Deodorization of Kerosene Using Activated Carbon as Adsorbent

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ABSTRACT

The secondary contaminant such as sulphur and other impurities represent one of the major threats to burning properties of kerosene and to environment. The sulphur contaminant produces a strong odor, which if not removed can cause some problems. Several method used to deodorized kerosene are extraction method by adding paraffin and solvent into kerosene, thereby removing the odor. In this study, activated carbon 10-50mm of particle size gotten from burnt woods was used to deodorize kerosene. The exercise was carried out using a specific quantity of untreated kerosene with different quantity of activated carbon at different contact time. Also iodometric method was used to test for sulphide level in the deodorized kerosene.

Key word: Deodorization, Activated carbon, Adsorption, Kerosene.

INTRODUCTION

Kerosene, one of the byproducts of petroleum was discovered in 1853 by Abraham Gesner. A British physician, Gesner developed a process to extract the inflammable liquid from asphalt, a waxy petroleum mixture. The term kerosene is derived from the Greek word keros. Kerosene is a combustible hydrocarbon liquid, widely used to power jet engines of aircraft (jet fuel) and some rocket engines. It is also commonly used as a cooking and lighting fuel for fire toys such as poi. Kerosene lamps are widely used for lighting in rural areas, where electrical distribution is not available or too costly for widespread use. Kerosene, a thin, clear liquid formed from hydrocarbons, with a density of 0.78–0.81 g/cm$^3$, is obtained from the fractional distillation of petroleum between 150 °C and 275 °C, resulting in a mixture of carbon chains that typically contain between six and 16 carbon atoms per molecule. Once the oil has been distilled into its fractions, further processing in a series of chemical reactors is necessary to create kerosene. Catalytic reforming, alkylation, catalytic cracking, and hydro processing are four of the major processing techniques used in the conversion of kerosene. These reactions are used to control the carbon chain distribution by adding or removing carbon atoms from the hydrocarbon backbone. These reaction processes involve transferring the crude oil fraction into a separate vessel where it is chemically converted to kerosene. Major constituents of Kerosene include n-Dodecane, alkyl benzenes, and naphthalene and its derivatives. The flash point of kerosene is between 37 and 65 °C (100 and 150 °F), and its auto ignition temperature is 220 °C (428 °F). Heat of combustion of kerosene is similar to that of diesel; its lower heating value is 43.1 MJ/kg (around 18,500 Btu/lb), and its higher heating value is 46.2 MJ/kg. Kerosene is immiscible in water (cold or hot), but miscible in petroleum solvents. Once the kerosene has been reacted, additional extraction is required to remove secondary contaminants that can affect the oil's burning properties. Aromatic compounds, which are carbon ring structures such as benzene, sulphur are class of contaminants that must be removed. The contaminants produce an offensive odor in the kerosene which the strong odor if not removed, can cause some problems.

This paper describes deodorization of specific volume of kerosene using activated carbon as adsorbent. The adsorption process occurred in a beaker at different contact time as a function of adsorption rate. In any adsorption process the material being adsorbed (e.g., a pollutant) is simply but effectively removed from one phase (e.g., odoriferous kerosene) and transferred to another phase (e.g., activated carbon). This means that adsorption is a physical separation process in which the adsorbed material is not chemically altered. Since the chemical characteristics of the adsorbed material are not changed, the use of adsorption in odoriferous kerosene treatment is
associated with the removal of obnoxious odor from the kerosene and its transfer to the activated carbon. This implies that the activated carbon now contains the hazardous material. Therefore, appropriate actions must then be taken to treat the spent activated carbon at the end of a cycle. After the adsorption processes, the carbon can be regenerated, disposed or destroyed.

Common Adsorbents

- Activated carbon - a char-like material with high surface area.
- Silica gel - hard, granular, porous material made by precipitation from sodium silicate solutions treated with an acid.
- Activated alumina - aluminium oxide activated at high temperature and used primarily for moisture adsorption.
- Alumina silicates (molecular sieves) – porous synthetic zeolites used primarily in separation processes.

As demand for kerosene and its byproducts increases, new methods of refining and extracting kerosene will become even more important. When it comes to attempting to filter out odors from the kerosene, there are two suggested methods. First, the kerosene is run through an activated carbon filter. This filter should catch some of the elements in the fuel that actually cause the odor, and by eliminating them, the smell is drastically reduced. A second approach is to add 1 cup M (about 330 grams) of powdered limestone to 1 G (3.785 liters) of kerosene. The mixture should be allowed to sit for three to five days; by then, any residue of the powder will have settled to the bottom of the container. The fuel should then be strained into a clean container. The limestone is said to absorb the odor causing properties of the kerosene, leaving the fuel to burn brightly and with almost no odor at all. The odor in kerosene can also be removed by liquid extraction with concentrated sulphuric acid as the liquid solvent. Multistage, countercurrent extraction process can be used. In this report, deodorization of commercial kerosene using activated carbon as adsorbent is discussed. Micro- and mesoporous granular rice husk activated carbon (RHAC) and micro porous granular coconut shell activated carbon (CSAC) are among the activated carbon that can be use to remove residual sulfur in form of Benzothiophenes (BTs) and dibenzothiophenes (DBTs) in commercial kerosene. From research, larger adsorption capacity of DBTs in volume basis was observed on CSAC, which was attributed to higher carbon content and larger ultramicropore volume of CSAC, while a larger adsorption capacity of BTs in volume basis appeared on RHAC.

The future of kerosene depends on the discovery of new applications as well as the development of new methods of production. New uses include increasing military demand for high-grade kerosene to replace much of its diesel fuel with JP-8, which is a kerosene based jet fuel. The diesel fuel industry is also exploring a new process that involves adding kerosene to low sulfur diesel fuel to prevent it from gelling in cold weather. Commercial aviation may benefit by reducing the risk of jet fuel explosion by creating new low-misting kerosene. In the residential sector, new and improved kerosene heaters that provide better protection from fire are anticipated to increase demand.

Previous Work

Most extraction processes are conducted in large towers that maximize the contact time between the kerosene and the extraction solvent. Solvents are chosen based on the solubility of the impurities. In other words, the chemical impurities are more soluble in the solvent than they are in the kerosene. Therefore, as the kerosene flows through the tower, the impurities will tend to be drawn into the solvent phase. Once the contaminants have been pulled out of the kerosene, the solvent is removed leaving the kerosene in a more purified state. A number of different additives can be used to reduce or eliminate the odor or it can be filtered to remove the element that causes the offensive smell. Several methods have been used by many to deodorize kerosene, they are as follows:

ANOZIE and OKAFOR (2005) proposed how odor in kerosene can be removed by liquid extraction with concentrated sulphuric acid as the liquid solvent. Multistage, countercurrent extraction process was used. The kerosene to sulphuric acid ratio and the number of liquid extraction stages required to completely remove the sulphur compounds causing the odor in kerosene were determined. They also determined specific gravity, aromatic content, smoke point, flash point, initial and end boiling points and the k-factor of the kerosene using standard procedures. They found that the optimum kerosene to sulphuric acid ratio was 50:50% (v/v) based on total acid used while the number of liquid extraction stages required to completely remove the sulphur compounds causing the odor in kerosene was five. The material balance of the five-stage, countercurrent extraction process was fully established.

MALCOLM TATUM (2003) stated that one of the oldest methods of creating deodorized kerosene is by adding paraffin oil. While the amount that should be added varies from one folk recipe to the next, most recommended one is using one part paraffin oil to two parts kerosene. Many people also believe that this combination will result in a fuel
that will burn brighter in an oil lamp. He also stated that if there is no paraffin available, using common rubbing alcohol is an option. Rubbing alcohol is actually isopropyl alcohol, and can be purchased at most discount retail stores. If the kerosene is destined for use in a camping lamp or heater, adding in 1 ounce (29.5 ml) of rubbing alcohol can often greatly decrease the aroma of 1 gallon (3.785 liters) of fuel. If rubbing alcohol is not readily available, a recipe of one part mineral spirits to three parts kerosene will yield the same result. Alternately, 20 drops of sassafras oil is said to cut the odor of 1 gallon (3.785 liters) of kerosene greatly.

KELOTH and KUTTY (1986) presented a model on how desulfurization and deodorization of sulfur-bearing liquid hydrocarbon feedstock such as kerosene was carried out by contacting such feedstock with sodium hydride at normal atmospheric pressure and at elevated temperatures. The resulting liquid is further contacted with a mineral acid such as sulfuric acid and an alkaline neutralizing agent such as caustic soda. He also stated that the liquid may also be contacted with an oxidizing agent such as sodium hypochlorite prior to being contacted with the neutralizing agent and with a dehydrating agent such as soda ash after being contacted with the neutralizing agent.

EXXONMOBIL One new method, developed by ExxonMobil, is a low-cost way to extract high purity normal paraffin from kerosene. This process uses ammonia very efficiently to absorb the contaminants. This method uses vapor phase fixed-bed adsorption technology and yields a high level of paraffin that is greater than 90% pure.

Theory of Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate) on the surface of the adsorbent. Or adsorption is the process through which a substance (Adsorbate), originally present in one phase, is removed from that phase by accumulation at the interface between that phase and a separate (Adsorbent) solid phase. In principle adsorption can occur at any solid fluid interface. Examples include: gas-solid interface (as in the adsorption of a Volatile organic compound on activated carbon); liquid-solid interface (as in the adsorption of an organic pollutant on activated carbon). Adsorption is usually described through isotherms, that is, the amount of adsorbate is a function of its pressure (if gas) or concentration (if liquid) at constant temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials. The first mathematical fit to an isotherm was published by Freundlich and Küster (1894) and is a purely empirical formula for gaseous adsorbates,

$$ \frac{x}{m} = kP^n $$

Where $x$ is the quantity adsorbed, $m$ is the mass of the adsorbent, $P$ is the pressure of adsorbate and $k$ and $n$ are empirical constants for each adsorbent-adsorbate pair at a given temperature. The function has an asymptotic maximum as pressure increases without bound. As the temperature increases, the constants $k$ and $n$ changes to reflect the empirical observation that the quantity adsorbed rises more slowly and higher pressures are required to saturate the surface. Adsorption is present in many natural physical, biological and chemical systems, and is widely used in industrial applications for purification.

Driving Force for Adsorption

The driving force for adsorption is the reduction in interfacial (surface) tension between the fluid and the solid adsorbent as a result of the adsorption of the adsorbate on the surface of the solid. The surface or interfacial tension, $\sigma$, is the change in free energy, $G$, resulting when the area between two phases, $A$, is increased. The definition of $\sigma$ is:

Interfacial tension ($\sigma$) = (dG/dA) T, P, n.

MATERIALS AND METHODS

Materials

Raw kerosene from PORT HARCOURT Refinery was deodorized. Activated carbon, gotten from burnt woods dried up and grinded into powdered form. The high surface area per unit volume Characteristic of activated carbon is
obtained with a two-step process used in carbon manufacturing: Pyrolysis of raw material (typically a high carbon source such as coal, wood, nut shells) to drive off (distill) the lighter fraction producing a charred, highly carbonaceous solid residue, activation of the charred residue via oxidation (typically with air or steam) to form a network of pores and passages with high surface area. Iodine solution, Starch and sodium thiosulphate bought in the market were also used as reagents Oyom).

**Equipment**

Triple beam balance, OHAUS 750-SO 610g was used to weigh activated carbon. Other equipments used are filtering paper, measuring cylinder, glass sample Bottle, conical flask, glass funnel, Beaker, Bunsen burner, Tripod stand and Holders for funnels.

**Method**

Adsorption method used in this experiment as already discussed in the theory on how it works. In this report, the adsorbent being the activated carbon is used to remove the adsorbates which are the odorants or impurities in the kerosene.

The method used is a Batch adsorption, consists of contacting finely activated carbon with the raw kerosene for a given period of time in a beaker. The activated carbon used in this process is typically supplied in a powdered form to maximize surface area for mass transfer and minimize agitation for suspension. Typical carbón particle size: 10 - 50 mm.

After the process completion, (typical contact time: 10 - 60 minutes) the spent carbon is separated from the kerosene (e.g., by filtration) and regenerated or disposed of.

A specific amount of activated carbon is weighed in a triple weighing balance to determine the weight, and poured into a beaker. 20ml of raw kerosene is poured into the beaker containing the weighed activated carbon and allowed for a given time to enable adsorption to take place. The adsorbent, been the activated carbon, adsorbed the adsorbate (impurities) in the raw kerosene, which leaves it partly or wholly deodorized. A filter paper with funnel was used to separate the purified kerosene from activated carbon.

**RESULTS AND DISCUSSION**

Deodorization of kerosene by desulphurization using adsorption process simply means removal of sulphur compounds like sulphide as in this case from product. The adsorption of sulphur in kerosene took place in a beaker containing weighed activated carbon. After a given time, the mixture was separated into purified kerosene and rich activated carbon using filter paper with funnel.

Iodometric method was used to test for sulphide in kerosene after the deodorization process. A clean conical flask was used to measure 5ml of deodorized kerosene. 0.75ml of 0.025N of iodine solution was added to kerosene and allowed for 10minutes observational time, the sample was titrated with 0.025N sodium thiosulphate, using starch as indicator. The change from blue black to colorless indicates the end point.

Converting the end point value from ml to mg/LS² is obtained by the following equation

\[
\text{Base} + 5\text{ml} = \frac{A(s) - (C \times D) \times 16000}{\text{Volume of Sample}}
\]

Where

- A = Volume of iodine solution
- B = 0.025 N (Normality of iodine)
- C = Volume of Na₂S₂O₃
- D = Normality of Na₂S₂O₃ = 0.025N

The result for the first batch of experiment is shown in table one. As indicated in the table one, the end point value increases as time and mass of activated carbon increases. The end point value 0.75ml indicates absent of sulphide in the deodorized kerosene. A successful removal of the contaminants leaves kerosene partly or wholly deodorized depending on the efficiency of the adsorbent and time taken.
Table 1: For first batch of experiment

<table>
<thead>
<tr>
<th>Mass of Activated carbon used</th>
<th>Volume of untreated kerosene Used</th>
<th>Contact Time of raw kerosene and carbon</th>
<th>End point Results (titration with iodine)</th>
<th>End point Results in mg/1S²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1g</td>
<td>20ml</td>
<td>26mins</td>
<td>0.70ml</td>
<td>4.0</td>
</tr>
<tr>
<td>2g</td>
<td>20ml</td>
<td>28mins</td>
<td>0.72ml</td>
<td>2.4</td>
</tr>
<tr>
<td>3g</td>
<td>20ml</td>
<td>30mins</td>
<td>0.75ml</td>
<td>0</td>
</tr>
</tbody>
</table>

The result for second batch of the experiment is shown in table two. From the table, the end point value is below 0.75ml. Although the value increases as the time and mass of activated carbon increases. The result of this experiment shows that sulphur compounds were still present in the deodorized kerosene due to long contact time between the adsorbent and kerosene.

Table 2: For Second Batch of experiment

<table>
<thead>
<tr>
<th>Mass of Activated carbon used</th>
<th>Volume of Untreated Kerosene Used</th>
<th>Contact Time of raw kerosene and carbon</th>
<th>End point Results (titration with iodine)</th>
<th>End point Results in mg/1S²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1g</td>
<td>20ml</td>
<td>56min</td>
<td>0.64ml</td>
<td>8.8</td>
</tr>
<tr>
<td>2g</td>
<td>20ml</td>
<td>58min</td>
<td>0.65ml</td>
<td>8</td>
</tr>
<tr>
<td>3g</td>
<td>20ml</td>
<td>60min</td>
<td>0.68ml</td>
<td>5.6</td>
</tr>
</tbody>
</table>

In figure one, the graph of time against sulphur present as shown in table one and two is plotted. The graphs represent two batches of experiment (batch one and batch two). From the first graph, total absence of sulphur is on the point zero (0) at 30minutes. From the result, second and third values indicated low amount of sulphur present.

![Graph of Time against sulphur present](image)

Figure 1: Graph of Time against Results (converted end point value in mg/1S²)

The second graph in figure 2 indicates high amount of sulphur due to longer time taken for kerosene to deodorize on the fix volume. Sulphur content in kerosene is lower at point 5.6mg/1S²; this is because a higher amount of activated carbon was used in the process.
CONCLUSION

Deodorization of kerosene using activated carbon did not only remove or reduces smell but also converted some other contaminants into harmless substances in the process which made it suitable for domestic purpose. The experiment was done in two batches and was noticed that some sulphur compounds were still present especially in the second batch. This was because the pore holes or walls of adsorbent got weak due to time taken for that batch of experiment. In that case, the longer the time taken, the weaker the strength of adsorbent depending on the volume of kerosene to be deodorized and the quantity of adsorbent used accordingly.

Nomenclature

T - Degree Celsius
M - Mass – gram
G - Gallon liters
RHAC – Rice husk activated carbon
CSAC – Coconut shell activated carbon
BTs – Benzothiophenes
DBTs – Dibenzothiophenes
P - Pressure
σ – Surface or interfacial tension
G – Free energy
A – Area – M²
ML – Milliliter
MM – Millimeter
N - Normality
V/V – Volume to Volume

REFERENCES

Anozie, Okafor - (2005) Deodorization and de aromatization of kerosene by liquid extraction method.
Freundlich, Kuster - (1894) Wikipedia, the free encyclopedia.
Malcolm Tatum - (2003) WWW.Wisegeek.Com “how Kerosene is Deodorized”.