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RESEARCH ARTICLE

PRODUCTION OF SILICON ETHOXIDE FROM NIGERIAN RICE HUSK

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ABSTRACT

Application of nanotechnology has been very limited in petroleum industry. However, in recent years, the importance of nano science to develop conventional methods in several branches of petroleum engineering has been highlighted. Despite the considerable surveys investigating different applications of nanotechnology in optimizing drilling fluid rheology in HTHP conditions and reservoir engineering (enhanced oil recovery techniques); far too little attention has been paid to producing these nano particles / additives locally in Nigeria. The petroleum industry has been the mainstay of Nigeria economy accounting for more 90% of our gross earning. The Nigerian Oil and Gas Industry Content Development Act 2010 seek to increase indigenous participation in the Oil and gas industry by prescribing minimum thresholds for the use of local services and materials. Due to the high silica content in rice husk, preparation of silica products is considered to be the most attractive utilization method at present. Amorphous silica is a basic raw material, which has found an increasingly wide market in industries. Rice husk is a well-known, abundant agricultural byproduct in rice-producing countries such as Nigeria. The disposal of rice husk has become a great environmental threat to the land and the surrounding areas where it is dumped. Therefore, recycling the waste and producing high-value materials is not only beneficial to the environment but is also a promising bio-resource technology. In this paper, an optimized process for preparation of nanosilica from rice husk is described. The characteristics of the nanosilica prepared are described and the silica content of the nanosilica reached a record of 94% purity in the method adopted. The nanosilica was further processed to form Silicon ethoxide which is an emulsifier that has its application in the industry. It can be deduced from the results that Silicon ethoxide is considered as a reversible surfactant because of its hydrophilic and hydrophobic nature. These chemical nature and functional group plays an important role in performance characteristic of a reversible mud.

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INTRODUCTION

According to Larbi (2010), biomass resources such as rice husk as a source for silica and silicon are being intensively studied for several applications in the industry. Agro waste / by-products with disposal issues which mostly lead to environmental nuisance are biomass resources; hence developing a product from them are in agreement with the global paradigm shift towards sustainable development. Polysilica have found several applications in different industries and can be produced in different forms such as colloidal silica, gel silica, fumed silica and aerogel silica. Though, biogenic silica has been said from literature to be a perfect alternative to synthetic silica. Rice husk has been

considered to be readily available agricultural bio-resource that can produce silica because of its cost effectiveness (Athinarayanan *et al.*, 2014). Polysilica have numerous potential applications and can be manufactured in several forms, including fumed silica, colloidal silica, silica gel, and silica aerogel. However, biogenic silica is an excellent alternative to synthetic silica because of its variable structure, density, and composition. Among the available agricultural bioresources, rice husk is considered to be a cost-effective and non-metallic bio-precursor for biogenic silica nanoparticle synthesis (Athinarayanan *et al.*, 2014). Recently, natural-resources-based silica has garnered considerable interest in the materials science and biomedicine fields because of the availability, low cost and eco-friendliness of these materials.

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Rice husk is an agro-waste which is produced in about 100 million of tons. About 108 tons of rice husks are generated annually in the world. In Nigeria about 2.0 million tons of rice is produced annually. Approximately, 20kg of rice husk are obtained from 100kg of rice. In Nigeria, proper utilization of agricultural waste has not been given due attention. The rice husk thereby constitutes an environmental nuisance as they form refuse heaps in the areas where they are disposed. During the harmattan (dry season) the rice husk dust is carried by wind to contaminate the environment. It burning generates rice husk ash which is rich in silica and can be an economically valuable raw material for production of natural silica. Industrial importance of rice husk (RH) is due to the presence of silica in hydrated amorphous form (Olawale *et al.*, 2012). Rice husk when burnt at low temperature below 700°C produces amorphous silica, while crystalline silica is produced at temperatures above 700°C. Rice husk ash is a major source of silicon dioxide. The ashes contain about 80% to 95% silicon dioxide and have low thermal conductivity and low mechanical properties. The ashes are also resistant to chemical etching and have high melting point of 1440°C. Crystallization in rice husk ash begins at temperature above 500°C; below this temperature rice husk ash is purely amorphous. The chemical properties of rice husk ash vary from one region to another. This variation is due to the condition under which rice is grown. These conditions include climate, soil, paddy (rice) variety and use of fertilizers (Onojah, 2013).



Plate 1 Rice Husk Hills in Ebonyi State, Nigeria

The surface properties of amorphous silica, which is considered to be an oxide adsorbent, in many cases depend on the presence of silanol groups. At a sufficient concentration these groups make such a surface hydrophilic. The OH groups act as the centers of molecular adsorption during their specific interaction with adsorbates capable of forming a hydrogen bond with the OH groups. The removal of the hydroxyl groups from the surface of silica leads to a decrease in the adsorption, and the surface acquires more and more hydrophobic properties. The hydrophilic nature of silica is mainly due to the presence of surface silanol groups. The -OH groups on the surface of silica cause silica particles to agglomerate and re-agglomerate. The rice husk ash so formed may contain several metallic impurities like Iron, Magnesium, Sodium, Potassium, Calcium which can decrease its surface area and purity. Several attempts are made to synthesize pure rice husk silica by eliminating these metallic impurities.

Ash Selection and usage

The selection of ash is important as the quality of ash determines the total amount as well as quality of silica recoverable. Ash which has undergone maximum extent of combustion is highly desirable as it contains higher percentage of silica (Davinder, 1997). High carbon present in rich husk ash can hinder the main silica digestion reaction and may change the product characteristics such as colour.

Experimental work

This section contains the information about materials and experimental procedures used in this study.

MATERIALS AND METHODS

The paddy residue or rice husk was obtained from rice mills in the eastern state (Ebonyi) and northern state (Nasarawa) of Nigeria.

There are various methods to prepare silica nanoparticles. Adam *et al.*, (2011) synthesized spherical nanosilica from agricultural biomass as Rice Husk via the sol-gel method. Jal *et al.*, (2004) synthesized nanosilica via the precipitation method. This study will adapt the method used by Gu *et al.*, (2013) to optimize the quality nanosilica produced from the rice husk obtained from Nigeria rice mills. Unlike the previous studies cited, in this study, the sample was first soaked in de-ionized water at room temperature for 24 hours. According to Gu *et al.*, (2013) the aim of the soaking pre-treatment was to remove most of the alkali metals and partial fixed carbon from rice husk to make the subsequent hydrolysis process.

This will ensure that the hydrolysis process is more efficient. X-ray fluorescence (XRF) characterization was performed to know the metal oxide compositions of the minerals that are present in the rice husk samples. Silica is the major constituent of rice husk ash and figure 1 and 2 below gave the typical composition of rice husk before and after pre-soaking treatment.

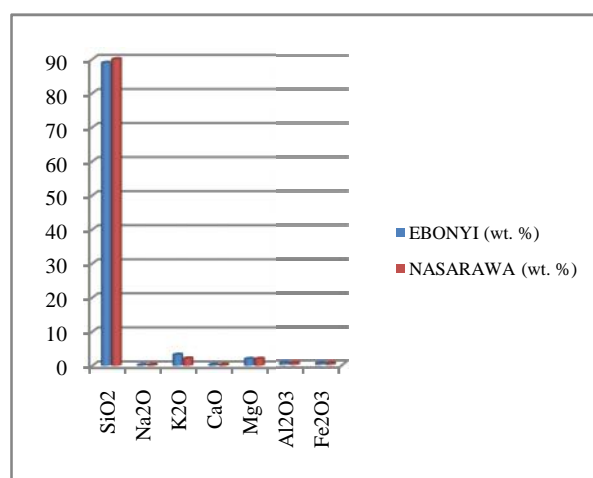


Figure 1 Metal Oxide content of the Rice Husks before Pre-Soaking

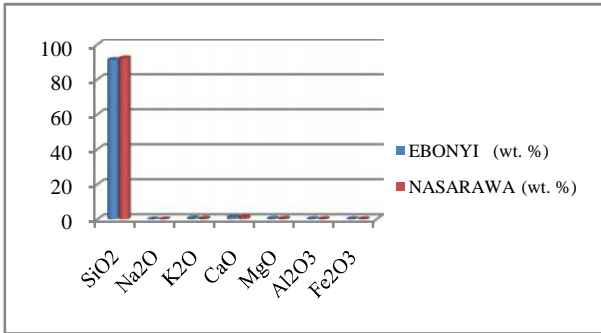


Figure 2 Metal Oxide content of the Rice Husks after Pre-Soaking

With such large silica content in the rice husk ash as shown in figure 2; it is economical to extract silica from the rice husk ash which has wide market and also takes care of ash disposal.

The method and apparatus used in this study to process the rice husk into rice husk silica or rice husk ash is shown in the process flow diagram below.

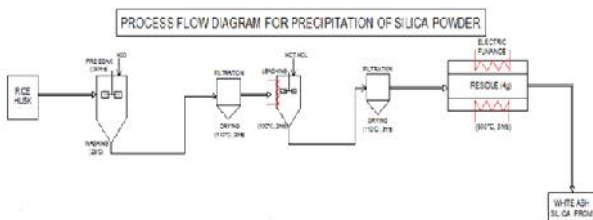


Figure 3 Process flow diagram for Extraction of Polysilica from Rice husk

During the extraction process, it was observed that for every 3g of the rice husk used; 0.75 – 0.80g of Silica Ash is produced from the furnace. The leaching of the rice husk using acidic reagent (HCl) was carried out in order to remove soluble elemental impurities and thus increase the purity of the silica content in the rice husk.



Plate 2 Rice husk sample (Before) and Polysilica Sample (After)

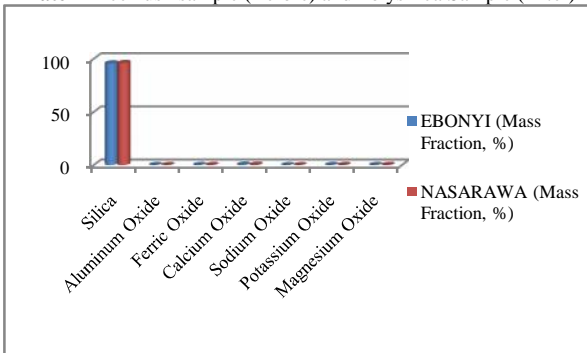
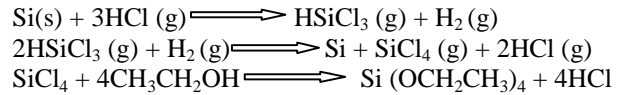


Figure 4 The Rice Husks Ash Composition

The overall reaction process can be represented by



Emulsifier

The field of surface chemistry is intricately connected to most processes of petroleum technology; from the drilling of crude oil to petroleum refining and petrochemical processing, as well as to allied and dependent applications and industries. All of these processes involve interfacial phenomena and surface chemical interactions. In the context of petroleum technology, surface chemistry deals with the surface properties of crude oil/air, crude oil/brine (or water) and crude oil/solid surfaces. Thus, surface tension, interfacial tension (IFT), contact angle, wetting and surface charge are the parameters that one measures for surface chemical studies (Kanicky et al., 2001).

A surfactant molecule has two functional groups, namely a hydrophilic (water-soluble) or polar group and a hydrophobic (oil-soluble) or non-polar group. The hydrophobic group is usually a long hydrocarbon chain (C₈-C₁₈), which may or may not be branched, while the hydrophilic group is formed by moieties such as carboxylates, sulfates, sulfonates (anionic), alcohols, polyoxyethylenated chains (nonionic) and quaternary ammonium salts (cationic) (Kanicky et al., 2001). Modern emulsifiers are additives and generally are classified in the group of so called tensides. These are substances that can reduce the surface tension. Emulsifiers have a variety of different structures and resulting from those also different fields of application.

Formulation of Silicon Ethoxide from the Extracted Nanosilica

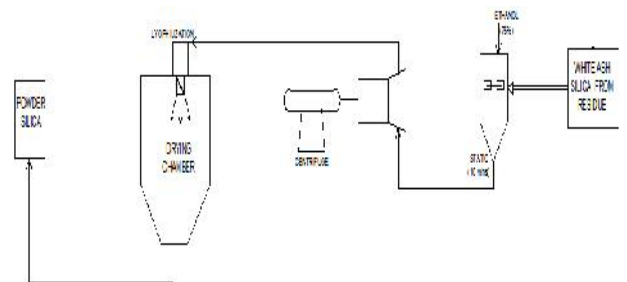


Figure 5 Formulation of Silicon Ethoxide



Plate 3 The Freeze Dryer and the Sample Curve Plot after Lyophilization Process

The silica extracted from the rice husk sample was gathered and grounded in a mortar until white silica powder was obtained. Ethanol was used to dilute the white silica followed by a mechanical fragmentation. The mixture was left static for 10 minutes at room temperature. Then centrifuged at 2600 rpm for 8 minutes and the deposit were refrigerated for 2 hours. After lyophilization, the Poly-silica powder is obtained.

Identification of the Polysilica Functional Group

The head and tale are two different functional groups that identify if the compound has a hydrophilic and hydrophobic nature needed for it to be reversible at a certain concentration.

Functional groups are the portions in an organic molecule that dictate how the molecule will react. To generate the IR spectrum, different frequencies of infrared light are passed through a sample and the transmittance of light at each frequency is measured. The transmittance is then plotted versus the frequency of light (which is represented in the somewhat unusual units of cm^{-1}). Different functional groups produce bond absorptions at different locations and intensities on the IR spectrum. Recognizing where the absorptions generated by the common functional groups occur will help to interpret IR spectra.

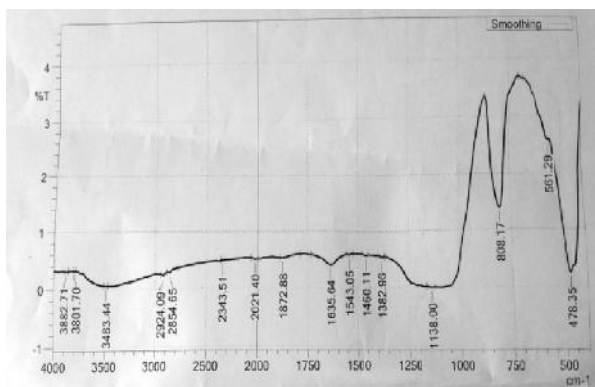


Plate 4 Identification of functional groups in Polysilica from Ebonyi State Rice Husk

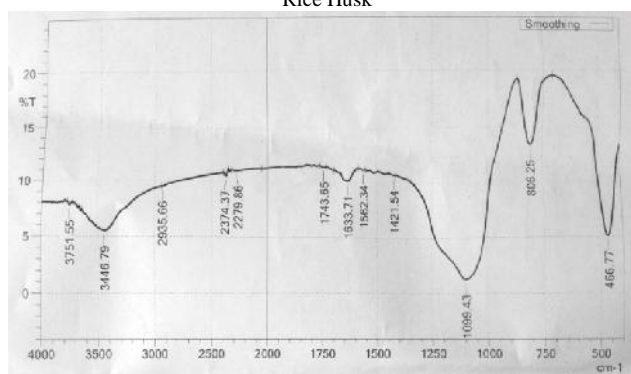


Plate 5 Identification of functional groups in Polysilica from Nasarawa State Rice Husk

DISCUSSION

The vibrational spectrum of a molecule (stretching or bending) is considered to be a unique physical property and is characteristic of the molecule. Infrared spectrum analysis was used in this study as a fingerprint for identification of

functional groups by the comparison of the spectrum from an “unknown” with previously recorded reference spectra. From literature, spectra-structure correlations for infrared analysis of organosilicon compounds identified that at frequency range of $810 - 800 \text{ cm}^{-1}$, amorphous silica is absorbed; in the sample from Ebonyi it was absorbed at 808.17 cm^{-1} while for Nasarawa it was absorbed at 806.25 cm^{-1} . The weak intensity Si-CH₂ band is identified at the frequency of 1138 cm^{-1} for Ebonyi and 1099.43 cm^{-1} for Nasarawa samples. The sharp band at 478.35 cm^{-1} and 466.77 cm^{-1} for Ebonyi and Nasarawa samples respectively, represent a strong Si-Cl group; while the sharp band at 1635.64 cm^{-1} and 1633.71 cm^{-1} for Ebonyi and Nasarawa samples respectively being a major bend indicate that a carbonyl group is attached to the silicon (C-O). The series of weak absorptions observed in both samples between 2000 and 1700 cm^{-1} indicates a simple aromatic compound.

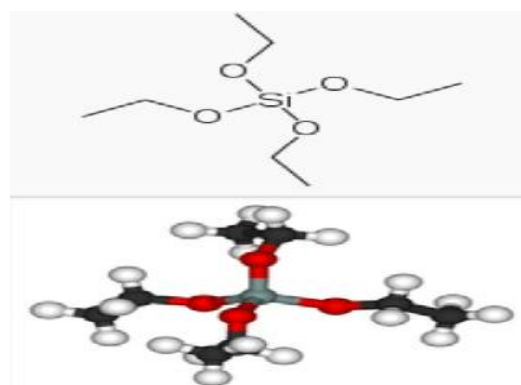


Plate 6 Structure of Silicon Ethoxide

CONCLUSION

Rice husk is one of the main agricultural wastes in milling processes that is abundantly available in Nigeria. Approximately, 20kg of rice husk are obtained from 100kg of rice. It burning generates rice husk ash which is rich in silica and can be an economically valuable raw material for production of natural silica. Industrial importance of rice husk (RH) is due to the presence of silica in hydrated amorphous form.

In this study, an optimized process was designed for the preparation of Polysilica from Nigeria rice husk. The soaking pre-treatment was observed to be an effective method to improve the purity of the Polysilica, due to the removal of metal oxides and partial fixed carbon during the process. Therefore, the soaking pretreatment made the subsequent hydrolysis more efficient. Also, for every 3g of rice husk treated; 0.82g of Nanosilica is obtained.

It can be deduced from the results that Silicon ethoxide is considered as a reversible surfactant because of its hydrophilic and hydrophobic nature. These chemical nature and functional group plays an important role in performance characteristic of a reversible mud.

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References

- A.D. Onojah, N.A. Agbendeh and C. Mbakaan (2013): Rice Husk Ash Refractory: The Temperature Dependent Crystalline Phase Aspects. *IJRRAS*, Vol. 15 Issue 2.
- Adam F., Chew T.S, and Andas J. (2011): A simple template-free sol-gel synthesis of spherical nanosilica from agricultural biomass. *J Sol-Gel Sci Technol*, 59:580-583.
- Davinder Mittal (1997): Silica from Ash - A Valuable Product from Waste Material. *RESONANCE*, July.
- Jal P.K., Sudarshan M., and Saha A. (2004): Synthesis and characterization of nanosilica prepared by precipitation method. *Colloids Surf Physicochem Eng Aspect*, 240:173-178.
- James R. Kanicky, Juan-Carlos Lopez-Montilla, Samir Pandey and Dinesh O. Shah (2001): Surface Chemistry in the Petroleum Industry. *Handbook of Applied Surface and Colloid Chemistry*. Edited by Krister Holmberg Center for Surface Science and Engineering, Departments of Chemical Engineering and Anesthesiology, University of Florida, Gainesville, Florida, John Wiley & Sons, Ltd USA.
- Jegan Athinarayanan, Vaiyapuri Subbarayan Periasamy, Mohammad Alhazmi, Khalid A. Alatiah, Ali A. Alshatwi (2014): Synthesis of biogenic silica nanoparticles from rice husks for biomedical applications. *Ceramics International* 41(2015) 275-28.
- Kingsley Kweku Larbi (2010): Synthesis of High Purity Silicon from Rice Husks. A thesis submitted in conformity with the requirements for the degree of Master of Applied Science Graduate Department of Materials Science and Engineering, University of Toronto.
- Olawale, Olamide, Festus Adekunle Oyawale (2012): Characterization of Rice Husk via Atomic Absorption Spectrophotometer for Optimal Silica Production. *International Journal of Science and Technology*, Volume 2 No.4, April.
- Shan Gu, Jingsong Zhou, Zhongyang Luo, Qinhuai Wang, Mingjiang Ni (2013): A detailed study of the effects of pyrolysis temperature and feedstock particle size on the preparation of nanosilica from rice husk. *Industrial Crops and Products* 50, 540- 549.

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