Comparative Study of The Adsorptive Capacities of Locally Synthesized Rice Husk and Coconut Shell Activated Carbons in The Desulfurization of Kerosene

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Abstract- Like every other petroleum fractions, kerosene is also accompanied by a number of impurities, chief of which are Sulphur compounds. These compounds are undesirable because they form So$_x$ during combustion. This sulfur compounds when burned have a devastating health effect and contribute greatly to depletion of ozone layer. The research project aimed at studying and comparing the adsorptive capacities of locally synthesized rice husk activated carbon (RHAC) and coconut shell activated carbon (CSAC) in the removal of these sulfur compounds from kerosene. The two adsorbents were first prepared from their respective precursors employing the one step chemical activation technique. Proximate analysis of the synthesized activated carbons was also done to gain a pre-knowledge as regards the suitability or otherwise of the activated carbon. Batch adsorption in a laboratory beaker was then carried out at different contact time and adsorbent dosage to desulfurize the kerosene. The contact time was varied for one hour at an interval of 10 minutes while adsorbent dosages of 1g, 2g and 3g were tested. The result shows that coconut shell activated carbon (CSAC) has a better adsorption capability in kerosene desulfurization when compared with rice husk activated carbon. This is seen from the highest removal efficiencies attained by both ACs. CSAC attains peak removal efficiencies of 57.32%, 66.22% and 65.11% at 1g, 2g and 3g respectively. This is far greater than the 32.21%, 39.01% and 51.57% attained by RHAC at the respective adsorbent dosages.

Indexed Terms- Activated Carbon, Adsorption, Rice Husk, Coconut Shell, Kerosene, sulfur, Desulphurization

I. INTRODUCTION

Kerosene is a larger and widely used source of energy in the world. It has a wide range of application in both domestic and industries. In the petrochemical industries, kerosene is the major feedstock in the production of linear alkyl benzene (LAB), a major component of both liquid and powdered detergents. However, like every other petroleum fraction, kerosene is also accompanied by a good number of certain contaminants. Chief among these contaminants is sulphur, typically in the form of organic sulphur compounds. Sulphur is the third most abundant element after carbon and hydrogen in fuels.

Sulphur compounds exist in various forms and can be classified into four main groups: mercaptans, sulphides, disulphides and thiophene. These compounds are very undesirable because when combined with atmospheric oxygen during combustion, they form Sulphur oxides SO$_X$. (Opara *et al.*, 2013)

The combustion of sulphur compounds are not only causing corrosion but also contributing considerably to acid rains and air pollution, deforestation, smog, and global warming, as well as several human health concerns such as cardiovascular disease, cancer, creation of asthmatic symptoms and other respiratory diseases. Sulphur compounds also deactivate some catalysts used in the further processing of the kerosene in the industry. For example, in the production of LAB, sulphur is capable of poisoning the molecular sieves of the MOLEX unit. Moreover, Sulphur compounds can cause several corrosion problems in pipeline, pumping, and refining equipment, as well as the premature failure of combustion engines and poisoning of the catalytic converters that are used in automotive engines. Today, the strongest motivation for the reduction of sulphur in fuels is due to environmental protection agency's regulation which is imposing stringent limits for sulphur levels in transportation fuels (Opara *et al.*, 2013).

Desulphurization prior to combustion has been viewed in recent years with the objective of ensuring clean fuel combustion and hence to avoid environmental degradation. In most chemical industries, the hydrodesulphurization (HDS) technique is usually employed to reduce the amount of sulphur present in fuels to the barest minimum. Nevertheless, the HDS technique is characterized by high cost of operation as it involves catalytic reaction of hydrogen and the sour fuel at an elevated temperature of about 400^oC.

Several polishing processes such as reactive adsorption, non-destructive adsorption, extraction, and oxidative desulphurization are suggested to supplement the conventional HDS process. Adsorption processes are some of the most economically attractive methods because of the straightforward operating conditions and availability of inexpensive and re-generable adsorbents.

Activated carbon, also widely known as activated charcoal or activated coal is a form of carbon which has been processed to make it extremely porous and thus to have a very large surface for adsorption or chemicals (Lorenc-Grabowska, 2016). It is characterized by high degree of micro porosity. A gram of activated carbon can have a surface area in excess of $500m^2$. The common method of development is thermochemical. The main concern is the removal of chemical component by adsorption from the liquid or gas phase (Khedr et al., 2014).

Recently, carbon has been one of the magnificent elements which have revolutionized material science. From carbon we obtain the best porous absorber (activated carbon) with excellent properties for large spectrum of industrial applications. Activated Carbon (AC) is the common term used for a group of absorbing substances of crystalline form, having a large internal pore structures that make the carbon more absorbent (Ting Lee, 2014).

These properties are obtained when a char is subjected to controlled gasification by oxidizing gases, or when a raw material impregnated with dehydrating agents is subjected to carbonization. Generally, the raw materials for the production of AC are those with high carbon but low inorganic contents such as wood, lignite, peat and coal (Lua and Guo, 2001).

Besides that, lot of agricultural waste and by product have successfully converted to AC for examples macadamia nutshell (Ahmadpour and Do, 1997), paper mill sludge (Khalili, et al., 2000). Today, activated carbon has been produced from various biomass such as corncob, cornstalk, dates etc., has attracted much attention. Among these carbon sources, corncob is a good precursor for preparing carbons with ultra-high specific surface area (Xie., 2013).

II. LITERATURES AND MOTIVATION

When kerosene is burned, the sulfur compounds in it combine with atmospheric oxygen to form SO_X thereby causing environmental pollution. The combustion of sulphur compounds contributes considerably to acid rains and air pollution, deforestation and global warming, as well as several human health concerns such as cardiovascular diseases, cancer, creation of asthmatic symptoms and other respiratory diseases. It is therefore necessary to develop efficient and affordable processes for desulphurization of kerosene before burning.

The disposal of agricultural wastes such as rice husk and coconut shell are becoming increasingly difficult making it imperative to device a means of effectively utilizing them.

Various experiments have been carried out to remove sulphur compounds in petroleum products by adsorption using activated carbon. Adsorption Process of Sulfur Removal from Diesel Oil using Sorbent Materials has been studied by Zubaidy *et al*., (2013). They used Date palm kernel powder for desulphurization process for diesel fuel. Gaurav and Daware, (2015) reduced sulphur contents of diesel by about 31% using Neem seed as adsorbent at different temperatures.

However, a comprehensive comparative study on the adsorptive capacity of the different types of the activated carbon as well as the effect of agitation and the quantity of the activated carbon on desulfurization of kerosene has not to my knowledge been documented. Therefore, in this study, we shall compare the adsorptive capabilities of rice husk activated carbon (RHAC) and coconut shell activated carbon (CSAC) in the desulfurization of kerosene.

III. MATERIALS AND METHOD

A. Materials

The materials used for the purpose of this study are outlined below:

Raw kerosene: Raw kerosene was sourced from A.Y.M Shafa filling station in Bauchi metropolis of Bauchi state, Nigeria. It is the contaminated adsorbate from which sulfur compounds must be removed through adsorption with activated carbon.

Rice husk: This also was collected in Bauchi metropolis, from a rice milling plant located at the railway industrial layout, Bauchi.

Coconut shell: Coconut shell was collected from Katagum market, Zaki local government of Bauchi state, Nigeria. This is also used as a precursor to produce the coconut shell activated carbon.

B. Equipment

Kiln: The kiln is used in the carbonization of the precursor material. The impregnated coconut shell and rice husk were subjected to elevated temperature in the kiln to produce the char.

Beakers: The batch adsorption of the sulfur compounds was carried out in a set of beakers. Activated carbon was contacted with the contaminated kerosene in the beaker.

Digital weighing balance: Digital weighing balance was used to measure the required amount of the activated carbon before being transferred into the beaker. Dosage of adsorbent was monitored with the aid of the digital weighing balance.

Measuring cylinder: This was used to measure the required volume of the kerosene. It was also used during the standardization of the KOH and HCl dilute solutions.

C. Reagents

Various reagents were used in the course of this xresearch project and they include the followings:

Potassium hydroxide (KOH): Dilute solution of 0.1M potassium hydroxide was used to impregnate the precursor materials (coconut shell and rice husk). The potassium hydroxide pellet was sourced from the chemical engineering department and made to standard using distilled water.

Hydrochloric acid (HCl): Hydrochloric acid solution was used to wash the carbonized activated carbon after cooling.

Nitrogen gas (N_2): Nitrogen gas was used to displace oxygen during the carbonization process. The flow of the N_2 was maintained at about 70ml/min throughout the carbonization time.

D. Production of Activated carbon

The procedure followed for the production of the activated carbon can be broadly classified under the following headings:

1. Precursor collection and preparation.

Two (2) precursor materials, coconut shell and rice husk were used for the research. Both precursors were sourced from Bauchi state. Coconut shell was collected from Katagum town, Zaki local government in a local market while rice husk was collected from a rice milling plant in Bauchi metropolis. The collected were sort, washed and sun-dried.

2. Size reduction.

The washed and dried precursors (coconut shell and rice husk) were then crushed to smaller size. This was achieved using a pestle and mortar. The materials were then sieved to collect uniform particles of size ranging from 3-4 millimetres. The collected particles were then impregnated using a solution of diluted potassium hydroxide.

3. Activation

The collected smaller sizes of the precursors were then impregnated with KOH at a temperature of about 76^{o}C. The weight ratio of ZnCl$_2$-to seed was considered 2. 10 mL deionized water was added to this mixture which was then dehydrated at 110 °C overnight.

4. Carbonization

The chemically activated precursors were then sent for carbonization. This was carried out in a kiln at a temperature of 750^{o}C. A kiln was used to achieve this temperature. During the carbonization, a flow of nitrogen into the kiln was maintained to displace hydrogen and produce an inert atmosphere.

E. Characterization

Some of the characterizations carried out on the produced activated carbon and the procedures followed were outlined as follows:

1. Ash Content (AC)

1 gram of sample was taken in a silica crucible. It was heated in a muffle furnace to 750˚c for 1.5hr. During this heating process the crucible was left open. After the required heating, the crucible was cooled in a desiccator and then weight of the ash was measured.

2. Moisture Content (MC)

Small amount of activated carbon sample (coconut shell) weight was measured and then taken in a petri dish. It was spread nicely on the dish. It was then heated in an oven at a temperature of 105-110^{0}C for 1.5hr. The petri dish was left open or not covered during heating process. After heating petri dish was removed and cooled in a desiccator. After cooling the weight of dried sample was measured, and the moisture content was calculated.

3. Volatile Matter (VM)

A known quantity of sample was taken in cylindrical crucible closed with a lid. It was then heated to 925˚c for exactly 7minutes in a muffle furnace. Then the crucible was cooled in a desiccator and weighted.

4. Fixed Carbon Content (FC Content)

To calculate the fixed carbon content, the percentage moisture content, ash content, and volatile matter are subtracted from 100, i.e.

$$F\ C\ content = 100 - (\%MC + \%AC + \%VM) \quad (1)$$

IV. RESULTS

A. Proximate Analysis

Proximate analysis was carried out where ash content (AC), moisture content (MC), volatile matter (VM) and fixed carbon content (FC content) were determined for the two precursor materials. Figure 1 compares the proximate parameters of the coconut shell and rice husk activated carbon.

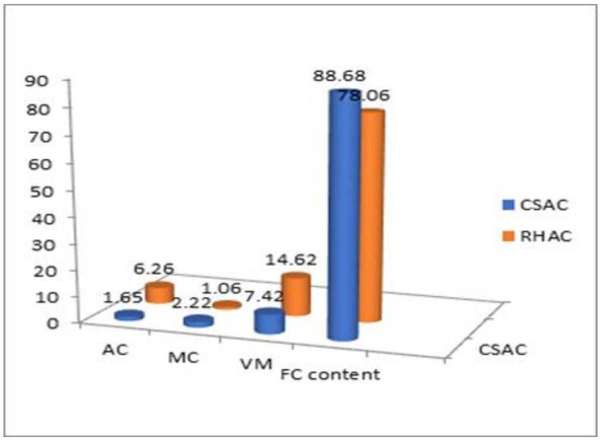

Figure 1. Comparison of the proximate analysis for the precursor materials

B. Desulfurization of kerosene with CSAC

The results for the desulfurization of the kerosene at varying contact time and dose of CSAC and constant volume (20ml) of kerosene are presented in Table 1 and Figure 2.

Table 1: Sulfur removal at 1g, 2g, and 3g of CSAC

Time [min]	Removal Efficiency (1g) [%]	Removal Efficiency (2g) [%]	Removal Efficiency (3g) [%]
0	0.00	0.00	0.00
10	16.67	19.44	27.78
20	22.22	23.33	33.33
30	33.33	36.11	41.67
40	52.78	55.56	69.44
50	63.89	63.89	61.11
60	75.00	72.22	58.33

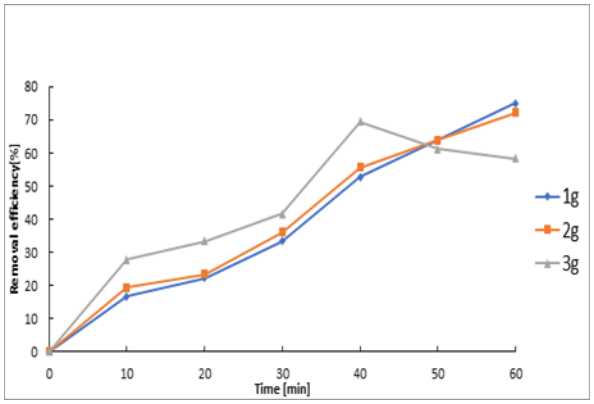

Figure 2. CSAC Removal efficiency vs Time at different dosage

C. Desulfurization of kerosene with RHAC

The results for the desulfurization of the kerosene at varying contact time and dose of RHAC and constant volume (20ml) of kerosene are also presented in Table 2 and Figure 3.

Table 2: Sulfur removal at 1g, 2g, and 3g of RHAC

Time [min]	Removal Efficiency (1g) [%]	Removal Efficiency (2g) [%]	Removal Efficiency (3g) [%]
0	0.00	0.00	0.00
10	9.38	6.32	10.42
20	11.98	13.65	16.92
30	13.47	23.02	31.04
40	24.72	33.26	36.74
50	30.80	37.92	34.20
60	40.21	51.01	37.57

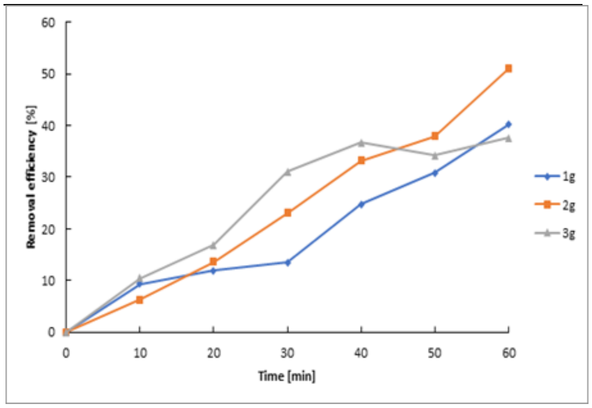

Figure 3. RHAC Removal efficiency vs Time at different dosage

V. DISCUSSION OF RESULTS

A. Proximate analysis result

The results obtained from the proximate analysis as presented in the tables and figures above shows that coconut shell is going to be a better precursor material for the preparation of the activated carbon. As earlier seen in the literature, activated carbons are best prepared from carbonaceous materials. This invariably implies that materials with reasonable amount of carbon content will make a better activated carbon than those with lower carbon.

From the table, it can clearly be seen that coconut shell activated has better carbon content when compared to rice husk. With a fixed carbon content of 88.68% against the rice husk's 78.06%, coconut shell activated carbon is expected to have a better adsorption capacity. Other properties of the CSAC that may give it an edge over RHAC is its low ash content, low moisture content and low volatile matter. CSAC was found to have 1.65%, 2.22%, and 7.42% for ash content, moisture content and volatile matter respectively. In the other hand, RHAC been of lower carbon content was found to greater ash content of 6.26%, moisture content of 1.06% and volatile matter of 14.62%.

B. Desulfurization with CSAC

From the results shown in Figure 2, one can say that coconut shell activated carbon (CSAC) was able to significantly reduce the amount of sulfur contained in the kerosene. Initially, it was found that the raw kerosene contains about 28.80mg/l of sulfur. Treating the kerosene with the CSAC brings about a progressive decrease in the sulfur. CSAC attains peak removal efficiencies of 57.32%, 66.22% and 65.11% at 1g, 2g and 3g respectively.

C. Desulfurization with RHAC

From Figure 3, it was clear that rice husk activated carbon (RHAC) was also able to significantly reduce the amount of sulfur contained in the kerosene. Initially, it was found that the raw kerosene contains about 28.80mg/l of sulfur. Treating the kerosene with the RHAC brings about a progressive decrease in the sulfur. RHAC attains peak removal efficiencies of 32.21%, 39.01% and 51.57% at 1g, 2g and 3g respectively.

Even though, both Activated Carbons were able to significantly adsorb the sulfur compounds contained in the kerosene, CSAC was found to have a greater adsorptive capacity when compared with RHAC. This is seen from the highest removal efficiencies attained by both ACs. CSAC attains peak removal efficiencies of 57.32%, 66.22% and 65.11% at 1g, 2g and 3g respectively. This is far greater than the 32.21%, 39.01% and 51.57% attained by RHAC at the respective adsorbent dosages.

Another thing that is evident from the results is that adsorption efficiency increases with an increase in the contact time up to a point where the active site of the adsorbent becomes saturated in which case equilibrium is set and in some cases desorption occurs as it can be seen in the case of 3g of CSAC. It was also established that increase in adsorbent dosage favours adsorptive efficiency and decreases the contact time.

CONCLUSION

In conclusion, it is safe to infer that that the aim of the research project was wholly achieved. Activated carbon was successfully prepared from rice husk and coconut shell and was subsequently used to desulfurize kerosene. The adsorptive capacities of these activated carbons were studied and compared, and it was found out that CSAC has a better adsorptive capacity when compared with RHAC. This further validated the proximate analyses results.

Contact time and adsorbent dosage were also varied and it was established that adsorption efficiency increases with an increase in the contact time up to a point where the active site of the adsorbent becomes saturated in which case equilibrium is set and in some cases desorption occurs as it can be seen in the case of 3g of CSAC. Same also applies to adsorbent dosage.

RECOMMENDATION

Subsequent researches in this area should focus on establishing the effect of other process parameters such as temperature and pressure. There is need to also test for the adsorptive capacities of other agricultural waste like palm kernel shell, egg shell and what have you.

The possibilities of designing an industrial scale adsorbers as well as commercial production of activated carbon from these agricultural wastes should also be looked in to.

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