Improvement of Nigerian Crude Residue

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Abstract

This research investigates how the properties of the Nigerian crude residue can be improved on to enhance its local usage. Chemical treatment was carried out on Nigerian crude residue and its rheological properties were tested. The physiochemical properties- specific gravity cum viscosity measured after the treatment gave 12.44% improvement in specific gravity and 17.92 times improvement in viscosity of untreated residue when oxidation technique was used while sulphurisation gave 9.5% improvement in specific gravity and kinematic viscosity was 15.24 times better than that of untreated bitumen. Blending and addition of polymer also improves the physiochemical properties considerably depending on the properties of blending additive used. With the application of this treatment technique, the properties of the Nigerian crude residue have been considerably improved and it was found to be suitable for construction purposes cum other uses.

Keywords

Crude Residue, Chemical Treatment, Rheological Properties

Introduction

Bitumen is a fossil fuel, which occurs naturally on its own or as a by-product of vacuum distillation of crude oil. It is also referred to as a viscous liquid, or a solid consisting essentially of hydrocarbons and their derivatives, and is soluble in carbon disulphide, substantially non-volatile and softens gradually when heated. It is blackish or brownish in colour and possesses water proofing and adhesive properties (Hobson and Pohl, 1973). Road pavement is the principal use of bitumen and it takes about 80% of the total bitumen consumption. The pitch lake on the island of Trinidad was the first large commercial source discovered but natural sources have since declined in importance, as vacuum distillation of crude oil is now the major source for the production of bitumen. This gives a cheaper and more readily available source. Moreover, the existing natural deposit alone cannot cater for the required existing high demand because of its numerous uses and the expected rise in rate of consumption as development progresses (Adegoke, 1988).

Bitumen properties are greatly influenced by the characteristics of its components, particularly the structure of asphaltene and the asphaltene/resin ratio of the bitumen sample. These, in turn, depend mainly on the nature of crude oil, constituents of the starting raw materials and the method of production. The properties of crude oils that indicate their suitability for bitumen manufacture are high weight percent of carbon residue, high specific gravity, sulphur content of more than 5 per cent weight, low wax content and high asphaltene content. Generally, Nigerian crude do not meet these characteristics; hence, bitumen from them do not meet international specifications (Obiaga, 1982). It has also been shown that the main limitation of the bitumen obtained by blowing Nigerian crude is its high susceptibility to temperature rise, thereby making it unsuitable for all weather road paving (Abraham, 1960).

Bitumen will continue to play an increasing role in our national development by way of its uses in the building industry and maintaining roads for easier and better communication, for construction of new airport runways and for other numerous uses. A large proportion of the bitumen consumed in our country is imported; this represents a great drain on our foreign reserve for a country that is a member of Organization of Petroleum Exporting Countries (OPEC). Nigeria therefore is faced with the following alternatives:(i) To continue to import her bitumen requirements;(ii) To import the heavier, more asphaltenic crude to feed her refineries in order to make bitumen, and, (iii) To obtain bitumen from her local crude.

None of the first two alternatives is as politically and economically desirable as the third alternative. These therefore call for the improvement of properties of bitumen gotten from Nigerian crude to stop dependence on importation and conserve her hard-earned foreign reserves. This improvement of properties also applies to all bitumen from medium, light, or low-sulphured crude, anywhere in the world.

Origin of Petroleum

Bitumen is obtained either from natural deposits, or as residue from the distillation of petroleum. Natural bitumen (also called Brea), is believed to be formed during an early stage in the breakdown of organic marine deposits into petroleum (Hobson and Pohl, 1973). Crude oil is a complex mixture of hydrocarbons that occur in the earth crust in liquid form. The term also includes natural gas and the viscous or solid form known as bitumen. The earlier hypotheses on the origin of petroleum postulated its generation from inorganic materials such as water acting on metallic carbides, or water and carbon dioxide interacting with alkali or alkaline earth metals (Kobe and Mcketta, 1962). Alternatively, because of the detection of hydrocarbon material in some meteorites and in the atmospheres of certain planets, suggestions were made that hydrocarbons present in the primeval earth gave rise to oil accumulations. Another hypothesis made was that petroleum is one of the products of volcanism (Abraham, 1960). Some arguments concerned the nature of the source material, whether it was animal or vegetable or both, while others were about the nature of the transforming agent, heat, bacteria, radioactivity and low temperature catalysis.

Animal and vegetable matter contains several main types of compounds, fats, protein and carbohydrates, the proportions and types varying with the organism. Fats are nearest in composition to hydrocarbons and there has been a tendency to consider them to be of prime importance in oil formation.

The complete breakdown by aerobic bacteria, and the less complete breakdown by anaerobic bacteria of organic substances might on the general grounds result in the formation of petroleum or substance closely akin to petroleum (Grudnikov, Ippolitov, Grudnikova, 2004). Moreover, recent investigations have shown that mineral catalysts and water affect reactions energized by heat or radioactivity involving crude oil or their possible antecedents.

Conclusively, should all these observations be generally applicable, it is reasonable to infer that some changes take place in the sediments beneath the earth crust. Circumstantial and experimental evidence suggests that the modest increase in temperature may play the principal role in causing the changes.

Nigerian Crude and Its Classification

Crude oil varies widely in appearance and composition from one geographical area to another; colour varies from yellowish-brown free flowing liquid to a black viscous semi-solid.Their differences are due to the different proportions of the various molecular types and sizes of hydrocarbon they contain. The classification of crude is based on whether it is paraffinic, asphaltic, or mixed based crude:

- Paraffin based crude: These contain paraffin wax but little or no asphaltic hydrocarbons. They consist mainly of paraffinic hydrocarbons, and, atmospheric distillation usually gives good yields of paraffin wax and high-grade lubricating oils. The gas oil fraction of this crude has low anti-knocking quality, kerosene of good burning characteristics and high grade lubricating oils.
- Asphaltic base crude: These contain little or no paraffin wax but asphaltic matter is usually present in large proportions. They yield lubricating oils that are more viscosity sensitive to temperature than those from paraffin base crude. It is usually dark, very viscous and gives a high yield of gasoline and kerosene of poor burning characteristics (Amu, 1970).
- Mixed base crude: They contain substantial amount of both paraffin wax and asphaltic matter with a proportion of aromatic hydrocarbons (Nelson, 1958). Another method used in classification is the API Gravity and specific gravity.

Characteristics of Nigerian Crude versus Suitable Crude for Bitumen Manufacture

Although it is not possible to predict with 100 percent accuracy whether or not particular crude will produce specification bitumen without actually separating the bitumen from the crude and running the tests, however, the properties of crude oils that normally yield high quality bitumen are compared with that of Nigerian crude as follows:

Table 1. Comparison between Nigeria and Foreign crude

Properties	Nigerian crude	Foreign crude
Specific gravity	High, above 1.0 / Low API of less than 25 degree	Low, below 1.0 / High API of between 35-40 degree
Weight percent of coradson carbon residue	High between 2-10 percent	Low, less than 3 percent
Weight percent of sulphur content	High, above 5 percent	Low, less than 1 percent
Weight percent of asphaltene content	High, above 5 percent	Low
Wax content	Low, less than 2 percent	High

Chemical Composition of Bitumen

Bitumen is chemically complex than the other petroleum fractions because of its higher molecular weight and the presence of large percentages of elements other than carbon and hydrogen. It has molecular weight of over 400.

The greater numbers of high-molecular weight isomers that occur make it exceedingly difficult to chemically define bitumen (Kobe and Mcketta, 1962). They worked on the constitution of bitumen and regard bitumen as a protected “lyophobe sol” the asphalt constituents was classified into: petrolenes (maltenes), asphaltous acids, anhydride resins, asphaltenes, carbenes, and pyrobitumens.

Asphaltenes, resins and oily constitutents are combined as a colloidal system, in which the asphaltenes are dispersed in the oily constituents and the solution is stabilized by the resin fraction which acts as a protective colloid (Abraham, 1960). Overall, bitumen consists of Asphaltenes, Maltenes and Carbenes (petrolenes), and Carboids (Adegoke, 1988).

The properties of the bitumen includes rheological properties in which variations in the amount and nature of the asphaltenes give rise to three broad groups viz: Newtonian (or almost Newtonian), Slightly elastic (non-thizotropic), and Strongly elastic (thixotropic) bitumens of PI* less than -2, between -2 and +2,and PI* greater than +2 respectively (Hobson,1973). Other properties include:(a) penetration, (b) Softening point (Allison,1975), (c) Viscosity, (d) Specific Gravity,(e)Flash point, and (f)Durability. PI* is the productive index.

Process involved in the improvement of bitumen property

This was done to be able to upgrade bitumen from the Nigerian crude to an acceptable standard. The method of improvement includes:

(i) Oxidation (Blowing)

The reaction is of the form:

$$C_xH_y + ½O_2 \rightarrow C_xH_{y-2} + H_2O$$

where x and y are integers such that C_xH_y represents a high molecular weight molecule of bitumen (Goppel and Knoteous, 1954).

(ii) Blending

The blending of “normal” grades of similar type is accurately represented by a linear relationship between the log penetration or the softening point of the blend and its components. Example of such relationship is:

$$\text{Log } P = a \log A + (1 – a) \log B$$

where P is the blend penetration required, a is the proportion of bitumen of penetration A, and (1-a) is the proportion of bitumen of penetration B.

(iii) Sulphurisation

This is a sulphur addition process in which yellow sulphur powder is added to a continuously heated residue. The process is maintained at about 240°C with continuous stirring. Hydrogen sulphide is a by-product of the reaction.

Experimental Technique

The experimental work involves obtaining the crude residue; oxidation (blowing) of distillation residue, sulphurisation of crude residue and blending. During the oxidation process, 2115g of sample residue from vacuum distillation was measured into the vessel and heated to 260°C on the electromantle. The flask was covered with a bored rubber cork, which has compressed air passed through it at the rate of $18.33 \cdot 10^{-6}$-$35 \cdot 10^{-6} m^3$/sec. (that is, 2.1 to 1.1

litter/min) into the preheated sample. This was run for about 8.167hours. Sulphurisation was carried out at atmospheric pressure, by adding 8g of sulphur to a batch of 100g of petroleum crude residue. The measured crude residue and sulphur were mixed vigorously in a flask containing boiling chips. The reaction took place in fume box and in a well-ventilated environment. The reaction mixture was heated up quickly to about 260°C and kept at this temperature for two hours. The heat was then turned off. The content of the flask was allowed to cool and was decanted. In the case of blending, it involves the blending of Nigerian petroleum crude residue with foreign petroleum residue and/or the blending of the petroleum residue with the naturally occurring bitumen. The required amount of each upgraded residue sample was measured. Heating was done at 45^{o}C and at constant stirring rate for 30 minutes.

Specific Gravity Determination

The washed empty specific gravity bottle was dried in the oven and weighed (A_g). This was then filled with water and reweighed (B_g). The specific gravity bottle was emptied, dried and filled with sample before weighing and recording the weight of bottle and sample (C_g). The ambient temperature was recorded. The specific gravity was calculated thus:

Specific gravity (s.g) = Weight of sample/Weight of an equal volume of water

$$s.g = C_g\text{-}A_g/B_g\text{-}A_g$$

Viscosity determination

The viscosities of the samples were determined using viscometer at temperatures of 40°C and 100°C. The temperature of the sample was increased before pouring it into the arm of the viscometer. The stopwatch was started when the sample reached the first timing mark and stopped when it reached the second mark. The various times were recorded and the average time taken. The kinematic viscosity of the crude oil sample using this method is obtained using "gravity-flow" of the sample and the kinematic viscosity is given by:

$$\nu = Kt$$

where ν = kinematic viscosity, K = calibration constant, and t = average time of flow.

The result can be converted to absolute viscosity by multiplying by the density of the crude, which is determined using the density bottle.

Results

The following results were obtained for the various treatment processes carried out on the crude residue.

Table 2. Variation of experimental parameters during oxidation

Reaction Time (min)	Temperature (°C)	Rate of air Flow (l/min)	Weight of sample (g)	Properties	
				Softening point	Penetration
0	260	2.1	2115	_	_
300	260	1.8	1845	49.4	123
360	260	1.6	1625	50.1	103
400	260	1.4	1390	50.1	88
490	260	1.1	1085	50.2	61

Table 3. Oxidation results

Properties	Before Oxidation	After Oxidation
Kinematic viscosity (100°C)	162.44	2911.52
Specific gravity (25°C)	0.9137	1.0274
Flash point (C.O.C, °C)	280	-

Table 4.Sulphurisation results

Properties	Before sulphurisation	After sulphurisation
Specific gravity	0.9137	1.0009
Kinematic viscosity	162.44	2475.72

Table 5. Blending results before improvement

Properties	Properties of foreign residue before blending	Properties of Nigerian Residue before blending
Specific gravity (25°C)	1.0055	0.9137
Kinematic viscosity (100°C)	442.23	162.44
Flash point (C.O.C, °C)	306	280
Carbon residue (C.C.R)	16.57	10.17

Table 6. Results after blending

Properties	80/20 Blend	90/10 Blend
Specific gravity (25°C)	0.9991	1.0013
Kinematic viscosity (100°C)	386.272	414.251
Flash point (C.O.C, °C)	290	300.8
Carbon residue (C.C.R)	15.29	15.93

Discussions

It was established from the tests carried out that Nigerian crude are either light or medium according to the API method of classification and residue from distillation are general of poor bitumen qualities. On experimenting with each of the improvement methods i.e. oxidation, sulphurisation and blending it was shown in the results that each of this methods has improved the properties of the crude oil residue (bitumen) considerably well as indicated by the improvement in specific gravity and viscosity among other physiochemical properties. Oxidation gave a12.44% improvement in specific gravity and 17.92 times improvement in viscosity of untreated residue (bitumen) while sulphurisation gave 9.5% improvement in specific gravity and improvement in kinematic viscosity was 15.24 times better than that of untreated bitumen. The tables of results showed that the properties of crude that indicate their suitability for bitumen production such as high weight percent of carbon residue, high specific gravity, sulphur content of more than 5 percent weight, low wax content, and high asphaltene content were improved using the treatment processes. Nigerian crude was made suitable for bitumen production when the results obtained were compared with the property listed in table1, which indicates the non-suitability of the crude.

Conclusions

The property of Nigerian crude residue (bitumen) was investigated with the purpose of establishing its suitability for local consumption that has wide and numerous applications.The research work has shown that despite the fact that Nigerian crude residue is of poor bituminious residue it is possible to produce asphaltic material with similar properties to that required for asphalts used industrially. This will reduce the need for importation of more asphaltic crude. The use of compressed air, sulphur and rubber shows that the process is not too expensive in terms of required raw materials. It is therefore concluded that oxidation, sulphurisation and blending caused improvement in the properties of bitumen, even if they are obtained from crude unsuitable for bitumen manufacture like the Nigerian crude.

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