IJBPAS, February, 2017, 6(2): 341-348

ISSN: 2277–4998

International Journal of Biology, Pharmacy and Allied Sciences (IJBPAS)

'A Bridge Between Laboratory and Reader'

www.ijbpas.com

DESULPHURIZATION POTENTIALS OF ACTIVATED CARBON ON KEROSENE

Oti Wilberforce J.O[1] and Eze Ilochi Nkechinyere Olivia[2]

[1]Ebonyi State University, Abakaliki, Ebonyi State, Nigeria

[2]Evangel University Akaeze, Ebonyi State, Nigeria

Received 12th Sept. 2016; Revised 20th Oct. 2016; Accepted 20th Dec. 2016; Available online 10th Feb. 2017

ABSTRACT

The ability of activated carbon prepared from locally sourced hardwood to reduce sulphur content in dual purpose kerosene (DPK)obtained from NNPC Mega Filling Station in Abakaliki, Ebonyi State. The concentration of sulphur in raw and desulphurized kerosene was determined using UV-Vis spectrophotometer (Genesys 1OS, Thermo-Scientific) at 460 nm. Results obtained showed that the concentration of sulphur in kerosene samples before and after desulphurization were 1.502 and 1.317 wt % respectively. The sulphur depletion was 0.185 wt % which was equivalent to 12.32 % desulpurization. This implied that the activated carbon prepared was able to remove a significant percentage of the original amount of sulphur in the raw kerosene, thus showing that activated carbon has the ability to extract sulphur from dual purpose kerosene (DPK) and can be potentially used in this regard.

Keywords: Kerosene, Acivated Carbon, Desulpurization, UV-Vis spectrophotometer, Petroleum

INTRODUCTION:

Petroleum is a non-renewable fossil fuel whose refined products are of high demand. Many countries such as Nigeria, Russia, Kuwait etc depend on oil as a major means of foreign exchange. Petroleum is a mixture made up of hundreds to thousands of hydrocarbons and non-hydrocarbons. The hydrocarbons present in petroleum may be grouped into three categories, namely: alkanes or paraffins, cycloalkanes or naphthenes, and aromatic hydrocarbons. About 90% by weight of the compounds present in petroleum are hydrocarbons (Anwar et al, 1990). Non-hydrocarbon components of petroleum exists as compounds of sulpur, nitrogen, oxygen and organometallic of mainly Ni and V. Analyses of samples of petroleum from different parts of the world show that the elemental composition of petroleum varies over the narrow range: 82-87% carbon, 11-16% hydrogen, 0-4% sulphur, 0-7% oxygen plus nitrogen, and a few parts per million metals (nickel, vanadium, etc). All the compounds in petroleum may be grouped into hydrocarbons and non-hydrocarbons(Jones, 1975).

One of the major products of petroleum refinery is kerosene which is a thin clear liquid containing mixture of carbon chains that typically contain 6 and 16 carbon atom per molecule and has a density of 0.78-0.81 g/cm^3 and flash point of 38 ^{o}C (Pillon, 2007). Kerosene is commonly used for cooking and lightening especially in rural areas, where electricity supply is not available or too costly. It is also used to power jet engines of aircrafts and some rocket engines. Kerosene can be used as both a solvent and lubricant. It is able to remove other petroleum products, such as grease with less risk of combustion when compared to using gasoline. Kerosene can also be used as a cooling agent in metal production and treatment. It is an effective pesticide, capable of killing insects, notably bed bags and head lice (Nwadinigwe and Nwaorgu,1999).

Petroleum from different locations vary considerably in their sulphur content, from less than 0.1% up to about 7% by weight sulphur. These percentage ranges refer to sulphur atoms which are chemically bonded to carbon chains and rings, and they do not include gaseous hydrogen sulphide (H_2S) which is associated with some crude oils within the reservoir. Some of such sulphur compounds include mercaptans or thiols (RSH), thiophenes or thiofurans (C_4H_4S), thiophenols (C_6H_5SH) and carbon disulphide (CS_2). Crude oil sample that have sulphur contents less than 0.5 % is classified as sweet crude while those containing greater than 0.5% are Sour crude (Udeme and Etim, 2012). Most of the Nigeria crude oils are classified as sweet since the sulphur content is less than 0.5% (Oyekunle, Famakin, 2004). The presence of sulphur in petroleum (crude oil fractions or product) poses great challenges because sulphur compounds are always objectionable. Sulphur-containing compounds are notorious in petroleum refining as they cause catalyst poisoning or inactivation, corrosion of refinery process equipment, and atmospheric pollution during combustion. Hence processes for desulphurization of petroleum fractions are very important in petroleum refineries (Speight, 1999).

Desulphurization of petroleum and its products is the process of removal of sulphur and its compound from petroleum and its products such as gasoline, kerosene and diesel (Gawande. and Kaware, 2014). Many methods have been used to address the problems associated with sulphur and its compounds in petroleum products but most of these methods previously used have a lot of limitations ranging from severe operating condition, high hydrogen consumption, expensiveness of catalyst used in the process, inability of some of those methods to remove sulphur to reasonable amount. In the past, many techniques have been employed in removing sulphur from petroleum and its products. This includes Doctor's process which involves oxidation of thiols to sulphides and disulphides. The process is considered a primitive technique, because it only eliminates the corrosion effects and obnoxious odour of elemental sulphur but not the sulphur compound itself. In other words, Doctor's process only deodorizes the petroleum but do not remove the sulphur (Knudsen, *et al.,* 1999). Later, hydro-desulphurization was employed in sweetening of petroleum. In this process, hydrogen is used to remove sulphur but it is a costly process due to cost of hydrogen and high pressure requirement of the process (Kwak *et al.,* 2000). Therefore, more economical and effective methods are being sought throughout the world as alternative means of achieving Sulphur-free fuels. These new methods include desulphurization using ionic solutions which does not involve any hydrogen consumption but the process is limited to desulphurization of lighter petroleum products (Knudsen *et al.,* 1988; Pillon, 2007). Petroleum products such as kerosene are not completely free of sulphur. Hence this study is an attempted to investigate the potential of using activated carbon prepared from locally sourced hardwood to desulpurize petroleum products specifically kerosene.

MATERIALS AND METHOD

Preparation of Activated Carbon: The wood was cut it into pieces, washed and dried. There after the wood particles were soaked with concentrated sulpuric acid solution for a period of 24 hours. Excess of the concentrated sulphuric acid solution was decanted and the wood particles were oven dried, after which it was carbonized in the muffle furnace at 150°C – 180°C. The ash (charcoal) was removed from the furnace, cooled and crushed into powdered form to maximize surface area for mass transfer and minimize agitation for suspension. Some phosphoric acid solution was added to completely soak the charcoal in powdered form for 24 hours. The acid solution was thereafter decanted and washed with distilled water to remove every traces of acid. The resultant slurry obtained was dried and used as the activated charcoal.

Collection of Kerosene Sample: One litre of kerosene sample was purchased from NNPC mega filling station in Abakaliki Ebonyi State.

Extraction of Sulphur from the Kerosene Sample: The process used in this work was adapted from (Tim, 2009) and (Gawande. and Kaware, 2014). 20 ml of raw kerosene was poured into the beaker containing 1g of activated carbon and allowed for 26 minutes to enable adsorption to take place. After which, a filter paper with funnel was used to separate the kerosene from activated carbon. The absorbance of the filtrate and the untreated kerosene sample and the calibration standards were measured at 460 nm using a UV-vis spectrophotometer.

Preparation of Calibration Standard: 10g of Na_2S was dissolved in small quality of distilled water and was made up to the mark with distilled water in a standard 100 ml volumetric flask to prepare 10 % w/v Na_2S solution. This stock solution contained 0.53 % sulphide. Serial dilution was made from the stock solution to prepare 1 %, 2 %, 3 %, 4 % and 5 %. A calibration curve was obtained by plotting the absorbance measured at 460 nm against the concentrations of the various calibration standards.

Determination of Sulphur Content in the Raw Kerosene and Desulphurized kerosene: Prior to measuring the absorbance of the raw and desulphurized kerosene, the absorbance of the various concentrations (1 %, 2 %, 3 %, 4 % and 5 %) of the calibration standards containing 10 % w/v Na_2S with minimum assay 99.6 % were measured to establish a standard calibration curve. The concentration of sulphur in the raw kerosene sample (before desulphurization) and the desulphurized sample were determined by measuring their absorbance at 460 nm using UV -visible spectrophotometer. The reason why 460 nm wavelengths was used was to minimize the interferences of other hydrocarbons and also because most sulphur compounds in petroleum products occur bonded to carbon (C-S) and sulphur in this form absorbs maximally at 460 nm (Verma, 2008). Distilled water was used as blank.

RESULTS

Tables 1, 2 and 3present respectively the results of the absorbance measurement from the calibration standards; the absorbance values of raw and desulphurized kerosene and Actual concentration of sulphur in raw and desulphurized kerosene (wt %). Figure 1 is a calibration curve of the standard sodium sulphide solution from where the actual sulphur concentrations in the raw and desulphurized kerosene samples were obtained while Figure 2 shows Sulphur content of kerosene before and after desulphurization.

Table 1: Mean of replicate absorbance of the calibration standards

Calibration standards (%w/v Na_2S)	Absorbance values at 460 nm		Mean
	1	2	
Blank	0.000	0.000	0.000
1	0.102	0.103	0.102.5
2	0.103	0.104	0.103.5
3	0.122	0.123	0.122.5
4	0.132	0.133	0.132.5
5	0.156	0.157	0.156.5

Table 2: Mean of triplicate absorbance of the raw and desulphurized kerosene

Samples	Absorbance values at 460 nm			Mean
	1	2	3	
Raw Kerosene	0.155	0.154	0.153	0.154
Desulphurized Kerosene	0.134	0.135	0.136	0.135

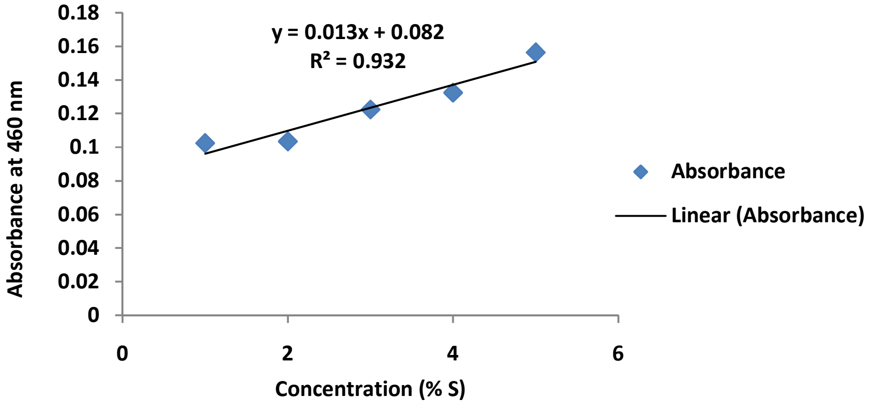

Fig. 1: Calibration curve of standard sodium sulphide solutions at 460 nm

Calculation: Sulphur content (wt %) was calculated using a factor obtained from the calibration curve as shown in Fig 1 above.

Sulphur content $= \frac{1}{0.1025} \times M_A$ **where M_A is the mean absorbance of each sample**

Table 3: Actual concentration of sulphur in raw and desulphurized kerosene (wt %)

Samples	Mean Absorbance (M_A)	Concentration of Sulphur (wt %)
Raw Kerosene	0.154	1.502
Desulphurized Kerosene	0.135	1.317

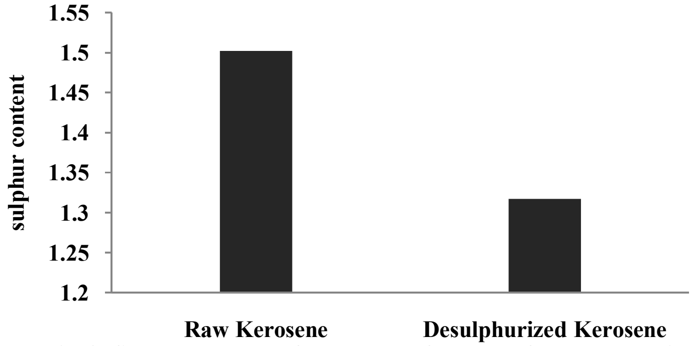

Fig. 2: Sulphur content of kerosene before and after desulphurization

Sulphur depletion = Sulphur in raw kerosene – sulphur in desulphurized kerosene

$$= 1.502 - 1.317$$

$$= 0.185 \text{ wt } \%$$

$$\text{\% Desulphurization} = \frac{\text{Sulphur depletion}}{\text{Sulphur content of raw kerosene}} \times 100\,\%$$

$$= \frac{0.185}{1.502} \times 100\,\%$$

$$= 12.32\ \%$$

DISCUSSION

The results obtained showed that the concentration of sulphur in the raw kerosene sample was 1.504 wt % while the sulphur content of the desulphurized kerosene was 1.317 wt % which means that the amount of sulphur in the raw kerosene was reduced by an amount equivalent to 0.185 wt %, which is 12.32 % reduction. The percentage desulphurization (12.32 %) are attributed to the properties such as surface area and nature of active sites of the activated carbon used which is a function of the way the activated carbon was prepared. The amount of sulphur extracted (sulphur depletion) by the activated carbon in this work represents all forms of sulphur bonded to carbon (C-S) in the kerosene sample which has their λmax at 460 nm (Valentina and Lina, 2013). These forms of carbon many classes of sulpur-containing compounds in petroleum include thiols (mercaptans); thia alkanes (sulphides); dithia alkanes (disulphides); thiophanes; thiophenes; benzothiophenes; dibenzothiophenes; sulphones; sulphonates, sulphates and sulphoxides. (Rasina *et al.,* 1988).

CONCLUSION

The results obtained in this study showed that activated carbon has the ability to adsorbed (extract) sulphur from kerosene and it has potential to do same for other petroleum products. However, the quantity of sulphur adsorbed depended on the relative surface interaction between activated carbon and the species of sulphur compounds which is a function of inherent properties of the activated carbon such as surface area and nature of active sites which further depends on the efficiency and method of its preparation. The materials for preparation of activated carbon are cheap and available and the method of preparation is relatively easy. Hence desulphurizing of petroleum or its products using activated carbon should be highly encouraged.

ACKNOWLEDGEMENT:

The authors wish to acknowledge Uguru Maureen who contributed immensely in the analysis of the samples.

REFERENCES

[1] Anwar, J., Nahid, F., and Kirmani, Z.U., (1990,) Determination of Trace Metals in Crude Oil Samples by Atomic Absorption Spectroscopy Using a Mixed Solvent System, *J. Chem. Soc. of Pak.*, Vol. 12, No. 3, pp. 249-52.

[2] Gawande, R. P. and Kaware P. J. (2014). A Review on Desulphurization of Liquid Fuel by Adsorption. *International Journal of Science and Research,* 3(7):2255-2259.

[3] Jones, P (1975) Trace Metals and Other Elements in Crude Oils, A Literature Study," BP Research Centre Sunbury, U.K.

[4] Knudsen, K. G; Cooper, B. H. and Topsoe, H. (1999). Catalyst and process technology for ultra low sulphur diesel. *Applied Catalysis A*, 189: 205–215

[5] Kwak, C; Lee, J. Bae, J. S. Choi, K and Moon, S. H. (2000). Hydrodesulphurization of DBT, 4-MDBT and 4, 6-DMDBT on fluorinated CoMoS/Al_2O_3 catalysts, *A pplied Catalysis A*, 200 (1): 233– 242.

[6] Madu, A. N; Njoku, P.C and Iwuoha, G. A. (2011) Extent of heavy metals in oil samples in escravous, Abiteye and Malu Platforms in Delta State Nigeria, *Learning Publics Journal of Agriculture and Environmental Studies* Vol. 2 (2).41- 44.

[7] Nwadinigwe C.A. and Nwaorgu O.N. (1999) Metal Contaminants in some Nigerian Well-head Crude Comparative Analysis *J. Chem Soc.* Nigeria 24, 118-121.

[8] Oyekuule, L. O. and Famakin, O. A. (2004). Studies of Nigeria Crudes I Characterization of Crudes oil

Mixtures Petroleum Sciences and Technology. 22(5): 665 – 558.

[9] Pillon, L. Z. (2007). Interfacial Properties of Petroleum Products, CRC Press. pp. 45-78.

[10] Rasina, M. G; Erikh, V. N and Rudin, M.G (1988). The Chemistry and Technology of Petroleum and Gas. Mir Publishers, Moscow. pp. 39-134.

[11] Speight, J. G (1999). The Chemistry and Technology of Petroleum. Third edition, Revised and Expanded, Marcel Dekker Inc, New York. pp. 215-357.

[12] Udeme, J. O. and Etim, I. U. (2012). Physiochemical Studies of Nigerian Crude Oil Blends Petroleum and Coal, 54(3):243-251.

[13] Tim, L. (2009). Analytical Techniques for the Determination of Sulphur Components in Fuel Gas, Fuel Gas and Natural Gas. Literature Thesis Chemistry Analytical Sciences, Vrije University, Faculty of Exact Sciences, Department of Analytical Chemistry and Applied Spectroscopy, De Boelelaan 1083108/ HV Amsterdam. pp. 1-35.

[14] Verma, R. M. (2008). Analytical Chemistry: Theory and Practice. Third Edition CBS Publishers, Darya Gani, New Dechi-India Pp.279-280.