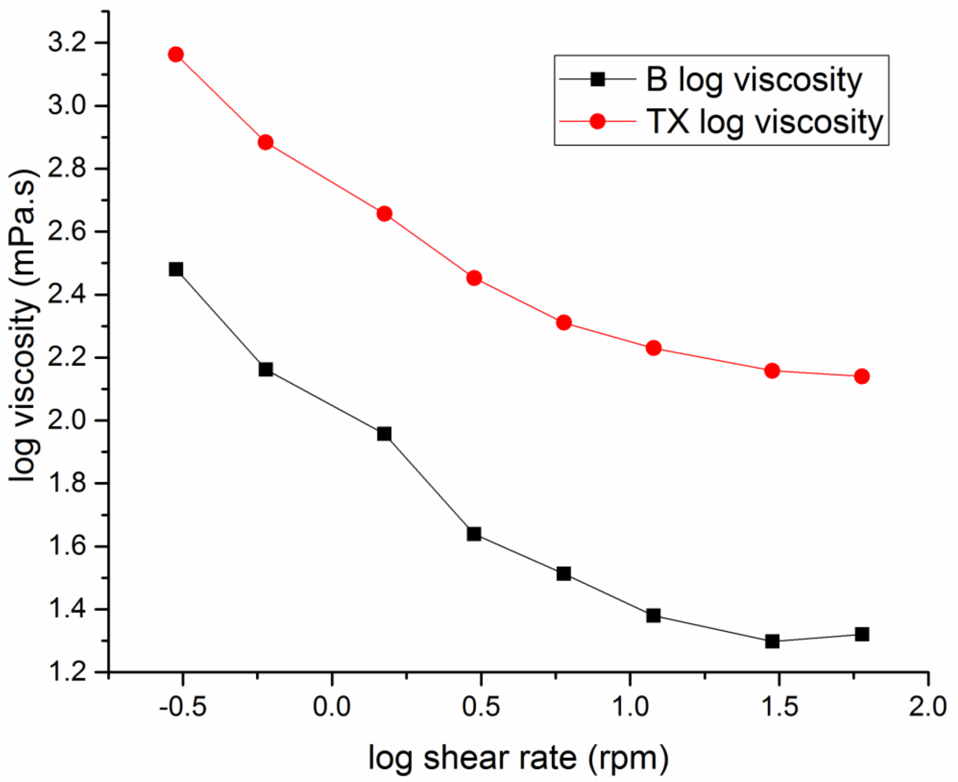


Figure 4. 82: Log of viscosity against log shear rate

Figure 4.12 shows the log-log plot of viscosity and shear rate which is similar to a shear thinning with yield stress curve shown by Khan et al. (1997). Benzene, toluene and xylene effluent stream acid tar are affected by the increase in the shear rate resulting in the acid tar waste thinning. This is in agreement with the results of the shear stress versus the shear rate pointing to visco-plastic behavior which then require modification to add the elasticity that is required by a pavement binder (Huang et al., 2011).

4.2.3.4 The effect of heating and cooling

The effect of temperature on the behaviour of acid tar waste is reported. This characteristic helps in the use of the acid tar waste in temperature changing environment.

4.2.3.4.1 Toluene and xylene effluent stream acid tar

Figure 4.13 shows the difference in the heating and then cooling of the toluene and xylene effluent stream acid tar, with the curves being far apart at temperatures 313K and 303K.

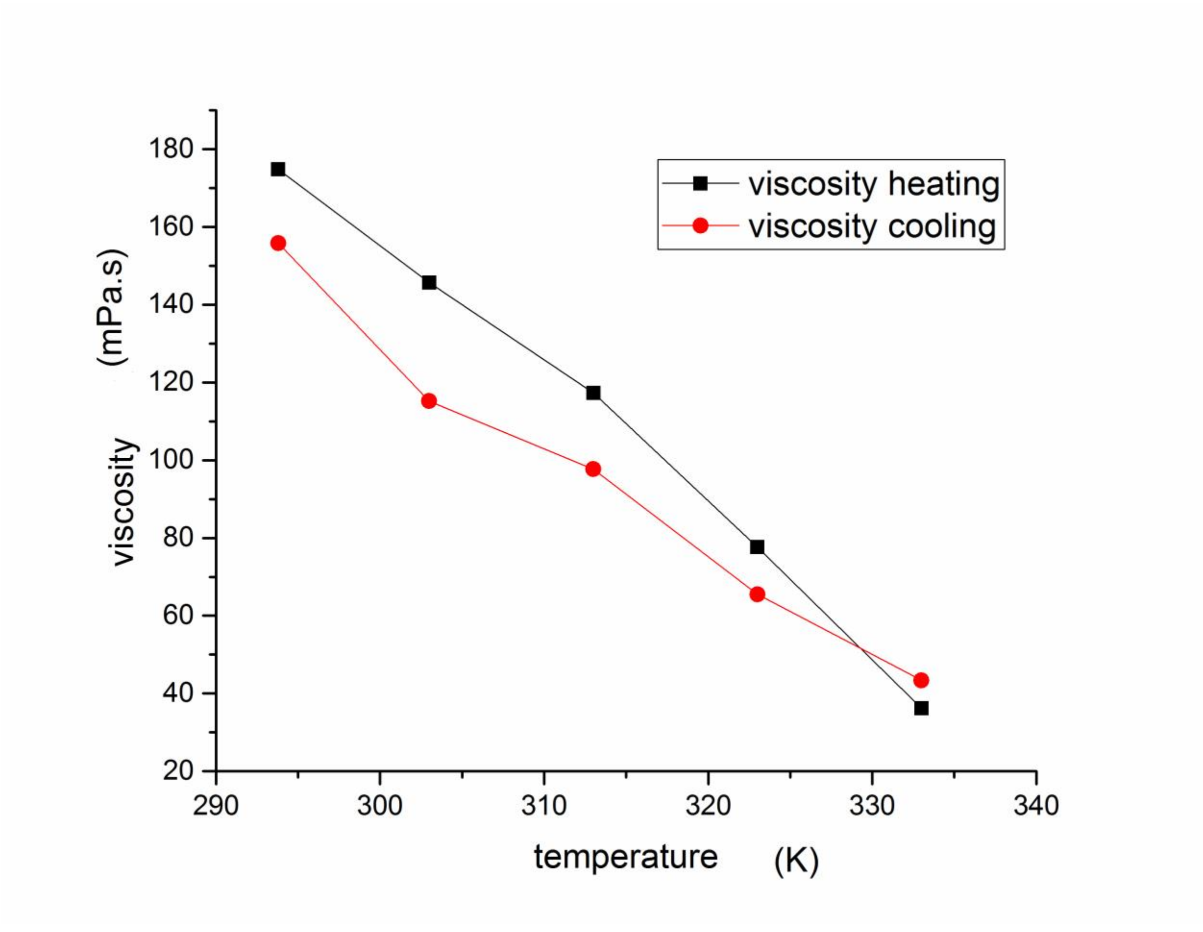


Figure 4. 93: Toluene and xylene effluent stream acid tar viscosity variation with temperature.

The two curves seem to be approaching each other at temperatures lower than 293.8K. Heat affected the viscosity from 174.8mPa.s at 293.8K to 36.2mPa.s at 333K. Cooling the sample did not yield the original viscosity values but there was approximately 10% decrease in viscosity at 293.8K. The difference is signficant at 95% confidence level with p = 0.02. Heating results in thinning of the acid tar waste. The toluene and xylene effluent stream acid tar seem to have some compounds contributing to viscoplastic nature which deform when heated. This could be a factor that can affect a pavement binder if this acid tar waste is used as a raw material, since everytime it is heated the viscosity will be reduced after cooling this will result in the binder bleeding instead of holding the agrigates together. Zimbabwe has most area that are hot in the afternoon and cool at night so such a binder might weaken on a daily basis.

4.2.3.4.2 Benzene effluent stream acid tar

Figure 4.14 shows the heating and cooling curve crossing at 307K and the resulting cooled benzene effluent stream acid tar has a higher viscosity than the original, but the difference between the viscosity at 293K before heating (28.1mPa.s) and that after heating (34.65mPa.s) is not significant at 95% confidence level with p = 0.15.

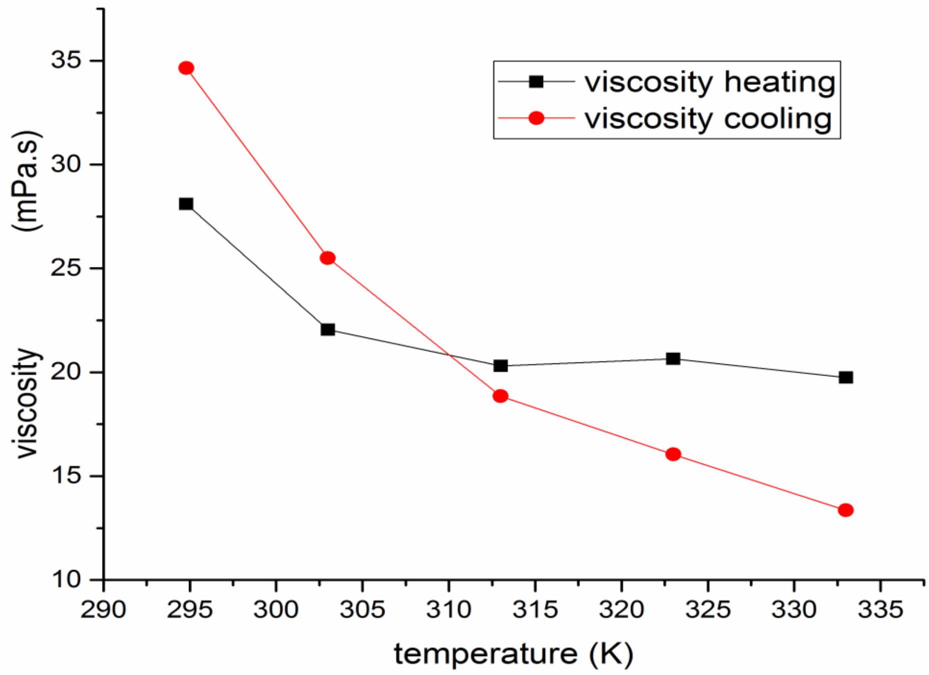


Figure 4.14: Benzene effluent stream acid tar viscosity variation with temperature.

Thus one can conclude that there is no significant chemical change brought about by heating. The heating curve shows very little variation, one can say the viscosity is within 19.75 - 28.1mPa.s while the cooling curve is from 13.35 – 34.65mPa.s.

The results show that there is very little in terms of plastic concentration thus the small variation being caused by heating. This acid tar waste will not affect the pavement binder in terms of viscosity change due to temperature variation, thus it will not contribute to decrease in stability. The consideration of viscosity dependence on temperature will assist further when considering the use of the two acid tar waste together or seperately.

4.3 Characterisation of neutralised acid tar waste

Investigation previously conducted (Frolov et al., 1985, Druzina and Perc, 2010) show that it is very difficult to work with freshly produced acid tar waste material because of the inherently high sulphuric acid content. Neutralisation, then becomes an important step, to not only control acidity of the acid tar waste, but can generate co-products with potential industrial and agricultural application.

4.3.1 Physical and inorganic analysis of neutralised acid tar waste

Figure 4. 15 shows that there is a significant difference in the temperature change of the two neutralising agents used, with calcium hydroxide having less temperature change compared with calcium oxide for benzene effluent stream acid tar and calcium hydroxide with higher temperature change than calcium oxide for toluene and xylene effluent stream acid tar.

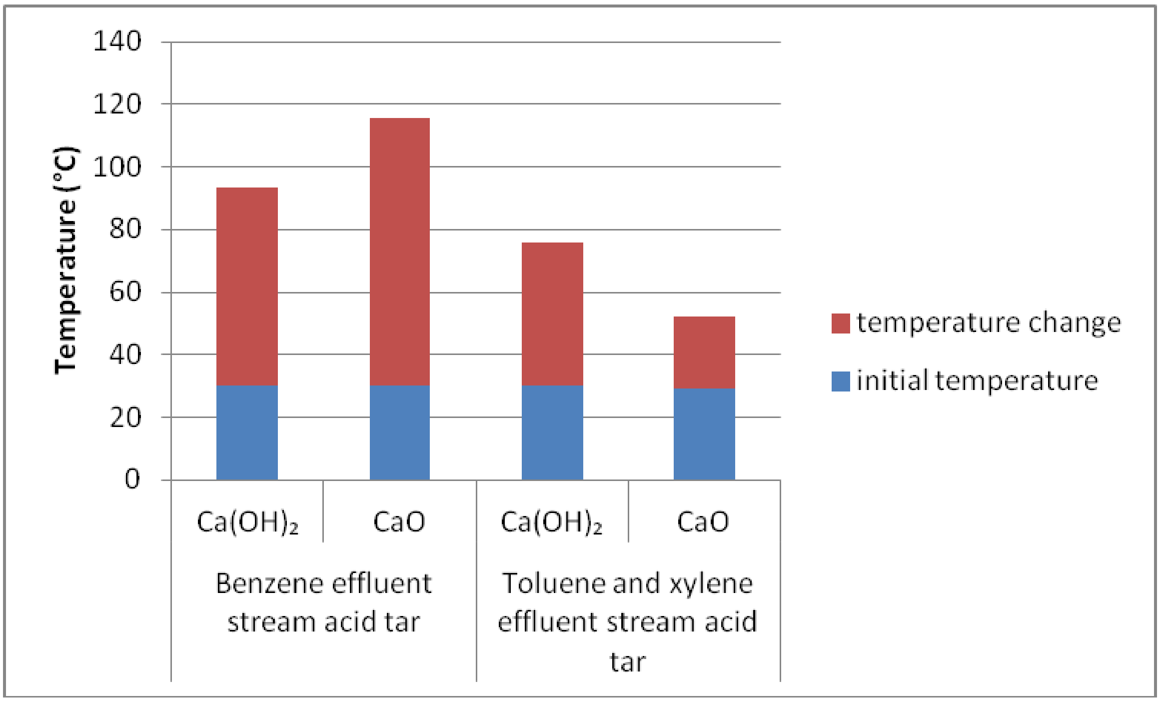


Figure 4. 15: Temperature change during neutralisation of acid tar waste with $Ca(OH)_2$ and CaO

Temperature change depends on the neutralising chemical used (Druzina and Perc, 2010), as is the case with these two chemicals. However, the results also show that the acid tar waste type affects the temperature change since it is difficult conclude that one base, for example, calcium hydroxide can produce same temperature change in both acid tar waste. For benzene, effluent stream calcium oxide (85.3^{0}C) had the highest temperature change whilst for toluene and xylene effluent stream acid tar the maximum temperature attained was 45.7^{0}C. Benzene effluent stream acid tar exhibited the higher temperature change for both the neutralising agents. This could be because of very little interference from the organic compounds present which was of low concentration. The benzene effluent stream acid tar was thus neutralised more rapidly than the toluene and xylene effluent stream acid tar. This then shows that there is so much interference from organic matter in the toluene and xylene effluent stream acid tar as compared to benzene effluent stream acid tar which has less organic compounds present. This also shows that benzene effluent stream acid tar has more mineral acid content than the toluene and xylene effluent stream acid tar.

The temperature changes can be used to determine the chemical to use for neutralisation of the acid tar waste that will minimise gas emissions, since temperatures which exceed 100^0C will lead to evaporation of sulphuric acid and sulphur trioxide from the mixture (Druzina and Perc, 2010). Benzene effluent stream acid tar will not produce these gases if calcium hydroxide is used for neutralisation at initial temperatures below 30^0C. However, the use of calcium oxide produced a less soluble salt because of the high temperature reached which lead to the evaporation of water, thus producing calcium sulphate anhydrite (Tlili et al., 2008). Kol'tsov (2014) states that during neutralisation water passes into the gas phase and some is bound by the products of reaction both physically and chemically in the form of capillary moisture. Thus high temperature for neutralisation of benzene effluent stream acid tar meant that most of the water produced vapourises into the air. From the equations (3.1) and (3.2) calcium hydroxide produce two moles as compared to calcium oxide with one mole of water thus, benzene effluent stream acid tar salt of calcium oxide is less soluble as compared to that of calcium hydroxide with more water moles.

Toluene and xylene effluent stream acid tar can use both calcium hydroxide and calcium oxide. Calcium hydroxide produced a less soluble salt and has high sulphate ion concentration. The starting temperature limit for this effluent stream is 50^0C, so that it does not exceed 100^0C during neutralisation.

Table 4. 8 shows that the concentration of sulphate ion for the particular acid tar waste is affecting the solubility with the high concentration leading to low solubility. The presence of sulphate ions in high concentration is not a guarantee that the solubility will be low as

shown in Table 4. 8. Thus for benzene effluent stream acid tar the calcium oxide salt has higher concentration of sulphate ions (8.5%) as compared to the calcium hydroxide salt (5.9%).

Table 4. 8: Solubility and anions concentration obtained for neutralisation of acid tar waste with calcium hydroxide and calcium oxide

Acid tar	Benzene effluent stream acid tar with		Toluene and xylene effluent stream acid tar with	
	$Ca(OH)_2$	CaO	$Ca(OH)_2$	CaO
Solubility in water (wt %)	50	30	45	55
Sulphate ion (wt %)	5.9	8.5	25.8	18.1
Carbonate ion (wt %)	<0.01	8.7	<0.01	9.2
Chloride ion (wt %)	1.77	0.17	0.56	0.38

For toluene and xylene effluent stream acid tar the calcium hydroxide salt had a higher concentration (25.8%) than that of calcium oxide (18.1%). This shows that the benzene effluent stream acid tar produced salts with lower sulphate ion concentration than toluene and xylene effluent stream acid tar despite the fact that the benzene effluent stream acid tar had sulphate ion concentration higher than toluene and xylene effluent stream acid tar. This is thus coming from 3-(1-methyl-1-phenylethyl) thiophene that was detected in the toluene and xylene effluent stream acid tar by the GC-MS. The presence of carbonate ion in the calcium oxide salt of both acid tar waste is because calcium oxide reacts with carbon dioxide to produce calcium carbonate (Men and Tao, 2007).

Though the benzene effluent stream acid tar salts have lower concentrations of sulphate ions, the salt of benzene effluent stream acid tar with calcium oxide has the lowest solubility as compared to all the salt produced. This has been reported by Chojnacki et al., (2005) and is associated with the presence of organic compounds that increase the solubility of the calcium sulphate produced; and that toluene and xylene effluent stream acid tar has more organic compounds than benzene effluent stream acid tar. On the other hand, the neutralisation of the acid tar waste has reduced the solubility of acid tar waste in water. Benzene effluent stream acid tar solubility has reduced from 94 to 30% and toluene and xylene effluent stream acid tar from 73 to 45%. This then means a reduced effect to the environment where most of the soluble compounds were going to end up in ground and surface water. This will however, contribute to a less soluble binder if the acid tar waste are first neutralised then modified.

The production of carbonate ion by the calcium oxide base for both acid tar waste shows that carbon dioxide is being produced from the heating of organic matter in the acid tar waste. The carbon dioxide reacts with the calcium oxide to produce the carbonate (Kalinkin et al., 2005). The toluene and xylene effluent stream acid tar had more carbonate ions than the benzene effluent stream acid tar. Toluene and xylene effluent stream acid tar had more organic compounds than benzene effluent stream acid tar thus it produces more carbon dioxide which will react to produce the carbonate ions.

4.3.2 Gas emission during neutralisation and heating of acid tar waste

The more soluble the salt, the more problems it exerts on the environment due to leaching. Zhernovaya and Onishchuk, (2005) discovered that heating the salt of acid neutralised with calcium based bases produced a more insoluble salt. Table 4. 9 show that heating of the neutralised acid tar waste produce more pollutants than the neutralisation of acid tar waste.

Table 4. 9: Gas emission during neutralisation and heating of acid tar waste

Parameters	Benzene effluent stream acid tar with		Toluene and xylene effluent stream acid tar with	
	$Ca(OH)_2$	CaO	$Ca(OH)_2$	CaO
Carbon monoxide during neutralisation (ppm)	0	0	80	80
Carbon monoxide during heating (ppm)	40	20	200	220
Nitrogen oxides during neutralisation (ppm)	0	0	120	40
Nitrogen oxides during heating (ppm)	80	20	400	360
Sulphur dioxide during neutralisation (ppm)	0	0	20	0
Sulphur dioxide during heating (ppm)	0	0	240	120
Solubility in water after neutralisation (%)	50	30	45	55
Solubility in water after heating the neutralised acid tar waste (%)	19.9	10.3	18.6	10.6

Toluene and xylene effluent stream acid tar has more gas emissions than benzene effluent stream acid tar during neutralisation and heating. This is because of the high concentration of organic compounds which decompose to carbon monoxide, nitrogen oxides and sulphur dioxide upon heating. The heating of the salt produced a less soluble salt than just neutralisation. Benzene effluent stream acid tar decreased from 30 to 10.3% and toluene and xylene effluent stream acid tar is from 55 to 10.6% for the calcium oxide base. Benzene effluent stream acid tar reduced from 50 to 19.9% and toluene and xylene effluent stream acid tar from 45 to 18.6%. The reduction is dependent on the base used with calcium oxide having the highest reduction. This could be because of the presence of carbonate ion in the salts produced by calcium oxide. The salt of calcium oxide for both acid tar waste after heating is less soluble (10.3-10.6%) than the salt produced by calcium hydroxide (18.6-19.9%) after heating. Thus the use of calcium oxide for neutralisation and heating can reduce the environmental effect of acid tar waste produced by ZIMCHEM Refineries before modification into a pavement binder.

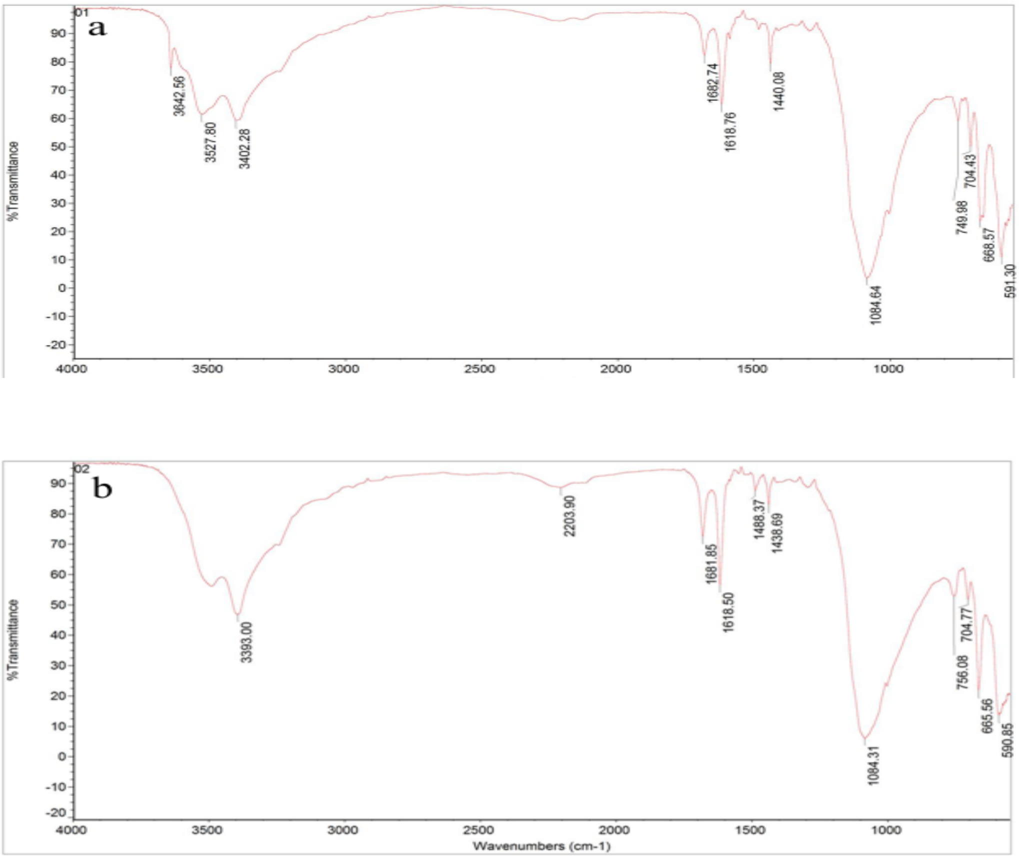
The high emission of sulphur dioxide by the toluene and xylene effluent stream acid tar is supporting the fact that there is sulphur containing organic compounds that release sulphur dioxide on heating. The high nitrogen oxides emissions from the salts of toluene and xylene effluent stream acid tar is also because of the four nitrogen containing compounds identified by the GC-MS which are: 2-phenyl-2H-1,2,3-benzotriazol-5-amine; phenylcarbamate; N-(2-phenylethyl)-benzamide; 2-benzoylamino-3-phenyl-N-(2-phenylethyl) propanamide. These are decomposed thus leading to a less soluble salt.

Calcium hydroxide produced more emissions for both acid tar waste materials despite the fact that calcium oxide with benzene effluent stream acid tar had the highest temperature change. Thus the gas emissions were not affected by the temperature change but by the base used.

4.3.3 Organic analysis of neutralised acid tar waste

The neutralisation has been reported to have resulted in increase in temperature and temperature has an effect on organic compounds. This section will highlight the effects the neutralisation had on the organic functional groups detected earlier.

Figure 4. 16 show the FTIR spectrums of salts of acid tar waste with calcium oxide and calcium hydroxide. The interpretation of the bands were done using Coates (2000).



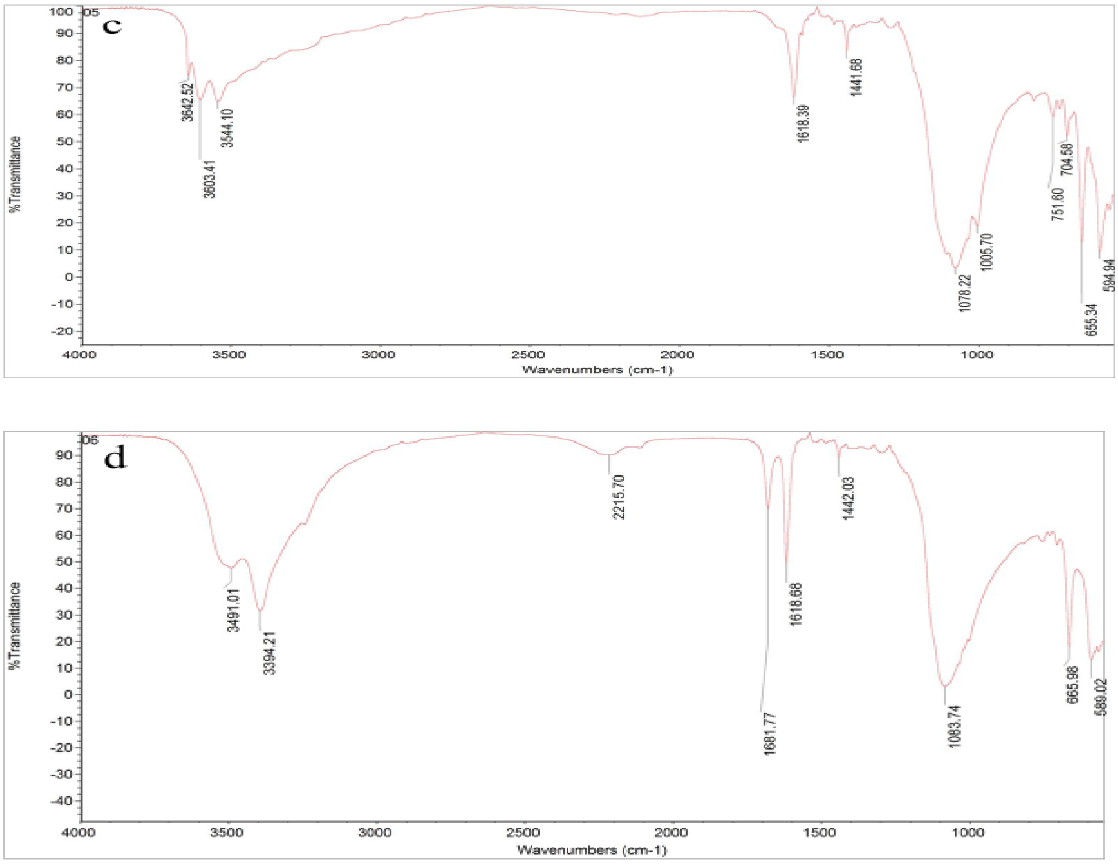


Figure 4. 16: FTIR of acid tar waste mixed with calcium oxide or calcium hydroxide.

In Figure 4.16 toluene and xylene effluent stream acid tar salt produced with calcium oxide (a)(first spectrum), toluene and xylene effluent stream acid tar salt produced with calcium hydroxide (b)(second spectrum), benzene effluent stream acid tar salt from mixing with calcium oxide (c)(third spectrum) and benzene effluent stream acid tar salt from mixing with calcium hydroxide (d)(fourth spectrum). The spectra for the two acid tar waste neutralised with calcium oxide exhibit similar bands except for 1682.74cm^{-1} for toluene and xylene effluent stream acid tar which is for ketones this makes it more favourable since ketones are polar compounds and can contribute to surface polarity which induces binding. The other difference is at 1005.7cm^{-1} which is more pronounced in benzene effluent stream acid tar as compared to toluene and xylene effluent stream acid tar band and is for alkanes.

The salts produced from calcium hydroxide for both acid tar waste also have similarities, with the differences found in the toluene and xylene effluent stream acid tar having three bands not found in benzene effluent stream acid tar (1488.37, 756.08 and 704.77 cm^{-1}which are for nitro compounds and aliphatic compounds respectively). This also indicates that the toluene and xylene effluent stream acid tar salt is a better raw material for pavement binder than benzene effluent stream acid tar salt. The differences across the bases used for toluene and xylene effluent stream acid tar, calcium hydroxide produced two bands that are not found in the calcium oxide salt (2203.9 and 1488.37$cm^{-1}$for the presence of calcium hydroxide and nitro compounds, respectively). The band at 3642.5cm^{-1} is only found in calcium oxide salt and is due to the presence of O-H bond from calcium hydroxide produced from calcium oxide and water (Kalinkin et al., 2005 and Galvan-Ruiz et al., 2009). Calcium hydroxide then will be more ideal for pavement binder production when it comes to the toluene and xylene effluent stream acid tar neutralisation before production.

Benzene effluent stream acid tar salt with calcium oxide has five bands that are not found in the calcium hydroxide salt (3642.52, 1005.7, 751.60 and 704.5cm^{-1}) Figure 4.16(c) and Figure 4.16(d). The calcium hydroxide has two bands that are not found in the calcium oxide salt (2215.7 and 1681.71cm^{-1}) which are for alkynes and alkenes, respectively. This shows that the high temperature produced by calcium oxide induced the breaking of these bonds resulting in the production of carbon dioxide which then lead to formation of carbonate ions.

There are two bands that are common in all the four salts and they represent the presence of sulphate ions 650-670cm^{-1} and 1050-1085cm^{-1}. The four spectra then show that there is less organic compounds in the salts as some might have reacted during neutralisation to produce inorganic compounds. The salts can thus be incorporated into pavement binder formation since what will have remained in the salt is resistant to heat.

4.4 Characterisation of modified acid tar waste

The results of the modified acid tar waste behaviour is reported in this section.

4.4.1 Effect of mixing acid tar waste with used engine oil on viscosity

Figure 4.17 shows that the mixing of acid tar waste with used engine oil is increasing the viscosity with benzene effluent stream acid tar having its maximum viscosity at 5:5 ratio and toluene and xylene effluent stream acid tar at 6:4 ratio. Benzene effluent stream acid tar required more used engine oil than the toluene and xylene effluent stream acid tar for the mixture to reach its maximum viscosity.

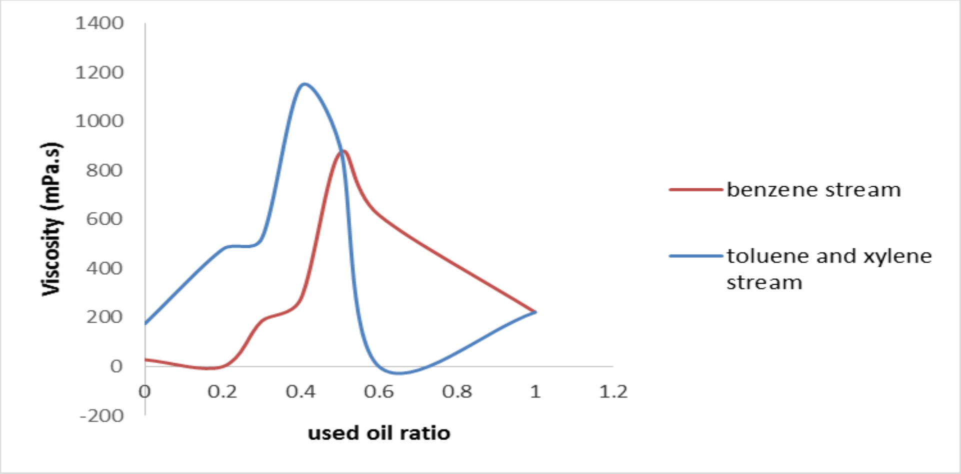


Figure 4. 17: Viscosity of acid tar waste mixed with used engine oil

This could because of less organic matter in the benzene effluent stream acid tar which lead to sulphuric acid being available to react with the used oil. The presence of polar compounds such as 2-chloro-2-norbornane carboxylic acid in toluene and xylene effluent stream acid tar could have influenced the formation of larger molecules with used oil which leads to the higher viscosity. The mixtures, however, separated after 24 hours for percentages of acid tar waste below 80%. Thus mixtures show the formation of asphaltene since the increase in concentration of asphaltene increase viscosity (Pokonova, 2003). This shows the possibility of using acid tar waste and used oil in pavement binder production. This contributed to the determination of the amount of used oil to be added in the modification of acid tar waste.

4.4.2 Dynamic viscoelastic parameters

The dynamic viscoelastic parameters include the complex viscosity, phase angle and the complex modulus. The effects of temperature and frequency on these parameters will provide the platform to assess the modified acid tar waste capability as a pavement binder.

4.4.2.1 Temperature sweep

Figure 4.18 shows how complex viscosity of the different modified acid tar waste material is affected by temperature.

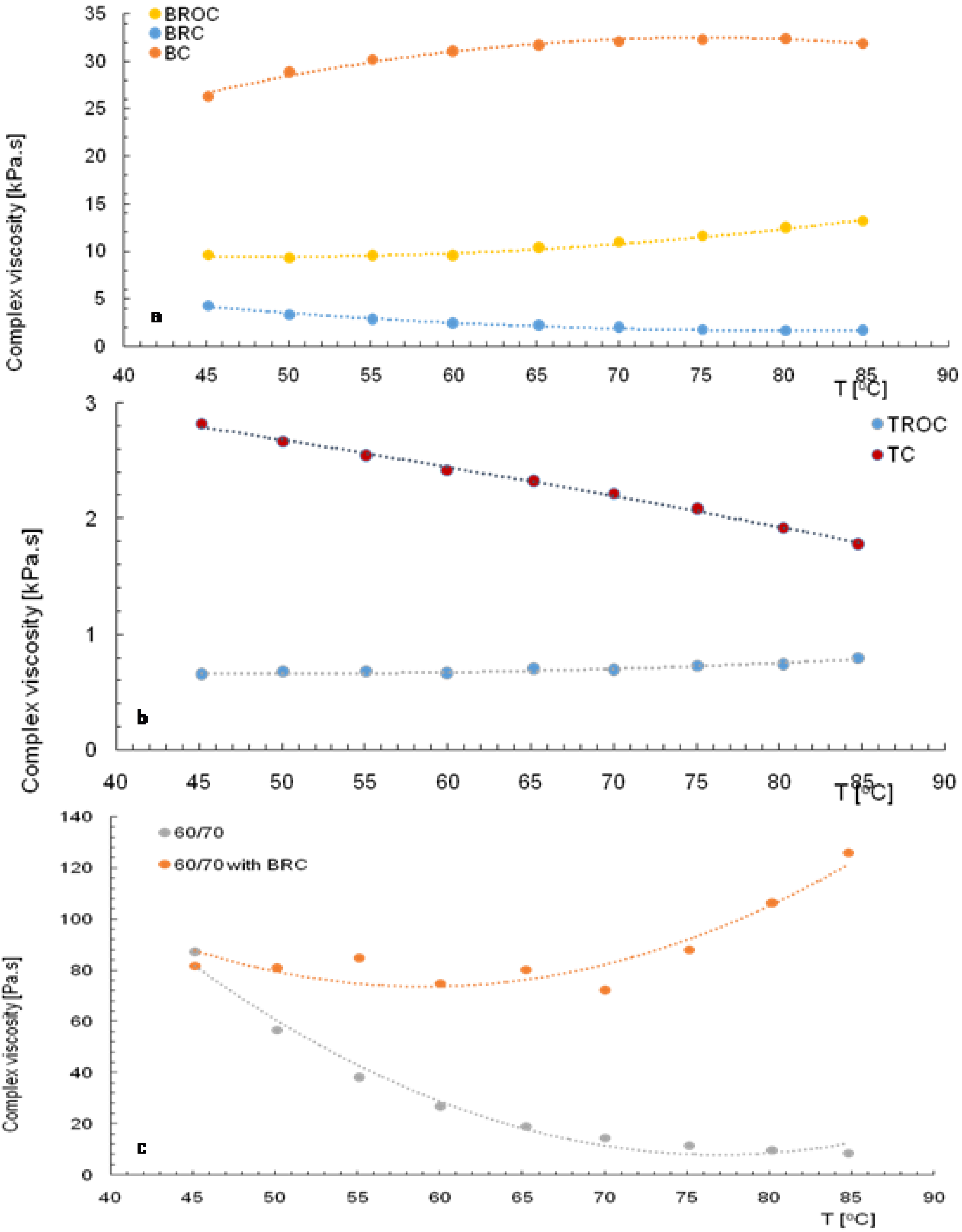


Figure 4.18: Effect of temperature on complex viscosity of the materials (a-benzene effluent stream acid tar modified materials, b-toluene and xylene effluent stream acid tar modified materials and c- 60/70 bitumen grade and 60/70 with BRC)

BC complex viscosity increased exponentially with temperature to about 75^{0}C then decreased slightly to 85^{0}C. This was because the sample hardened as the temperature increased due to evaporation of volatile substances resulting in a dry hard solid material. BRC and 60/70 complex viscosity decreased exponentially with temperature showing that it weakened with an increase in temperature. This could be attributed to the cleavage of intermolecular forces leading to melting and becoming more liquid. This is good for application, which is made easy by the reduced resistance to flow, making it easy to apply at high temperature. 60/70 had lower complex viscosity than BRC at each given temperature, making BRC stronger in terms of intermolecular forces than 60/70. BROC, TROC and 60/70 with BRC complex viscosity increased with temperature. In these mixtures, there seem to be swelling of the rubber component. BROC and TROC could be the presence of used oil which at high temperatures could be absorbed by the rubber causing swelling which then increases the viscosity. The mixture 60/70 with BRC did not behave as either BRC or 60/70 under these conditions indicating that the mixture of these two formed a product with a different structure to them hence the different pattern. TC complex viscosity decreased linearly with temperature showing that it had intermolecular forces weakened by the increase in temperature. BRC and TC are the modified acid tar waste that show potential for use in the pavement binder.

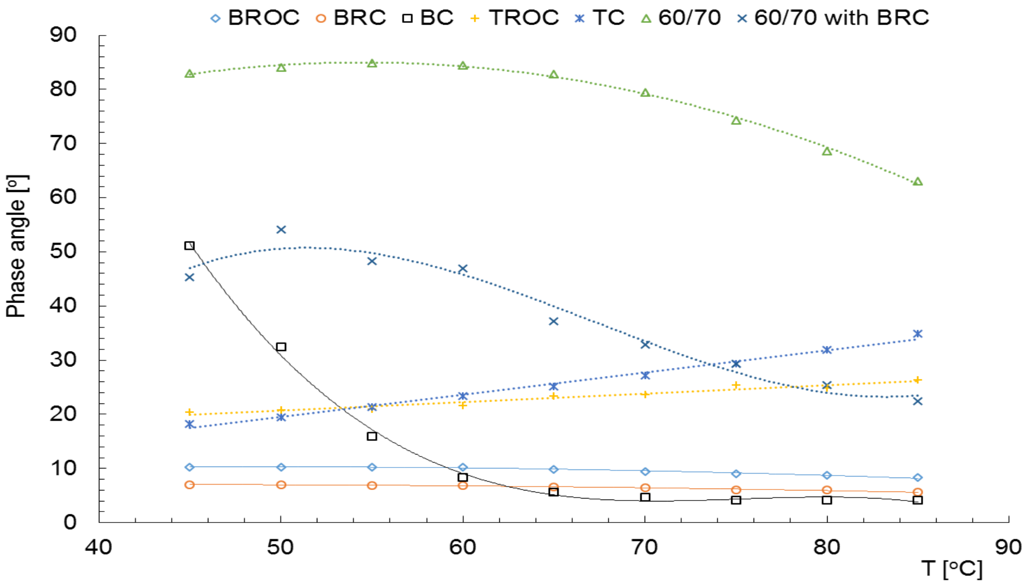


Figure 4. 19: The effect of temperature on viscoelastic behavior of the material.

Figure 4.19 shows the variation of viscoelasticity of the material under study. BC and 60/70 with BRC at low temperatures was close to 50 percent viscous as it is elastic, but as the temperature increased it became more elastic. BRC and BROC had a constant value of phase angle throughout the temperature range of 45 to 85^0C. BRC being more elastic than BROC though both proved to be more elastic than they are viscous. TC and TROC increased their viscous nature as the temperature increased which was expected so that it does not crack at high temperature. This behavior is similar to the one reported by Wang et al. (2012) for rubber modified asphalt from 45 to 75^0C. TC δ increased with increase in temperature while G* decreased with increase in temperature which is a pattern that was reported by other researchers for modified and unmodified pavement binders (Airey, 2004, Hafeez and Kamal, 2009, Kumar et al., 2009, Hafeez et al., 2012 and Pareek et al., 2012). 60/70 decreased the viscous nature at high temperature, though it is highly viscous as compared to the other products made from acid tar waste. 60/70 with BRC shows that in terms of temperature effect on viscoelastic behavior it retained the 60/70 pattern. The reduction of viscous nature however, points to the role that BRC has contributed in improving the elastic nature of the asphalt.

4.4.2.2 Rutting parameter

The modified acid tar waste has also been tested to determine the temperature at which the material will fail under normal load and the results are described in this section.

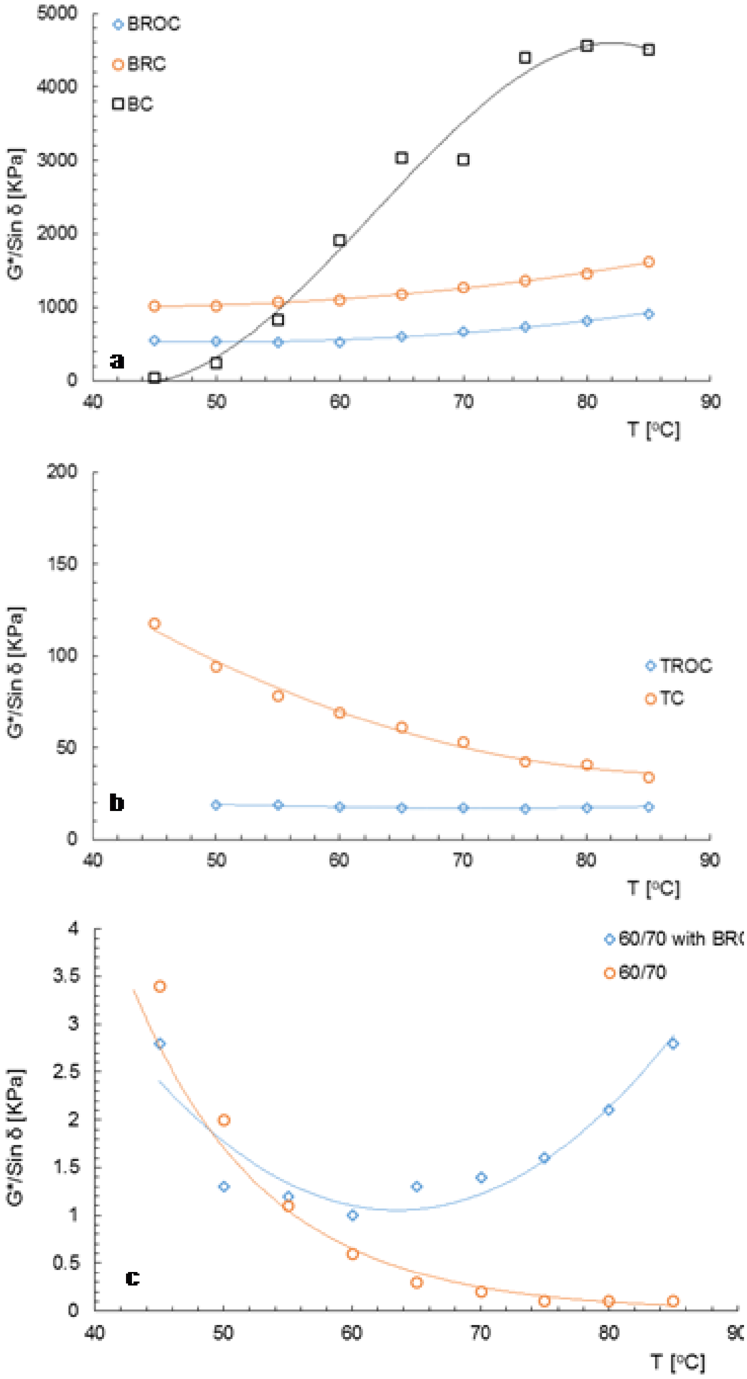


Figure 4. 20: The effect of temperature on the rutting resistance of materials (a- benzene effluent stream acid tar modified materials, b-toluene and xylene effluent stream acid tar modified materials and c- 60/70 bitumen grade and 60/70 with BRC)

Figure 4. 20 show the rutting resistance parameter of the modified acid tar waste material. The modified acid tar waste mixtures all show a rutting resistance above 1.0 kPa. Benzene effluent stream acid tar modification products show an increase in the rutting

resistance parameter with increase in temperature which is a good behavior since rutting is most experienced at high temperatures. Toluene and xylene effluent stream acid tar modification products, however, show a decrease in the rutting resistance parameter with increase in temperature. 60/70 also shows a decrease in the rutting resistance parameter with increase in temperature and at 60^0C it was already below 1.0 kPa. There is need therefore to modify bitumen as alluded to by other researchers (Airey, 2004; Kumar and Garg, 2011; Babalghaith et al., 2016; Yu et al., 2016). The modification of 60/70 with BRC produced a product which had lower values of rutting resistance parameter from 50 to 80^0C as compared to BRC though they were higher than the 60/70. The mixture also shows that at lower temperatures the 60/70 behavior is dominating whilst at high temperatures the BRC behavior is predominant. All in all the mixture had improved 60/70 asphalt. TC and 60/70 behaviour is similar to what was obtained by Xu et al. (2016) for the binders they tested. 60/70 had a failure temperature of 56^0C while Kumar and Garg, (2011) had a failure temperature of 57.9^0C and Babalghaith et al. (2016) was 64^0C for the same grade but different source. This shows that grading using only penetration and viscosity is not sufficient.

4.4.2.3 Frequency sweep

The effect of changing the frequency at constant temperature on the viscosity modulus, phase angle and the complex modulus of the acid tar is reported. Figure 4.21 shows the response to the increase in frequency. All the modified acid tar waste products show a decrease in complex viscosity as the frequency is increased.

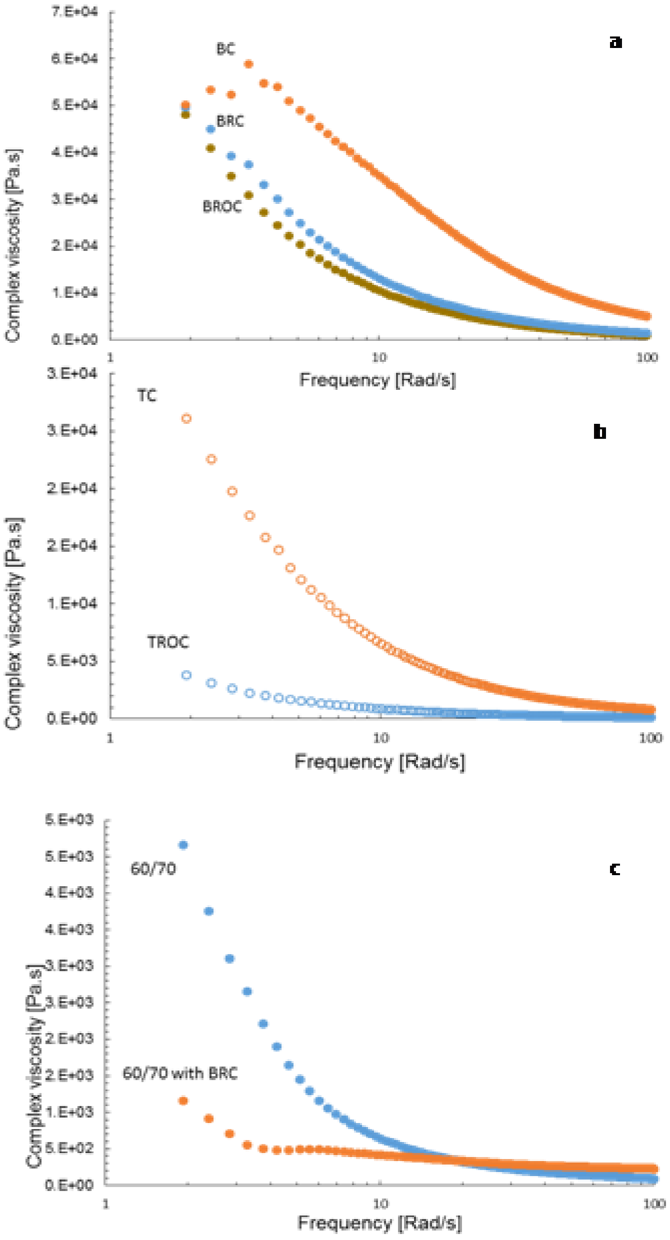


Figure 4.21: The effect of frequency on the complex viscosity (a-benzene effluent stream acid tar modified materials, b-toluene and xylene effluent stream acid tar modified materials and c- 60/70 bitumen grade and 60/70 with BRC).

This shows that inter molecular forces of the samples are affected by the increase in frequency (shear thinning) and this combination is suitable for roads that are in remote areas where there is low traffic. BC, BROC and BRC having higher complex viscosity are at an advantage as compared to the toluene and xylene effluent stream acid tar products as it will take more time to reach zero complex viscosity. This could be because the benzene effluent stream acid tar is more reactive and has produced better matrix with the calcium oxide and the rubber than the toluene and xylene effluent stream acid tar. Zhu et al. (2009) when comparing modifiers also commented that a good interaction between modifier and bitumen could result in high complex viscosity. The 60/70 with BRC proved to be better at high frequencies than 60/70.

Figure 4.22 shows the viscoelastic response of modified acid tar waste products and 60/70 bitumen grade to the increase of frequency. BRC, BROC and TROC decrease in viscous behaviour at low frequency to a constant which is more elastic than TC, 60/70, BC and 60/70 with BRC. BC and TC have a sharp decrease in viscous behaviour at low frequency then as the frequency increase there is gradual decrease in viscous behaviour to a more elastic nature. 60/70 has a decrease in viscous behaviour but not significant thus it remains more viscous at high frequency. The 60/70 with BRC was more elastic at low frequency and at high frequency gaining more balanced viscoelastic behaviour. Huang et al (2011) had commented that the elastic and viscous nature of asphalt was equally important. The behaviour of 60/70 with BRC shows the move towards more viscoelastic balanced at high frequencies, which helps the material to return its structure after such load is removed. BRC and 60/70 are extreme opposites with BRC being more elastic while 60/70 is more viscous at both low and high frequencies.

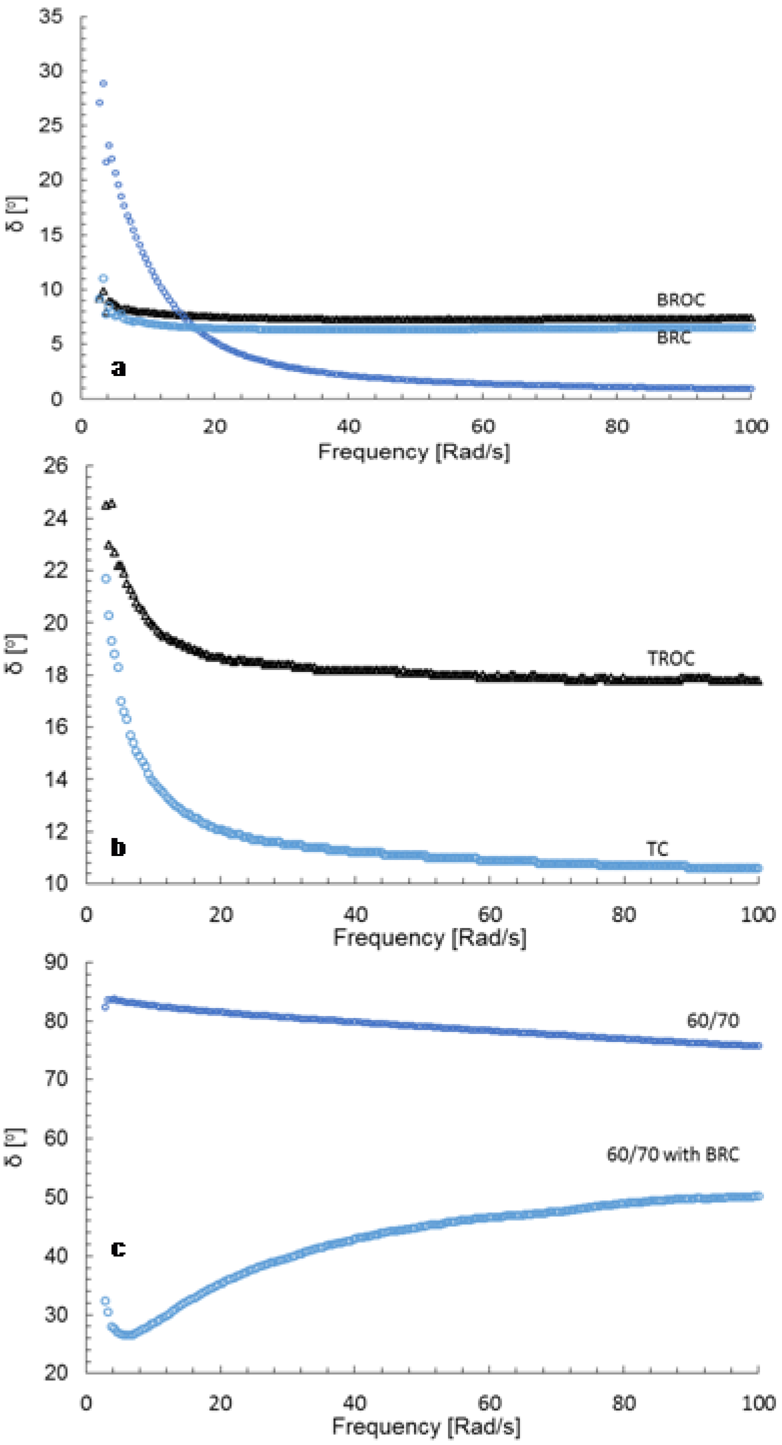


Figure 4.22: The effect of frequency on the viscoelastic behavior (a-benzene effluent stream acid tar modified materials, b-toluene and xylene effluent stream acid tar modified materials and c- 60/70 bitumen grade and 60/70 with BRC).

Figure 4.23 shows the stiffness response of the material under study to frequency. BRC, TC and 60/70 stiffness increased with increase in frequency with BRC having the highest complex modulus of the three. This pattern is similar to what Zhu et al. (2009) obtained when analyzing modified asphalt.

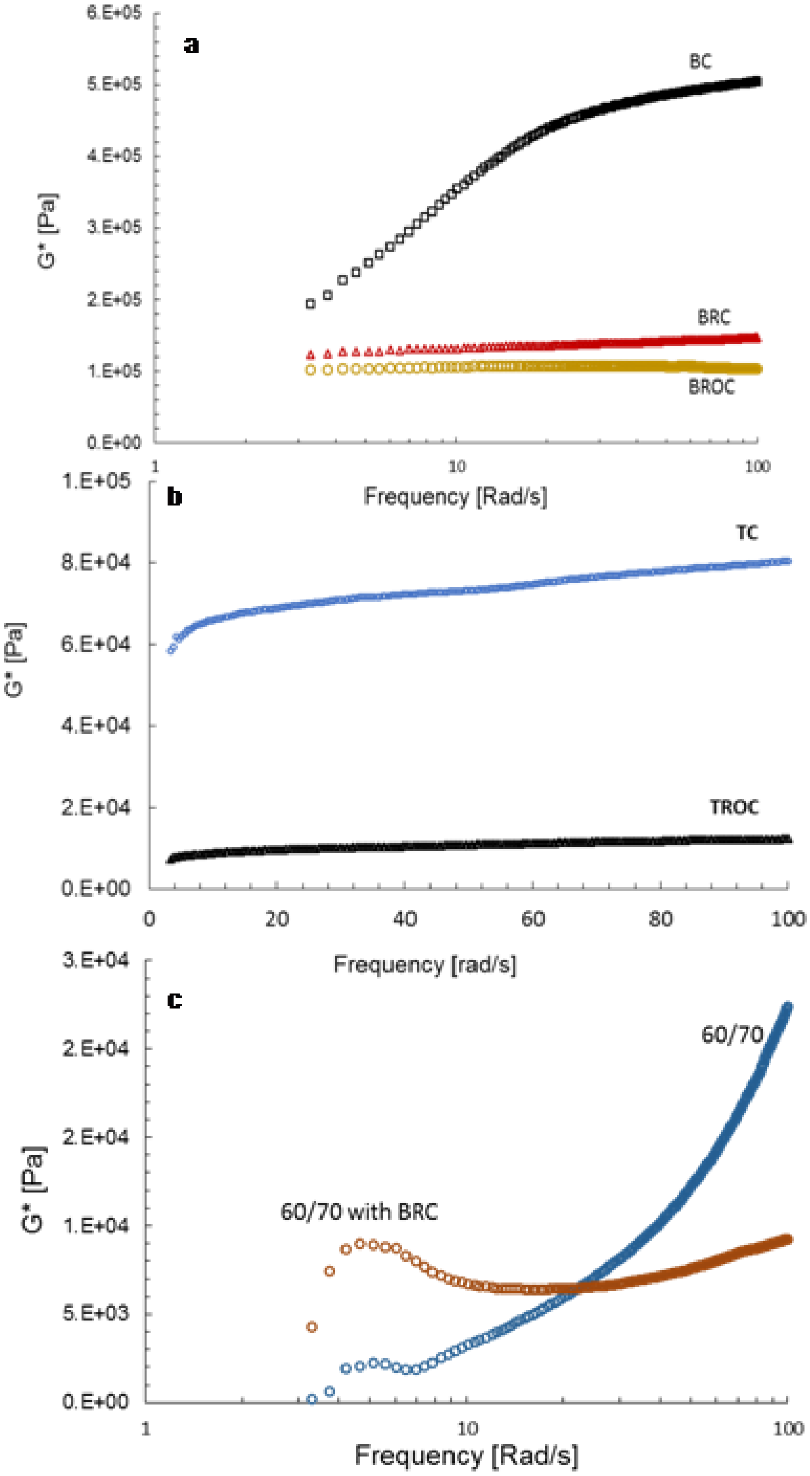


Figure 4.23: The effect of frequency on stiffness of material (a-benzene effluent stream acid tar modified materials, b-toluene and xylene effluent stream acid tar modified materials and c- 60/70 bitumen grade and 60/70 with BRC).

BC stiffness increased rapidly with increase in frequency up to medium frequency and then leveled off. BROC stiffness increased at low frequencies and then decreased from mid to high frequency indicating that it reaches a point where it is weakened by frequent deformation. 60/70 stiffness increases sharply with the increase in frequency. 60/70 with BRC was stiffer than 60/70 at lower frequency which can be related to what Ye and Wu, (2009) observed when they modified asphalt using fiber additives, a stiffen effect more significant at low frequencies. Navarro et al. (2007) also commented on the increase in the complex modulus values in the low frequency region and a slight decrease in the high frequency zone when rubber is added to bitumen. Thus the effect of rubber in the BRC is more pronounced here than the acid tar waste or the calcium oxide. At 10rad/s 60/70 with BRC has G* greater than 60/70 making a better asphalt.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Introduction

From the results and discussion in Chapter Four conclusions and recommendations have been reached, these are mentioned in detail in this chapter. The conclusions are arranged according to:

1. Characterisation
2. Neutralisation
3. Modification

5.2 Conclusion

Characterisation of benzene and toluene and xylene effluent streams leads to the following logical reasoning:

a. Toluene and xylene effluent stream acid tar had nine organic compounds identified while benzene effluent stream acid tar had six organic compounds.

b. Organic compounds present in the two acid tar waste are not only different in amount but also in the functional groups.

c. Benzene effluent stream acid tar contains alkyne, quinoline (nitro compound), cyclo compound, amine, phenol and benzyl while toluene and xylene effluent stream acid tar contains amide, amine, carboxylic acid, pyrrole, thiophene, indine and benzyl.

d. Despite their difference, both acid tar waste had alkane, alkene, ketone and ether.

e. Thus the acid tar waste have some functional groups found in asphalt and there is a possibility that when modified can produce pavement binders which are for toluene and xylene effluent stream acid tar: pyrrole, carboxylic acid and ketone while benzene effluent stream acid tar: quinoline, ketone and phenol.

f. Toluene and xylene effluent stream acid tar has more polar inducing functional groups, thus more interactions are expected. The binder from toluene and xylene effluent stream acid tar is thus able to adhere to surfaces more than that of benzene effluent stream acid tar.
g. The acid tar waste show that they contain very little inorganic compounds with sulphate ions being in high concentration.
h. Benzene effluent stream acid tar had higher sulphates ion than toluene and xylene effluent stream acid tar.
i. The sulphate ions are from sulphuric acid which was 24.2% for benzene effluent stream acid tar and 23.7% for toluene and xylene effluent stream acid tar.
j. Toluene and xylene effluent stream acid tar had higher viscosity (183.0mPa.s) than benzene effluent stream acid tar (28.6mPa.s).
k. The acid tar waste were all visco-plastic with benzene effluent stream acid tar (0.162) being less than toluene and xylene effluent stream acid tar (0.435).
l. Benzene effluent stream acid tar behaved as the Herschel-Bulkley model while toluene and xylene effluent stream acid tar pattern followed the Bingham model thus they were all non-Newtonian fluids.
m. The presence of organic matter also affected the rate of thinning of the acid tar waste with toluene and xylene effluent stream acid tar thinning much faster when exposed to heat than benzene effluent stream acid tar.
n. The visco-plastic nature of the two acid tar waste indicates that they can be used for binder production.

From the characterisation of neutralised acid tar waste the following conclusions were drawn:

a. The salts produced from neutralisation of toluene and xylene effluent stream acid tar had high concentrations of sulphate ions (25.8%) than that of benzene effluent stream acid tar (8.5%) and this could be used for gypsum production.
b. The benzene effluent stream acid tar salts were less soluble in water than that of toluene and xylene effluent stream acid tar an important improvement for binder formation.
c. Toluene and xylene effluent stream acid tar was able to be neutralised with calcium hydroxide and calcium oxide at temperature changes less than 50^0C however the gaseous emissions were higher than what the benzene effluent stream acid tar produced.
d. The solubility of the salts in water was further reduced by heating at 150^0C. This reduces the risk of leaching of chemicals into the environment if the waste is to be used for binder production though heating means an increase in gaseous emission.
e. Calcium oxide salt for both acid tar waste had lower solubility (10.3%) after heating while calcium hydroxide salt for both acid tar waste had approximately 20%.
f. Calcium oxide proved to be the best base in terms of gaseous emissions as well as the production of a less soluble salt. Calcium oxide became the base used in the binder production as neutralising agent.

The acid tar waste modified products characteristics were influenced by the type of the acid tar waste. The following elaborates further:

a. Benzene effluent stream acid tar had products which were stiffer and more elastic than those produced from toluene and xylene effluent stream acid tar.

b. Toluene and xylene effluent stream acid tar produced material which behaved like 60/70 bitumen grade even if it was stiffer than the bitumen.

c. TC performed better than TROC in the rheological test performed, thus it is the best product to be considered for pavement binders.

d. BC was very stiff and hardened during test making it unsuitable for pavement binding.

e. BROC was not stiff in comparison with BRC and the fact that it hardened when exposed to high temperatures making it difficult to use at high temperatures for application on pavements. This makes BRC the best material for benzene effluent stream acid tar.

f. BRC was stiffer than TC but could not be compared to other binders in the way it behaved after it had been subjected to deformation. This makes TC the best product from the five materials produced from acid tar waste.

g. Acid tar waste can be used in the production of pavement binders as shown by the mixture of BRC and 60/70 which, showed improvement for both BRC and 60/70 bitumen grade, in:

    i. Rutting resistance where it had no failing temperature

ii. Viscoelastic were it was more balanced than both materials used to produce it.

5.3 Recommendations

a. Calcium oxide should be used to neutralise both the toluene and xylene effluent stream acid tar and the benzene effluent stream acid tar before production of pavement binders. This is because it gives less water soluble product with low gas emissions which is environmentally friendly.
b. BRC and TC can be used in pavement binder production if the elasticity is reduced while improving the viscous nature.
c. The material produced should then be used in roads that have low traffic.
d. The combination of the acid tar waste with 60/70 bitumen grade also needs further consideration.
e. The issue of the percentage of bitumen to the acid tar waste mixtures using the rheological and conventional methods to characterise the material also requires further investigation.

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APPENDIX: Publications and conference presentations from this work

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Characterization and utilization of acid tar waste from crude benzol processing for environmental sustainability

C. Danha[1], C. H. Chihobo[2], D. Musademba[2], D. J. Simbi, P. K. Kuipa & E. Jonathan
[1]*Environmental science, Chinhoyi University of Technology, Zimbabwe*
[2]*Fuel and energy, Chinhoyi University of Technology, Zimbabwe*

Abstract: *This paper reviews the utilization of acid tars with the overall aim of reducing or eradicating the environmental problems associated with acid tar landfill disposal at a local crude benzol refinery in Zimbabwe .The review focused on disposal, characterization, composition and utilization of acid tars. Peer reviewed journal and conference papers from 1980 to the current year were considered. The papers reviewed were mainly from petroleum processing since the acidic nature of the tar can be assumed to be similar to that of crude benzol processing and the databases used were Science direct, Hinari and Agora .The effects of the disposal of acid tar in lagoon were reviewed. The utilisation of acid tar waste is dependent on the chemical composition hence work on the characterization of acid tars was reviewed. The use GC-MS was common in the characterization of acid tars as compared to other analytical techniques. Some of the utilization processes which were reviewed included among others the conversion of acid tar to asphaltenes, production of pavement binders, energy utilisation, acid tar co-processing, membrane technology, ion exchangers and carbon adsorbents technique. The utilization of acid tar waste hinges on effective treatment methods owing to its complex chemical composition.*

Keywords: *Crude benzol, Acid tar, Refining, Lagoons, Characterisation, Asphaltenes, Energy, membrane technology, Remediation, Disposal*

I. Introduction

Acid tars are basically derived from three processes namely re-refining of spent lubricating oils, refining of petroleum fractions and in crude benzol refining. The refining of crude benzol involves washing with concentrated sulphuric acid which sulphonates the more undesirable compounds and allows easier separation and recovery of the Benzene, Toluene and Xylene fractions. The Acidic tarry waste material generated is regarded industrially as a product of low commercial value and is disposed off in lagoons; however, acid tars from crude benzol can be feedstocks for the synthesis of other valuable products. The focus in European, American and Asian countries is on the remediation of acid tar lagoons created by former gas works sites, benzol refining, refining petroleum fractions and in oil re–refining. The remediation activities were mainly centred on reclaiming the land, burning and utilisation of the acid tars. In Africa and Zimbabwe in particular there is no literature in support of the remediation and utilisation of the acid tars. The main objective of this literature review was to make a close analysis of the various technical and scientific ways of utilising acid tars.

II. Environmental effects of acid tar disposal

Disposing acid tar in open lagoons expose the environment to different impacts since the effects are dependent on the temperature and moisture content [1]. For example acidification of groundwater and mineral oil was observed with high levels of sulphates in areas close to the Pesniski Dvor dumping site [2]. Environmental risks such as volatiles in the air, dust blow off from exposed and weathered tar surface, leaching to the ground water and surface water are expected from open lagoons [1]. The leaching of the waste affects the ground water and the evolution of gases from the waste also affects the atmosphere which might lead to acid rain which will in turn affect surface water. During storage in holding ponds, the chemical composition of the acid tar changed as a result of leaching of the acid from the tar by rainfall, evolution of sulphur dioxide and condensation of the substances present in the acid tar [3]. [4] Also supports this when he observed the inconsistent chemical composition of the acid tar that changes with time due to the reaction of the organic components with atmospheric oxygen and sulphuric acid. The use of quick lime to neutralise acid tars in lagoons has been found to be environmentally unacceptable since it produces emissions which will lead to environmental problems such as acid rain and global warming [1]. Acid tars contain sulphuric acid thus the effects of sulphuric acid on the environment are the major ones that need to be considered followed by those of organic chemicals such as benzene and other volatile organic compounds. From the literature reviewed, the environmental effects of acid tars disposed in lagoons, have been given little attention.

III. Techniques for characterising acid tars

The proper utilisation of acid tars in any application requires an in depth understanding of the chemical composition of acid tar. The composition of acid tar has been determined using gas chromatography-mass spectrometry (GC-MS) [5], while gas chromatography with a thermal conductivity detector is said to be suitable for analysis of organic compounds [6]. Mass spectrometry detection simplifies the analysis by eliminating the need for standards to identify the organic groups. In another research organic compound content of spent sulphuric acid from benzol refining process was analysed using gas chromatography with flame ionisation detector [7]. The use of Fourier transform infrared (FTIR) spectrometry with gas chromatography-mass spectrometry for characterisation of organics and coal by-products was common [8]; [9]; [5] and [10]. According to [4], FTIR is used to further confirm the presence of organic groups detected by GC-MS. [10], used gas chromatograph and a mass selective detector along side FTIR to determine the organic composition of crude benzene. [8] Used GC-FTIR system were the FT-IR at a frequency range of 4000 to 580cm^{-1}at resolution of 8cm^{-1}was used as a detector. The role of the GC was to separate the organic components using oven temperatures adapted to each mixture (alkanes, branched alkanes, cycloalkanes and aromatics the temperature range was 28 to 270^{0}C). There are some investigations that just relied on FTIR for characterisation [11]; [12] and [13]. [11] Used FTIR at frequency range of 4000 to 500cm^{-1} at a resolution of 4cm^{-1} at room temperature.
The use of FTIR for organic acid analysis in aqueous solutions requires pH monitoring as the spectra vary with pH. The presence of one molar sodium chloride of pH 8.5 ensures that all the organic acids are present in their fully de-protonated form [14]. There is need for pre treatment of the sample so as to avoid co eluting of organic compounds. A sample of coal tar is passed through silica gel and alumina in a column to separate various types of organics using the difference in their ability to adsorb and the difference of polarity between various eluents [15]. Common eluents used are pentane, benzene, ethyl acetate and methanol to end up with aliphatic, aromatics, esters and polar organic compounds [15]. Hexane, benzene and ethanol are solvents which are used to extract different groups of organic compounds from acid tar so that the analysis become easy since different groups differ in their solubility for every solvent [16].

In an investigation for analysis of crude oils and petroleum products, 100% n-hexane for saturates, 5% benzene/95% n-hexane for mono aromatics, 15% benzene/85% n-hexane for di-aromatics and 60% methanol/20% diethylether/20% benzene for poly aromatics was used for elution on a silica gel column prior to FTIR [17]. Soxhlet extraction with 1:1 volume of acetone and dichloromethane is used to extract the organics from acid tar [5]. The acid tar is also separated into toluene soluble and insoluble fractions. Toluene soluble is further separated into asphaltene and maltenes using heptanes precipitation [5]. Maltenes are separated into saturates, aromatics and resin through silica gel packed column chromatography using n-hexane, 20% (v/v) dichloromethane/ n-hexane and 50% (v/v) dichloromethane/methanol, solvent is then removed in a fume hood [5]. Due to the complexity of the acid tars various techniques are used as has been shown in the literature available.

IV. Composition and properties of acid tars

The following table summarises the work by various researchers on the composition of acid tars.

Table I: Composition of acid tars

Researcher	Composition of acid tars (%)					
	Sulphuric acid	Water	Organic oil	resins	Ash/other impurities	Asphaltene
[3]	45±5	5.38±2.63	41.25±3.75	-	0.076	-
[3]	0.026±0.01	6.7±4.3	80.5±5.5	12.1±2.7	0.93±0.33	-
[3]	12.3	28	42	22	5.9	-
[18]	48.2	-	49.5	-	-	-
[19]	44	6	50	-	-	-
[20]	-	-	73	24	-	3
[16]	0.014	3.21	52.15	6.29	0.14	37.85
[7]	63.8	-	6.9	-	29.3	-
[5]	-	9.3±1.1	32.5±1.5	0.5±0.02	-	19.3±0.6
[5]		7.25±1	3.1±0.3	1.8±0.1		2.3±0.2

Generally the results from Table I indicate that the percentages of organic oils in the acid tars are higher than corresponding sulphuric acid present in the samples. Fresh acid tar has a high percentage of sulphuric acid as compared to the pond acid tar. The composition of acid tar is time dependent. This is also supported by [3] when he observed that the percentage of sulphuric acid decreased with time in storage tanks where a solid film had formed on the surface of the acid tar. [21] Have also shown that there is a decline in sulphuric acid in ponded tars when he observed that the composition of the gas after decomposition of pond acid tar had 28.6 mol % of hydrogen sulphide and less than 1.2 mol % of sulphur dioxide. The differences in the percentages of the sulphuric acids may be explained by the fact that the acid is either being consumed by chemical reactions or evaporating into the air, thus there is need to find out what happens to the acid tar the minute it is produced to about a year in a monitored environment. The percentage of sulphuric acid varies from sample to sample. The presence of resins and asphaltenes in ponded acid tars supports that chemical reactions will have taken place over time. The water content is very low in both fresh and pond acid tar.

The character of acid tars is complex. In the characterisation of acid tars, [5] observed two acid groups as evidenced by the two plateaus shown in figure 1, suggesting the presence of both organic acids and inorganic acids in the acid tar.

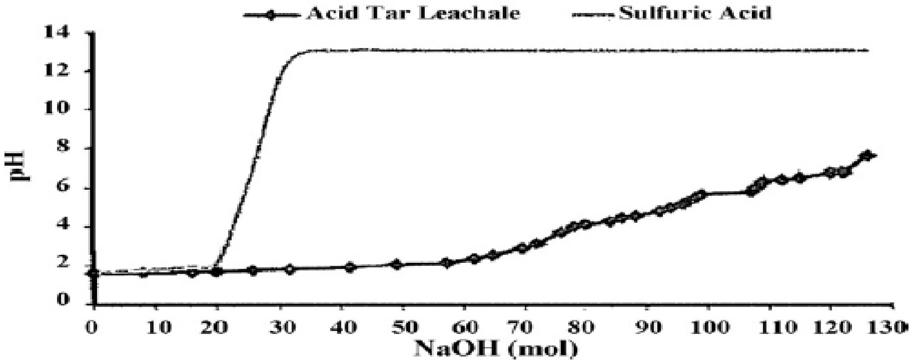

Fig. I: The titration of sodium hydroxide against acid tar [5]

[18] Previously observed that freshly produced acid tars consisted of mainly sulphuric acid, sulphonic acid and carboxylic acid. The pH of acid tar is variable and depends on the process by which the acid tar is generated, the amount and strength of the sulphuric acid used in the process and pre-treatment prior to disposal [22]. This implies that there is need to determine the composition of acid tar for each set of raw materials used. In studying the Hoole Bank Lagoon in Europe, [19] observed evidence of particles settling at the bottom of the lagoon, and in analysing the acid tars he found that the density of acid tars ranged from 1.2 to 1.4 g/ml and the viscosity varied with temperature. In a similar research at the D.I. Mendelev Yaroslav in Russia, [23] observed high ash content of approximately 6.5% and high viscosity for the bottom layer of acid tars. Ash could be the major part which is being deposited at the bottom.

V. Utilization and processing of acid tars into asphaltenes

The processing of fresh acid tar was said to be more difficult than that of acid tar from lagoon due to the high percentages of sulphuric acid [3]. In normal state sulphuric acid mixed with organics does not react with the organic part of the mixture [24]. This then makes the mixture difficult to deal with when fresh and yet once in lagoons reaction with air and water can take place thus reducing the acidity of the mixture. Polymers and inorganic cement techniques were attempted in the 1970s in UK but the processes proved to be more expensive than the neutralisation and landfill dumping of acid tars [22]. Neutralisation is done under controlled temperatures and emissions monitoring since it increases temperature which leads to sulphuric acid and sulphur trioxide evaporating from the mixture if the temperature exceeds 100°C [25]. [3] proposed a method for the production of paving asphalt: a three key step process which involved neutralisation of the acid tar with technical calcium oxide at temperatures between 90 and 100^0C; evaporation of water from the reaction mass at 100 to 130°C and oxidation of the neutralised mass with air at 160 to 190°C in a thermostatic metal reactor with stirrer. In another method by [26] acid tar was converted to asphalt using the thermal cracking method. The resulting product from this method was found to be temperature dependent such that low penetration was observed at high temperatures (460- 480^0C) when the product was exposed for 10 minutes. When acid tars are exposed to high temperatures for more than 10 minutes coke formation is prompted instead of asphaltenes and resin which are responsible for the viscosity characteristics of the product. This type of processing requires the control of emissions since the lowest temperatures were 400 to 420^0C [26]. Thin film cracking of acid tars at $350\text{-}400^0$C resulted in asphaltene material of 65-70%, liquid hydrocarbons of 20-25% and gas of 5-10% and at 500^0C coke at 18% and liquid hydrocarbons 75% produced [27]. A technology for processing acid tars with the aim of obtaining solid fuel, resins and general use medium oils was proposed by [4]. The proposed technology is based on the use of membrane methods of separation of hydrocarbons and comprises the following steps: heating and filtration to remove acid water and particulate contaminants; neutralisation of the filtered acid tars with an alkali solution; two stage de-asphalting and subsequent series of separation of oil and resin in membrane units. The auxiliary stages of the process involved neutralisation and treatment of the acid waters generated and the recovery of the solvents used. Acid tars of the following composition were processed in an experimental set up: acid number, 14mg KOH/g, 21.7% paraffin and naphthalene; 5.9% aromatics; 12.9% resins; 47.1% residue (oxidation products, carbenes, carboids, and solid residue) and 12.4% asphaltenes. The yield from the process was 60% solid fuel, 12.5% resin and 26% oils (industrial type).

VI. Acid tar use in pavement binder production

Basic properties of bitumen are softening point (°C), penetration (mm) and ductility (cm) [28]. Softening point, penetration, brass breaking point, morphology and rheological properties play a part in the performance of the bitumen [29]. Natural bitumen from Iran consisted of 13% ash 60% volatile matter, 28% fixed carbon and 1-5% moisture content [29]. The natural bitumen is black in colour, specific gravity of 1.1-1.2g/ml, softening point of 119°C and penetration of 0-2mm [29]. The natural bitumen, however, requires modification to improve its penetration properties. Asphalt that was produced from acid tar meet the requirements of the Russian standards for bitumen grade 60/90 paving asphalt with respect to penetration, softening point, breaking point, flash point and adhesion to marbles but has low ductility of 3.9cm at 25°C instead of 61 [30]. The adhesive properties of the bitumen are improved when mixed with polymers [31]. Copolymer of divinyl with styrene, atactic polypropylene, and co-polymer of ethylene with vinyl acetate, polychloroprene, polyisobutylene and natural rubber are polymers that are preferable for bitumen modification. From analysing the results by [31 and [29] natural bitumen can be mixed with asphalt to complement each other. In another research by [32] mixed asphalt with natural rubber to improve the viscosity. More viscose asphalt was found to have high softening point and this reduces the deformation, bleeding and increased pavement stability at high temperatures [32]

VII. Energy utilization of acid tars

Table II gives the energy values of acid tars obtained from various tar lagoons. The variation in the energy content reported in the Table 2 is actually a function of the acid tar composition. The energy content depends mainly on the combustible carbon content. The energy values indicate that acid tars can be used as a source of fuel.

Table II: Energy values of acid tars

Researcher	Place	Composition	Energy value
[23]	Mendeleev Yaroslavl Oil Refinery (Russia	79%Organics, 3% water, 11,5%H_2SO_4, 5% Sulphur, 6.5% ash content	33.5 MJ/Kg
[33]	Sydney Tar ponds. (Nova Scotia Canada	51%Moisture , 20.62% ash, 18.14% C, 7.37%H, 0.55%N, 1.12%S	9.47 MJ/kg
[34]	Avonmouth England	34.90%C, 5.50%H, 6.35% O ,0.30%N, 2.12%S, 9% Moisture, 4.03%Ash, 25 to 50%w/w Lead in ash, 5000 Cp Viscosity and 1.3 Specific gravity	18.648kJ/kg

[35] Patented a process for the manufacture of boiler fuel from solid and high viscosity acid tars mixed with a straight run petroleum fraction. The resultant boiler fuel yield was found to be 92-97.4 wt %. In another research, [27] showed that high yields of light petroleum products could be obtained from the thermal cracking of the organic components of the acid tars. The designed process by [27] yielded gaseous hydrocarbons (primarily, C_1 -C_4) as well as liquid hydrocarbons that corresponded with the boiler or furnace fuel by composition. An enriched organic matter solid fuel was derived from acid tars using an organic admixture [36] and [37]. The admixture was pulverized and simultaneously heated to 200 – 300^{0}C, it was observed that the organic matter of the acid tar when heated to 200-300^{0}C behaves as a reducing medium for sulphuric acid. Apart from processing the acid tars into a suitable fuel, some researchers tried to use the raw acid tar as a basic fuel. [23] Investigated the possibility of utilising the bottom layer of the acid tars which had been ponded for over a century at D.I Mendeleev Yaroslavl's oil refinery. The ponded acid tar had separated into three layers and the potential energy from the bottom layer was estimated at 16.76*10^9 GJ [23]. Their attempt to utilize the bottom layer as a basic fuel for the manufacturing energy carriers in ordinary boilers was a challenge due to the relatively high ash content of about 6.5%, and the viscosities which did not allow burning in traditional boilers with fuel nozzles. However, with improved combustion technologies such as the circulating fluidised bed, combustion of the acid tars was found to be feasible. The technology proved to be effective in burning fuels with high moisture content and sulphur content without using expensive systems for scrubbing Nitrogen and Sulphur oxides from gases [38]. [39] Noted that the development of such fluidised bed technology on poor quality fuels

was demonstrated way back in the 1960s. [40] attempted co-combustion of acid tars with coal in a bubbling fluidised bed combustor with a total heat input of about $2MW_{th}$, with the share of the acid tar being about a half. A surprising result of 99% combustion efficiency was attained. The use of a fluidised bed combustor for burning acid tar, however, required that limestone be added to the bed material in order to provide some degree of sulphur capture [40]. By applying the limestone to the bed material, around 417ppm as opposed to 600ppm SO_2 emission limit as stipulated by the Commission of the European Communities was achieved using this method [40]. It can, therefore, be concluded from such an experience that the burning of viscous and sulphur containing wastes such as the acid tars can be demonstrated with a minimum effect on the environment. [41] Noted that the incineration of acid tars in fluidised bed technologies as a fuel substitute have not been well investigated.

VIII. Ion exchangers and carbon adsorbents

[42] Extensively studied the utilisation of acid tars in the synthesis of new reactive feed stocks for the manufacture of cationic exchangers. The feedstock for the manufacture of cationic exchangers was obtained from the redox reaction of oily acid tars and asphaltenes from naphtha deasphalting. Mixing acid tars from the treatment of transformer and automotive oils and naphtha deasphalting asphaltite produced a secondary petroleum residue with a group composition constituting 18.3% oils, 16.1% resins, and 65.6% asphaltenes. Sulphurisation with 20% oleum, produced a powdered sulpho cation exchanger with the following properties: static exchange capacity (SEC), 3.8 meq/g; dynamic volume capacity (with 0.0035N calcium chloride solution at unit load of 10 litres /litre.h), 489meq/g; bulk mass of air dried product, 0.59g/ml; moisture content, 23.4%; swelling in water, 39.2%; and mechanical strength, 92% [42].

Analysis of sulphurisation kinetics data showed very high reactivity of resins and asphaltenes from the acid tars and asphaltite. With respect to the properties the powdered cation exchanger made from petroleum resins and asphaltenes, [42] proposed their use in preliminary water treatment with metal gauze asbestos gravity filters at nuclear power plants.

In a technological process described by [42], acid tars can be utilised in the synthesis of polycondensates used as basic stocks for adsorbents. The resins and asphaltenes in acid tars can be used as additional source of feedstock, while the spent sulphuric acid can be used as a catalyst which solves the environmental problems of oil refineries. A mixture of cracking residues, furfural and acid tars in the ratio 33:25:22(wt) was used to fabricate the copolycondensate (furan –formolite). The stock for the adsorbents consisted of coal dust, furan –formolite, and wood tar in the ratio 39:39:22(wt). The adsorbents obtained were characterised by a high C.H ratio and molecular size pores. The sorption studies showed that they sorb gases – methane, carbon dioxide and xenon to a much higher degree than industrial adsorbents. The adsorption, separating and selective properties of the cracking residue adsorbents were superior to industrial adsorbents for approximately the same pore size. The adsorbents obtained can be used for the treatment of difficulty sorbed and polar gases

IX. Conclusion

A review of studies on acid tars has revealed that the environmental impacts of acid tars have not been fully explored and the constituents of the acid tar obtained by the various researchers differed. No resemblance in terms of the composition by weight can be drawn from these studies; however, the basic characteristics of acid tars remain similar despite the process by which the acid tar was derived. Analysis of acid tar requires pretreatment and the use of gas chromatography equipped with mass spectrometer detector is common. Various methods for the processing of acid tar into utilisable product have been tried in an attempt to reduce the long standing environmental problems associated with the disposal of acid tar in lagoons. Some of the utilisation processes which were reviewed included among others the conversion of acid tar to asphaltenes, production of pavement binders, energy utilisation, acid tar co-processing, membrane technology, ion exchangers and carbon adsorbents technique. These techniques, however, have not been conclusively investigated owing to the complexity of the acid tar. Accordingly, the deep-seated need for environmental sustainability still remains. Therefore, the problems experienced with the land fill disposal of highly corrosive acid tar wastes mean that an effective treatment method and utilisation techniques is needed for existing acid tar lagoons and the quantities that are still being generated by both crude petroleum and coal carbonisation processes world-wide.

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Characterization of acid tar waste from benzol purification

Danha, C., Simbi, D.J. and Kuipa, P.K.

Chinhoyi University of Science and Technology
Department of Environmental Science and Technology,
P. Bag 7724, Chinhoyi, Zimbabwe

ABSTRACT

The use of concentrated sulphuric acid to purify benzene, toluene and xylene produces acidic waste known as acid tar. The characterization of the acid tar to determine the composition and physical properties to device a way to use the waste was done. There were three acid tars two from benzene (B acid tar), toluene and xylene (TX acid tar) purification streams and one which was from the storage tank (HT acid tar). The viscosity and density varied greatly amoung the three acid tars with B acid tar having the lowest viscosity (28.3mPa.s) and HT acid tar having the highest viscosity (63.592Pa.s). For density HT had the lowest (1.43g/ml) and TX had the highest (1.549g/ml). The sulphuric acid % concentration was 15.4% for HT, 23.7% for TX and 24.2% for B acid tar. The solubility test also showed a difference in the three acid tars, B acid tar was more soluble in water than in methanol while the other two were more soluble in methanol than in water. GC-MS and FT-IR results showed that TX and HT acid tars had weak organic acid such carboxylic acid, alcohols and aldehydes. The B acid tar had few organics as compared to TX and HT. The results show that the sulphuric acid is being lost in the holding tank and the physical and chemical properties of B and TX acid tar are different thus the need to treat differently if they are to be treated separately. The HT acid tar has properties that make it easier to work with; an example is the high viscosity and the high organic content.

Key words: Acid tar, benzol processing, sulphuric acid, organic acids, characterization and viscosity

INTRODUCTION

Acid tar is waste produced from purification of benzene, toluene and xylene using sulphuric acid. The benzene, toluene and xylene are from benzol processing. Benzol is a by product of coal carbonization. Acid tars are mainly from three processes namely re-refining of spent lubricating oils, refining of petroleum fractions and in crude benzol refining. The refining of crude benzol involves washing with concentrated sulphuric acid which sulphonates the more undesirable compounds and allows easier separation and recovery of the Benzene, Toluene and Xylene fractions. The Acidic tarry waste material generated is regarded industrially as a product of low commercial value and is disposed off in lagoons; however, acid tars from crude benzol can be feed stocks for the synthesis of other valuable products. In Zimbabwe acid tar waste is generated at Zimchem Refineries (PVT) LTD situated at ZISCO Steel in Redcliff. The waste is contained in lagoons lined with sealing tar which expose the waste to air and rain. The acid tar is sometimes mixed with lime at the lagoons. There are two streams that produce acid tar at Zimchem. The benzene purification, which uses oleum (100% sulphuric acid) and the toluene and xylene purification which uses 98% sulphuric acid are the two streams. The acid from the two streams is then directed to a holding tank before taking the acid tar to the lagoons. Under normal production the company disposes about 40 tons of acid tar a month. Kwekwe River is situated at the bottom of the mountain where the lagoons are. The river is a source of water for Redcliff town. Disposing acid tar in open lagoons expose the environment to different impacts since the effects are dependent on the temperature and moisture content (Catney, *et al,* 2005). Leaching of acid tar affects ground water for example acidification of groundwater was observed with high levels of sulphates in areas close to the Pesniski Dvor dumping site (Zilic-Fiser *et al.*, 2010). Evolution of gas from the waste also affects the atmosphere which might lead to acid rain which will in turn affect surface water. During storage in holding ponds, the chemical composition of the acid tar changed as a result of leaching of the acid from the tar by rainfall, evolution of sulphur dioxide and condensation of the substances present in the acid tar leading to the inconsistent chemical composition of the acid tar that changes with time due to the reaction of the organic components with atmospheric oxygen and sulphuric acid (Frolov *et al.*, 1981 and Burtanaya *et al.*, 2007). The use of quick lime to neutralise acid tars in lagoons has been found to be environmentally unacceptable since it produces emissions which will lead to environmental problems such as acid rain and global warming (Catney *et al.*, 2005).

The proper utilisation of acid tars in any application requires an in depth understanding of the chemical composition of acid tar. The composition of acid tar has been determined using gas chromatography-mass spectrometry (GC-MS) (Leonard *et al.*, 2010). Mass spectrometry detection simplifies the analysis by eliminating the need for standards to identify the organic groups. In another research organic compound content of spent sulphuric acid from benzol refining process was analysed using gas chromatography with flame ionisation detector (Chojhacki *et al.*, 2005). The use of Fourier transform infrared (FTIR) spectrometry with gas chromatography-mass spectrometry for characterisation of organics and coal by-products was common (Kempe *et al.*, 2005, Ku *et al.*, 2005, Leonard, *et al.*, 2010 and Semenova, *et al.*, 2007). FTIR is used to further confirm the presence of organic groups detected by GC-MS (Burtnaya, *et al.*, 2007 and Semenova *et al.*, 2007). GC was used to separate the organic components using oven temperatures adapted to each mixture (alkanes, branched alkanes, cycloalkanes and aromatics the temperature range was 28 to 2700C) (Kempe *et al.*, 2005). There are some investigations that just relied on FTIR for characterisation (Hu, *et al.*, 2012, Rincon, *et al.*, 2005 and Semenova *et al.*, 2012).

Generally the results obtained indicate that the percentages of organic oils in the acid tars are higher than corresponding sulphuric acid present in the samples (Frolov *et al.*, 1981, Leonard *et al.*, 2010, Chojnacki *et al.*, 2005, Kolmakov *et al.*, 2006, Frolov *et al.*, 1986, Nichol, 2000 and Aminov *et al.*, 1989). Fresh acid tar has a high percentage of sulphuric acid as compared to the pond acid tar. Percentage of sulphuric acid decreased with time in storage tanks where a solid film had formed on the surface of the acid tar (Frolov *et al.*, 1981). The differences in the percentages of the sulphuric acids may be explained by the fact that the acid is either being consumed by chemical reactions or evaporating into the air, thus there is need to find out what happens to the acid tar the minute it is produced to about a year in a monitored environment. The percentage of sulphuric acid varies from sample to sample.

In the characterisation of acid tars, two acid groups were observed as evidenced by the two plateaus obtained in the acid base titration, suggesting the presence of both weak acids and strong acids in the acid tar (Leonard *et al.*, 2010). In their further characterization they obtained methyl phenyl benzoic acid, naphthalenyl propenoic acid, phtalic acid, naphthalene acetic acid and phenathrene carboxylic acid.

Freshly produced acid tars consisted of mainly sulphuric acid, sulphonic acid and carboxylic acid (Frolov *et al.*, 1986). The pH of acid tar is variable and depends on the process by which the acid tar is generated, the amount and strength of the sulphuric acid used in the process and pre-treatment prior to disposal (Nancarrow *et al.*, 2001). Chojnacki *et al.*, (2005) characterized petrochemical sulphuric acid from benzol refining and observed that sulphuric acid was 63.8 mass%, organic was 3.547mass% and the inorganic impurities constituted the rest. Sulphuric acid content ranged from 29.5 to 41.1% for the acid tar from various oil treatments (Purings *et al.*, 1990). In studying the Hoole Bank Lagoon in Europe, it was observed that particles settled at the bottom of the lagoon, and the density of acid tars ranged from 1.2 to 1.4 g/ml and the viscosity varied with temperature (Nichol, 2000). In a similar research at the D.I. Mendelev Yaroslav in Russia, high ash content of approximately 6.5% and high viscosity for the bottom layer of acid tars (Tumanavskii *et al.*, 2004). The research aims at coming up with physical and chemical characteristics of the acid tars produced at Zimchem Refineries so as to deduce ways to utilize the waste.

MATERIALS AND METHODS

Materials

Acid tar samples

Three different acid tar samples from crude benzol processing were used. The sample denoted as TX acid tar was from the toluene and xylene purification with 98% sulphuric acid. This sample was brown and viscous. The second one was from benzene purification with oleum. This sample was black and less viscous than the first one and was assigned the name B acid tar. The third one was from the holding tank were the first two streams are collected into. This sample was dark brown and more viscous than the first two and was assigned the name HT acid tar. The three acid tars were very acidic such that the pH had to be measured after dilution with distilled water (1g/100ml).

Method

Viscosity and density

Viscosity was measured using NDJ-85 viscometer at 25°C. Density was measured using specific gravity bottle at 25°C.

Titration of acid tar

1g of acid tar was placed into 100ml volumetric flask and was diluted with distilled water to 100mls. 20 mls was withdrawn and titrated with 0.1M sodium hydroxide, after a Lasany L1-702 pH meter was immersed. pH was measured after every 2mls of base and a record was made. Plot of volume versus pH were made from which the volume at pH 7 was obtained. The concentration of the acid was then calculated.

Solubility of acid tar in various solvents

1g of acid tar was diluted with 100mls of two solvents (water and methanol). The mixture was filtered after agitation for 30 minutes. The percentage soluble was

obtained from the initial and final weight.
% of soluble = [(Initial grams – grams of sample on filter paper)/initial weight]x 100

Gas Chromatography – Mass Spectroscopy (GC-MS)

Liquid- liquid extraction

Acid tar was dissolved in water then filtered and the water soluble organics were extracted using pentane and hexane. The solid part was dissolved in methanol, dichloromethane and in toluene. The samples were also refluxed with toluene. Then the samples were analysed using GCMS-QP2010 Ultra Shimadzu. The solvents were used for baseline determination. The GC was operated in split mode ratio 2:1. Helium gas flowed at 47.1cm/sec and this was the carrier gas. The capillary column was 30m by 0.25mm and was programmed at 60ºC for 5 minutes and increased to 300ºC at 10ºC/minute, was held at 300ºC for 2 minutes, which resulted in 31 minutes total running time. The MS scanning was between 35 and 500m/z with an inlet line temperature of 250ºC, ion source temperature of 200ºC and electron ionization mode of 70eV. All this was done to identify the organic compounds found in the acid tar.

Fourier transform infrared spectroscopy (FTIR)

Samples were filtered and analysed using the Agilent 600 FTIR. The samples were analysed in solid form. The results were interpreted using (Coates, 2000).

RESULTS

Viscosity and density

Table 1 shows the viscosity of the acid tars and their density and the more viscous acid tar has a lowest density. HT acid tar has the highest viscosity and the lowest density. This can be because the acid tar is not fresh as the other two are and is a mixture of the two which might have resulted in chemical reaction. This means that the reaction that occur in the tank lead to production of polymers which are more resistant to motion. These polymers will be light since it has low density. TX and B acid tar has viscosities lower than HT acid tar, but their densities are higher than that of HT. TX acid tar is more viscous and denser than B acid tar. TX acid tar has more particles which are causing resistance to motion applied and these are also increasing the density.

Table 1: Viscosity and density of three acid tars.

Acid tars	Viscosity (mPa.s)	Density (g/ml)
B	28.6±0.7	1.519±0.002
TX	183±2.3	1.549±0.004
HT	63592	1.43±0.020

Titration of acid tar

Fig 1 shows that despite the difference in concentration of acid in the acid tar the two plateaus are showing in all the three acid tars just like Leonard et al., (2010) obtained using sodium hydroxide.

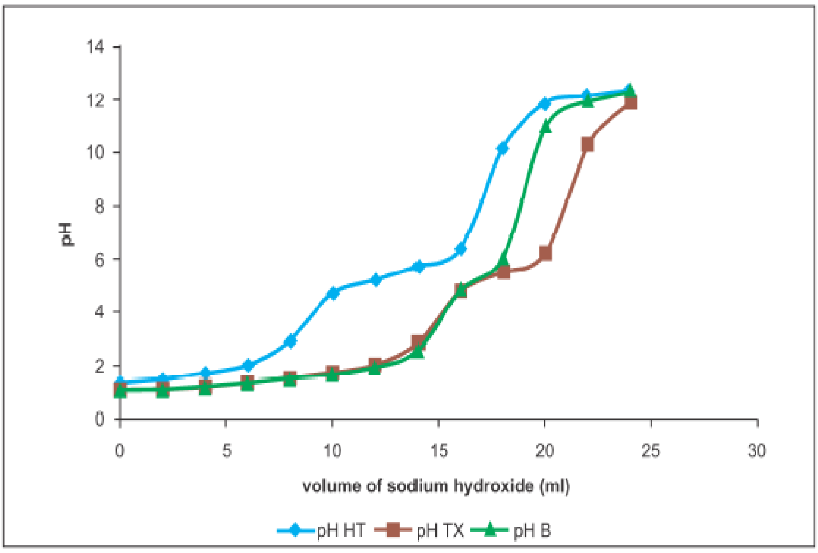

Figure 1: acid tar titration with sodium hydroxide of the three acid tars.

There is a strong possibility of the presence of both organic (weak) acids and inorganic (strong) acids in the acid tar since they behave differently with weak acids partially dissociating and strong acids completely dissociating. The first sharp raise at pH of 4 is as a result of complete neutralization of the strong acid (sulphuric acid). The second sharp raise is then from the weak organic acid which take time to dissociate due to the fact that equilibrium will have been reached between the acid and the dissociated ions. This is what causes the drag that is seen after the first sharp rise. The drag from the first plateau though is different with the HT having the longest followed by the Toluene and xylene then the Benzene one as the shortest. This then indicates that HT acid tar has more organic acids than the other two acid tars. TX acid tar has more organic acid than B acid tar as shown by the difference in the drag.

Table 2: Acidic concentration of acid tars

Acid tars	Acid concentration (mol/l)	Sulphuric acid concentration(mol/l)	% of sulphuric acid in sample	Organic acid concentration (mol/l)
B	9.5	7.5	24.2	2
TX	10.5	7.5	23.7	3
HT	8.5	4.5	15.4	4

The results in Table 3 show that the acid tar concentration from the Holding Tank is less than the one from benzene, toluene and xylene streams, this might be due to the vaporization of the acid into the atmosphere since the tank is open. The pH after dilution of 1g into 100mls of water is HT 1.34, B 1.02 and TX 1.10. The anomaly is the B acid tar; it should have a higher acid concentration than the TX since it has the lowest pH. Fig 1 and the results in Table 3 show that the B acid tar has the same concentration of sulphuric acid with TX acid tar this maybe due to the amount used in the purification since these are fresh acid tars. Thus the same amount of sulphuric acid is being used in the purification of benzene, toluene and xylene. The two acid tars differ in the concentration of organic acids. TX acid tar has more organic acid than B acid tar this can be because B acid tar has fewer organic compounds as compared to TX acid tar. The organic acid at this point can not be as a result of reaction between sulphuric acid and organic compounds in the two fresh acid tar. HT acid tar has the lowest concentration of sulphuric acid and the highest concentration organic acid. This acid tar is not fresh and the concentration of sulphuric acid is expected to be the same as the B and TX acid tar since it is a mixture of the two. But because of the fact that it is exposed to the atmosphere the concentration of sulphuric acid is low. The sulphuric acid has been consumed in the production of the organic acid (acidification of organic compounds) and some might have been lost into the atmosphere.

Solubility

Table 3 shows that a higher percentage of acid tar is soluble in water with benzene stream having the highest (94.31%), toluene and xylene stream having the second (73.44%) and Holding Tank having the least (70%).

Table 3: Acid tar solubility in %

Solvent	TX acid tar	B acid tar	HT acid tar
Water	73.44±0.21	94.31±1.18	70
Methanol	94.2±1.3	87.0±1.4	96.0±0.6

In the entire solubility test TX seems to be very similar or close to the HT acid tar. B acid tar is different from the other two; their solubility is increasing as you go from water to methanol while for B acid tar the increase in solubility is from methanol to water. This shows that b acid tar has less organic compounds than TX and HT acid tar.

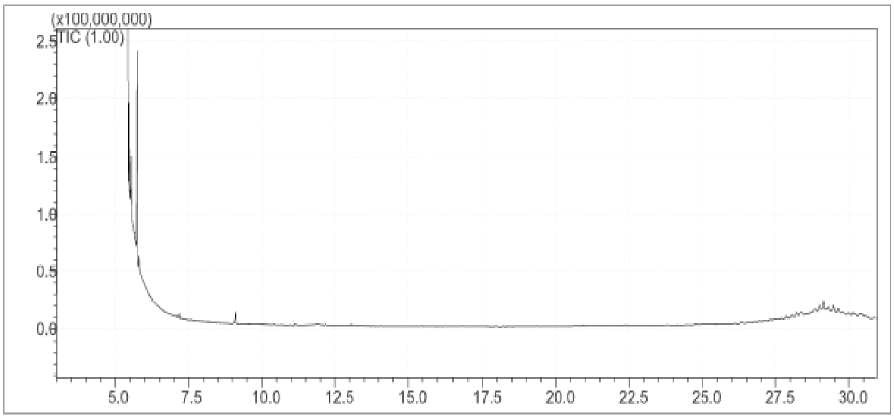

Figure 2: B acid tar chromatography

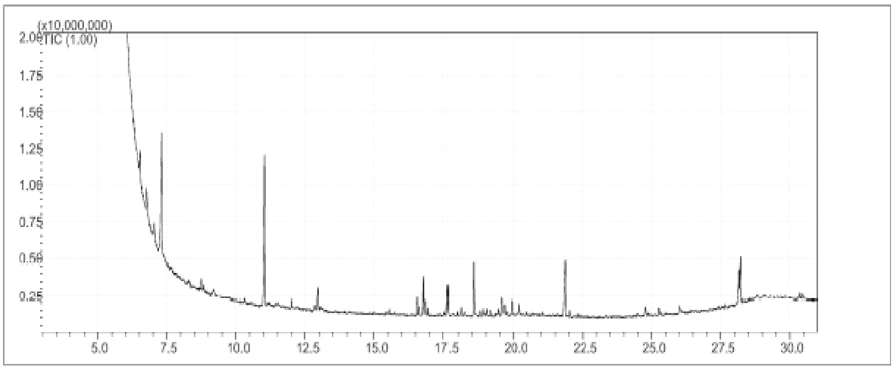

Fig 3: TX acid tar chromatography

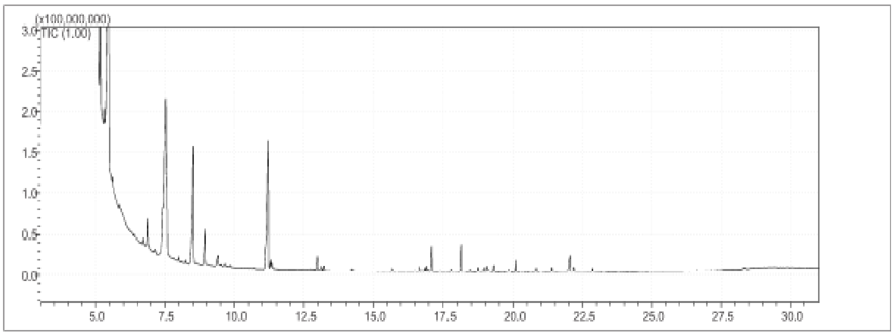

Figure 4: HT acid tar chromatography

Fig 2, Fig 3 and Fig 4 show the chromatograph of the three acid tars dissolved in toluene. The chromatograph can be used to estimate the difference in the amount of organic chemicals soluble in toluene of the three acid tars. B acid tar has the least with TX acid tar being average and HT acid tar having the most of organic compounds soluble in toluene. Compound two in Table 4 under the B acid tar column also was found in HT acid tar and is compound one in the HT acid tar column. TX acid tar had a compound that was also in HT, compound eight in the TX column and is compound twelve in the HT acid column. The two scenarios show that both B and TX acid tar represented in the HT acid tar. Table 4 shows that there are more organic compounds in HT acid tar than there are in B and TX acid tar.

Table 4: Organic compounds in the three acid tars.

	B acid tar	**TX acid tar**	**HT acid tar**
1.	3-[(5-Amino tetrazol-1-ylimino)-methyl]-phenol (Alcohol)	2-Phenyl-2H-1,2,3-benzotrial-5-amine (Amine)	3-Ethylidene-2-methyl-1-hexen-4-yne (Alkyne)
2.	3-Ethylidene-2-methyl-1-hexen-4-yne (Alkyne)	Phenyl carbamate (Amide)	Benzonitrile oxide (Nitro compound)
3.	Cyclooctyne (Alkyne)	1-Methylene-1H-indene (Alkene)	5-Nitro-2-(4-nitrobenzylidenamino)-toluene (Nitro compound)
4.	Isobutyl 2-ethoxy-1(2H)-quinolinecarboxylate(Ester/ether)	2-Chloro-2-norbornanecarboxylic acid (Carboxylic acid)	3-Methyl- phenol (Alcohol)
5.	2-Methoxy-2-(2-nitroethoxy) propane (Nitro compound)	3-(1-Methyl-1-phenylethyl)-thiophene (Sulphur compound)	N-[(Phenylmethoxy)carbonyl]-DL-alanine (Carboxylic acid)
6.	E-1, 5, 9 Decatriene (Alkene)	5-(1,1-dimethylethyl)-2,3-dihydro-3,3-dimethyl-1H-inden-1-one (Ketone)	N-(4-Nitrobenzylideno)-quinolin-6-amine (Nitro compound)
7.		1,4-Dimethyl-2-phenoxybenzene (Ether)	Benzenepropanal (Aldehyde)
8.		N-(2-Phenylethyl)-benzamide (Amide)	Benzocyclo heptatriene (Alkene)
9.		2-Benzoylamino-3-phenyl-N-(2-phenylethyl) propanamide (Amide)	1,2-dimethyl-4-(phenylmethyl)–benzene (Aromatic)
10.			1-(o-Ethylphenyl)-1-phenyl- ethane (Aromatic)
11.			2-(1,3-Dihydro-3,3-dimethyl-1-phenyl-3,4-benzofuran-1-yl) acetic acid (Carboxylic acid)
12.			N-(2-Phenylethyl)-benzamide (Amide)

Fourier transform infrared spectroscopy results

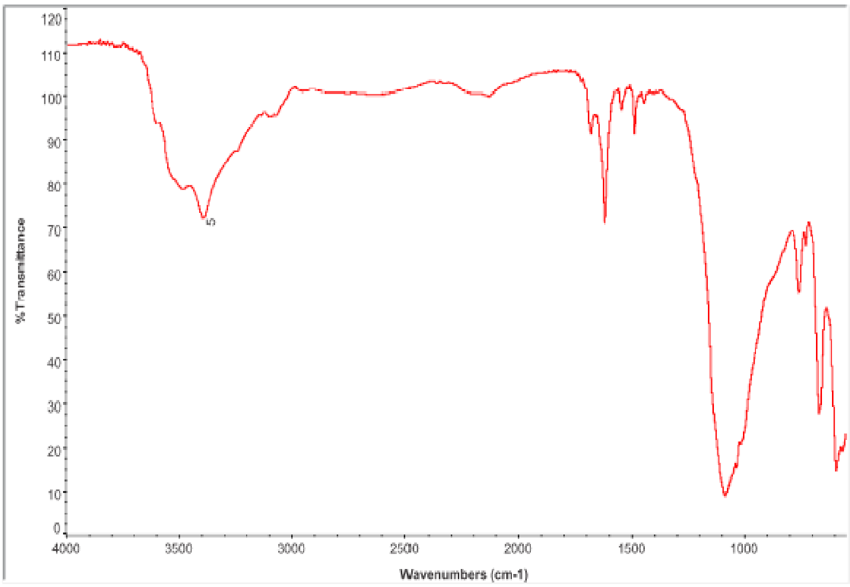

Figure 5: FTIR benzene acid tar

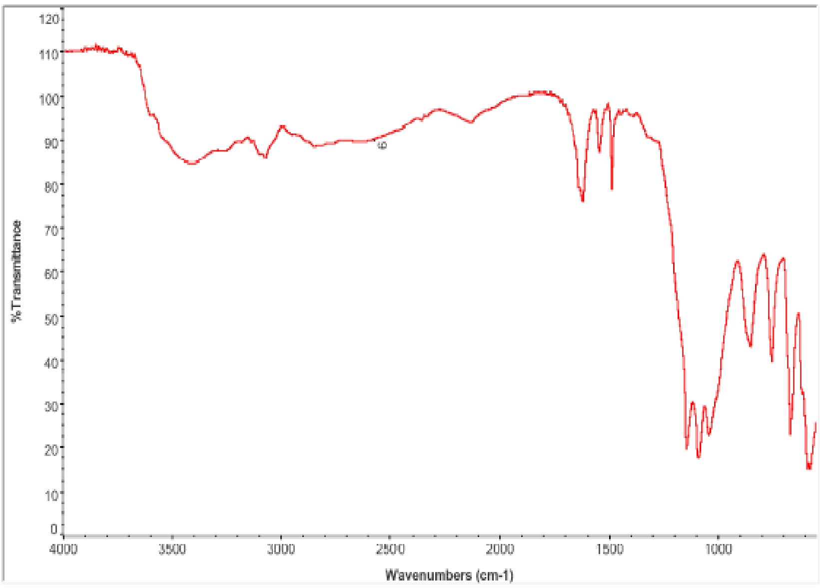

Figure 6: FTIR of Toluene and xylene acid tar

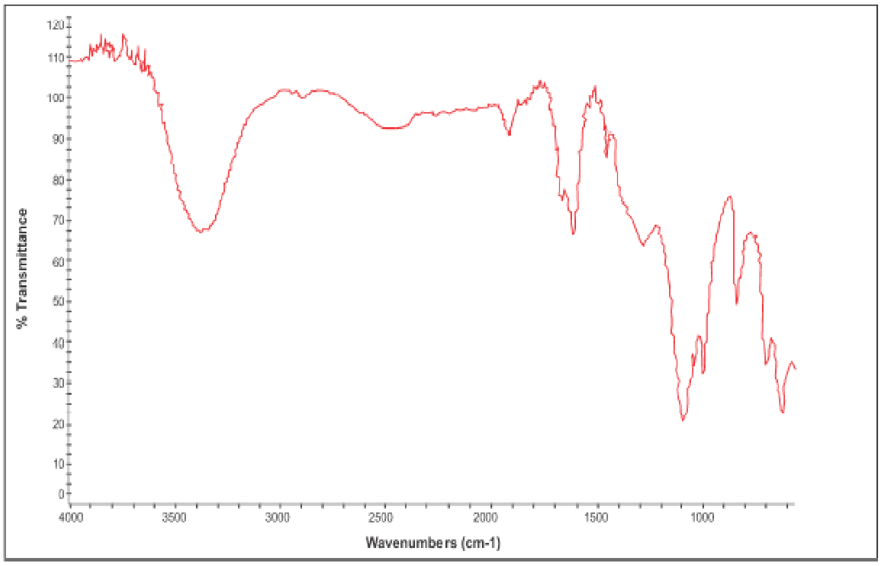

Figure 7: FTIR of holding tank acid tar

Fig 5, Fig 6 and Fig 7 show the spectrum for the three acid tars with common bands of wave number being observed in the three spectrums. The first band is at 1600cm-1 which is for alkenes thus the three acid tars have an alkene or –C=C-. HT acid tar has a more reduced transmittance as compared to B and TX acid tars at this wave number showing it has more alkenes than B and TX acid tars. This is also supported by the number of compounds (3) that have a -C=C- bond in Table 4 under the HT acid tar column. The other common band was 1100cm-1which is for alcohols and is found in all the three acid tars. TX however has no alcohol and Coates (2000) also indicated that it can be due to the presents of secondary amines. TX and HT have one at 1050cm-1 which is for amines. B acid tar had bands at 3510 and 3400cm-1, TX had a reduced transmittance at 3440 and HT at 3350cm-1 all representing the presence of nitro compounds in the three acid tars. For aromatic compounds B and TX acid tars had a ban

CONCLUSION

B acid tar has the lowest viscosity (28.6 ±0.7) and HT acid tar has the highest viscosity (63592). TX acid tar has the highest density (1,549±0.004) and HT acid tar has the lowest density (1.43±0.020). The fresh acid tars have sulphuric acid concentration that is higher than the HT acid tar and yet the HT has the highest concentration of organic acid. The sulphuric acid concentration for all the acid tars is less than 25% thus recovery of sulphuric acid will be difficult. The organics that are contributing to acidity in the three acid tars are not the same. B acid tar had an alcohol and an ester while TX had carboxylic acid and ketone and HT acid tars had two carboxylic acids, an alcohol, and an aldehyde. This then explains the drag that is after the neutralization of sulphuric acid in TX and HT acid tars, which is bigger than that of the B acid tar. B acid tar has the lowest number of organic compounds followed by TX then HT acid tar. d stretching from 3150-3000cm-1while the one for HT was at 1480cm-1.

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Characterization of acid tar using shear rate and temperature dependence of viscosity

Danha C*, Simbi D J and Kuipa P Kº

Chinhoyi University of Technology, Zimbabwe

[*cdanha@cut.ac.zw](mailto:cdanha@cut.ac.zw)

ºpkkuipa@cut.ac.zw

Introduction

Acid tar is formed as waste product from the purification of benzene, toluene and xylene with sulphuric acid. The process produces two streams which result in two types of acid tars, one derived from toluene and xylene purification with 98% sulphuric acid and the other from benzene purification with oleum. The fresh acid tars are fluid with a viscous appearance, the toluene and xylene acid tar appearing to be more viscous than benzene acid tar. In acid tar, being an organic fluid, there is an inclination towards making it a raw material for pavement binders. Thus the flow characteristic of the waste is needed to label it suitable or not suitable raw material for pavement binders. The objective of the study is to determine the rheological properties of the two acid tars using shear rate and temperature dependence of viscosity.

The viscosity of Newtonian liquids decreases with increase in temperature according to the Arrhenius relationship [1]. The investigation carried out by [2] on the rheological properties of acid tars from the pond; gave an activated energy value of 61.1 x 10^3J/mol using the plot of logarithm of the viscosity versus the reciprocal of temperature. The viscosity decreased with increase in temperature (range 20-80ºC).

Newtonian, power law, Bingham, Herschel-Bulkley and Casson behavior are some of the fluid behaviors that are based on the effect of shear rate on shear stress [3,4].

The viscosity and shear rate plot is known as the flow curve. If it is shown on a log-log plot it can help to differentiate between the Newtonian, shear thinning, shear thinning with yield stress and shear thickening [5]. Newtonian (since the viscosity is constant) gives a horizontal line at the value of the viscosity. Shear thinning shows a Newtonian behavior at the low shear rate values and at high shear rate values it exhibitsa decrease in viscosity as shear rate increases. In shear thinning with yield stress the material shows a decrease in viscosity with increase in shear rate at values above yield stress and at low shear rate there is a characteristic slope of -1. Materials that show this behavior are visco-plastics. Shear thickening is where the viscosity increases over a range of shear rate, this is not that common but found in concentrated colloidal dispersions and some polymer solutions.

2.0 Experimental methods

2.1 Materials

Two different acid tar samples from crude benzol processing were used. One was from the toluene and xylene purification with 98% sulphuric acid. The other one was from benzene purification with oleum.

2.2 Experimental technique

The two acid tars were measured using a NDJ-85 viscometer, which is a rotational viscometer. Benzene acid tar required the use of spindle 1 and toluene and xylene acid tar spindle 2 at 25^0C using a water bath.

The viscosity was determined at 293K to 333K at 10K intervals using a heating mental with temperature control probe [2]. a, b, k and r^2 were obtained using the Origin 2015 software by fitting the data to exponential equations and the equation with the r^2 closest to 1 was picked to represent the relationship of viscosity and temperature.

The shear stress in % torque was measured against shear rate in rounds per minute from 0.3 to 60 rpm at 298K [6]. The data was fit into the five models. The correlation coefficient and chi square were obtained using Origin 2015 software. The models used in the software were Newtonian, Power law, Bingham, Herschel-Bulkley and Casson.

Viscosity was measured against shear rate from 0.3 to 60 rpm to help determine the behavior of the acid tar using the flow curve on a log-log plot at 298K.

3.0 Results

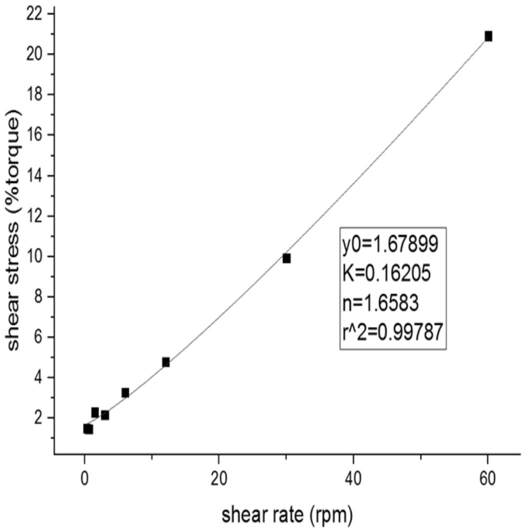
3.1 Temperature effect

Arrhenius equation did not fit the two acid tars point for temperature dependency. This then showed that the acid tars did not behave like Newtonian fluids.

3.2 Shear rate effect

3.2.1 Benzene acid tar

Herschel-Bulkley model has the best fit to the experimental data. The correlation coefficient of 0.99787 is closest to one than the other four and it has the smallest chi square value.



The relationship is $\tau = 1.67899 + 0.16205\dot{y}^{1.6583}$ as shown in Figure 1. The value of n is greater than one meaning the benzene acid tar exhibit shear thickening qualities [7]. This then explains why the benzene acid tar takes longer to reach zero viscosity as compared to toluene and xylene acid tar despite the fact that it has lower viscosity than toluene and xylene.

3.2.2 Toluene and xylene acid tar

The Bingham model has the best fit since the correlation coefficient is the one closest to one and the chi square value is the smallest as compared to the other four models. The relationship is $\tau = 1.44563 + 0.43535\dot{y}$ as shown by Figure 2. The plastic viscosity of toluene and xylene acid tar is 0.435 which is greater than that of benzene acid tar which is 0.162. The rheogram shows no curvature and is a typical Bingham model as shown in Figure 2.

Figure 3 shows the log-log plot of viscosity and shear rate which is similar to a shear thinning with yield stress curve shown by [5]. The two acid tars benzene, toluene and xylene acid tar are affected by the increase in the shear rate resulting in the acid tars thinning. However both of the curves do not have a slope that is -1 which would have confirmed that the fluids are shear thinning [5].

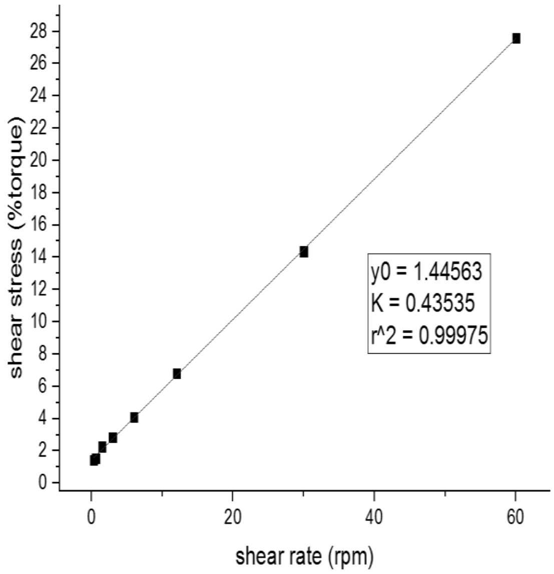


Figure 2: Bingham model graph for toluene and xylene acid tar

3.3 Viscosity shear rate relationship

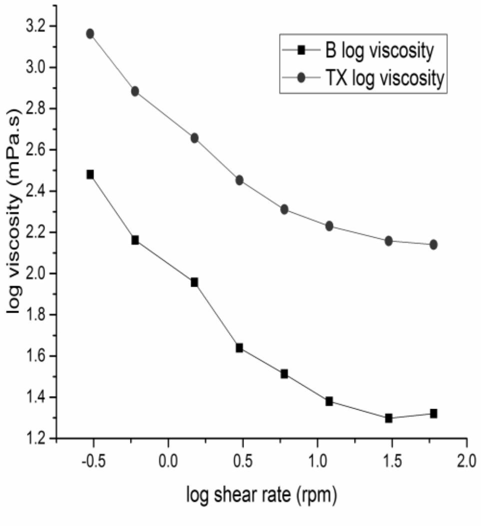


Figure3. Log of viscosity against log shear rate

Conclusion

Acid tar derived from toluene and xylene purification with 98% sulphuric acid is more viscous (183±2.3 mPa.s) than acid tar derived from benzene purification with oleum (28.6±0.7mPa.s). Toluene and xylene acid tar viscosity decreases with temperature increase at a much faster rate than benzene acid tar viscosity.

The Shear stress relationship with shear rate showed that benzene acid tar behaved more as a Herschel-Bulkley fluid and the toluene and xylene acid tar was more of a Bingham fluid. The viscosity shear rate log-log plot supports the shear stress shear rate relationship results that the acid tars are visco-plastics. Benzene acid tar (plastic viscosity of 0.162) is less visco-plastic than toluene and xylene acid tar (plastic viscosity of 0.435). Toluene and xylene acid tar would need less material to increase its plasticity and the viscosity as compared to benzene acid tar.

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