Determination Of Nitrogen And Sulphur Oxides Produced During Combustion Of Jatropha Cake Bio-Pellet

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Abstract

Jatropha cake is a promising renewable source of energy, its use as a combustible fuel makes it an important source of potentially harmful gases to the environment and the health of the users. It is important to determine the level of pollution caused by the Jatropha cake bio-pellet so as to take the necessary precautions to prevent the dangers that may be associated with the use of the fuel. Oiled and de-oiled Jatropha cake samples were burnt in a furnace to determine the amount of nitrogen oxides (NO\textsubscript{x}) and sulphur dioxide (SO\textsubscript{2}) produced during combustion. The effect of combustion temperature on the production of these gases was also investigated. NO\textsubscript{x} and SO\textsubscript{2} were collected in a mixture of aqueous ammonia and hydrogen peroxide and quantified as nitrates and sulphates. The amount of ash produced during combustion was determined at the temperature of 500\textdegree\textsuperscript{C}. The experiment also aimed at determining the alkaline metals contained in the ash. The results showed that the production of NO\textsubscript{x} and SO\textsubscript{2} increased with increasing temperature with the highest amount of NO\textsubscript{x} at 1200\textdegree\textsuperscript{C} and that of SO\textsubscript{2} at 800\textdegree\textsuperscript{C}. The metal content in the ash was found to be 10.9, 2.0, 9.0 and 1.1% of potassium, sodium, calcium and magnesium respectively.
1.0 Introduction

Biological material from living, or recently living organisms, most often referring to plants or plant-derived materials is known as biomass. This material may be classified into four groups: wood and agricultural products, solid waste, landfill gas and biogas, and alcohol fuels. As a renewable energy source, biomass can be used as it is or converted into another type of energy product such as biofuel. The Jatropha curcas plant has been used as a source of biofuel in some countries including Zimbabwe. The dry seed from the plant contains about 38-42% weight of oil which can be extracted by chemical or mechanical means (Singh et al., 2008). The cake that remains after extraction of oil from the seeds is classified as biomass.

Biomass can be converted to energy in three ways: thermal conversion, chemical conversion, and biochemical conversion (Houshfar et al, 2012; Raja et al., 2009; Jingura et al., 2010). Most biomass used today is home grown energy. Since biomass is combustible, its use of as a source of energy is important due to the continuous depletion of fossil fuels. However, combustion of fuels is associated with the production of smoke, particulate matter, soot volatile organic compounds and other air pollutants (Fine et. al., 2004). Although biomass is said to be carbon dioxide (CO₂) neutral, combustion of these sources releases the following measurable pollutants which may be used to estimate health risks; carbon monoxide (CO), hydrocarbons (CₚHₚ), nitrogen oxides (NOₓ), sulphur oxides (SOₓ), soot, dust, particles and formaldehyde. Nitrous oxide (N₂O) is also present in lesser amounts in combustion air, and this gas is important from a global warming perspective (Meiqiu and Yahui, 1994).
Biomass is an important renewable energy resource. In recent decades, several reasons have led to the dramatic increase in the utilization of biomass. First, biomass is a renewable resource, the availability of biomass is unlimited, and its regenerative process runs well. Second, the extraction of biomass energy can be carried out more flexibly; the biomass can be burned directly without the use of advanced technology (Pambudi, 2010). The recovery of energy from biomass and non-recyclable waste products by combustion has become important due to the mentioned advantages.

Other than the emissions from the combustion of biomass, ash is also produced which comprises inorganic salts. It has been noted that determination of chemical composition of biomass has been restricted to elemental composition because focus was mainly on its agricultural use (Misra et al., 1993). Even though wood ash composition has been determined, very little is known about the composition of ash from combustion of Jatropha cake although it has been known and used to improve soil fertility (Singh et al., 2008).

Jatropha cake which is a waste product from the production of bio-diesel is a promising source of energy. Its use as a combustible fuel makes it an important source of the mentioned air pollutants and many others. This study seeks to determine the calorific value of the local Jatropha cake and some of the factors that may affect this value, such as moisture content and oil content. The pollutants produced during combustion of the cake will also be quantified so as to determine the contribution of the Jatropha cake to pollution when it undergoes combustion. The focus will be mainly on the nitrogen oxides and sulphur dioxide which have a significant effect on health and
the environment. The effect of the combustion temperature on the production of the gases will also be monitored. There will also be a comparison between cake obtained by mechanical extraction and that obtained by chemical extraction. It will also be important to quantify the ash produced per given amount of sample. Characterization of the ash will then follow to determine the amounts of inorganic elements present. The elements of interest are sodium, calcium, magnesium and potassium.
1.1 Justification of the study

Recovery of energy from biomass by combustion has become important worldwide because they are thought to cause less air pollution than the fossil fuels. The biodiesel production process gives Jatropha cake as a by-product and it would be advantageous to obtain the energy from the cake through combustion rather than to put in more energy and resources into converting it to other forms which may seem useful in other areas.

Exposure to emissions from fossil fuels, mainly CO, NO$_x$, SO$_x$, suspended particulate matter which can be inhaled, and hydrocarbons is of serious public concern because of diseases of the respiratory system such as lung infections (Smith, 1993). Biofuels are called CO$_2$ neutral because the carbon in biofuels was recently extracted from atmospheric carbon dioxide by growing plants. However, combustion of all kinds of materials results in emissions that may be harmful to the environment, combustion devices and human health. There is emission of alkaline compounds and acidic gases. Nitrogen and sulfur oxides are also emitted during combustion of biofuels. (Venkataraman et al., 2005; Amand et al., 2006).

Studies have shown that combustion of biofuels such as wood, agricultural waste and dried animal manure in cooking stoves is the largest source of black carbon emissions and greenhouse gases in the South Asian region (Venkataraman et al., 2005). In a study by Pandey et al., (1989), rural areas in developing countries had high morbidity and mortality rates from acute respiratory infections owing to the high levels of indoor air pollution due to biofuels. It has also been found that continual exposure of the early man to campfires used as heat sources in enclosed areas
contributed to increased incidences of nasal cancers (Gaffney and Marley, 2009). Most of the information on the gaseous and particulate pollutants from wood is available (Venkataraman et al., 2005; Amand, et al., 2006); but very little is known about the components of the gases and the amounts that are produced during combustion of the Jatropha cake.

As a fuel that will probably be used for cooking, Jatropha cake has a high potential to be used indoors at domestic level. It is important to determine the level of pollution possible if Jatropha cake is used as a fuel so as to protect the environment and the health of the users. Knowing these levels of pollution may assist in taking the necessary precautions to prevent the dangers that may be associated with its use. However, combustion of biomass may be beneficial in that it results in ash that can be used to increase soil fertility (Singh et al., 2008). The ash contains elements that are useful to plants such as potassium and phosphorus. The ash may also be used for soap making as it contains the alkali earth metals which are important in the saponification process.
1.2 Hypotheses

The full energy potential of the Jatropha cake may be released if it is used as a fuel; however, like all other fuels smoke is emitted that contains acidic gases such as the nitrogen oxides and sulfur dioxide which may be harmful to the environment and humans. The ash resulting from combustion of the cake may be useful for soap making.

1.3 Main objective

The main objective is to burn oiled and de-oiled Jatropha cake samples in a controlled environment and determine the amounts of nitrogen and sulphur oxides produced during combustion of the fuel and to characterize the resulting ash from the combustion.

1.4 Specific Objectives

1. To use chemical extraction to determine the amount of oil remaining in the cake after the mechanical extraction process and to determine the calorific value of the cake before and after removing the oil.

2. To quantify NO$_x$ and SO$_2$ gases produced from combustion of Jatropha cake by collecting in aqueous ammonia.

3. To determine amount of ash produced per given amount of sample and quantify Na$^+$, K$^+$, Mg$^{2+}$ and Ca$^{2+}$ in the ash.
2.0 Literature review

The Jatropha *curcas* plant grows quickly from cuttings and it is a tropical plant that can be grown in low to high rainfall areas. It is a multi-purpose plant with many attributes and considerable potential apart from it being an important source of biofuel. It has been grown to reclaim land and also as a living fence around fields to protect crops from the grazers, due to the toxicity of most of the varieties to animals (Gubitz *et al*., 1999). The plant’s hardiness and rapid growth makes it a prime candidate for erosion control and land reclamation. It has been reported that the plant has been grown in Cuba for reasons including prevention of soil erosion by wind and water and improvement of soil fertility, (Openshaw, 2000).

The Jatropha cake is a result of pressing of Jatropha seeds to extract oil for biodiesel production. The mechanical extraction yields 30% - 38% of crude oil which may be used as crude or after its trans-esterification. (Forson *et al*., 2004). The cake is generally about 50-70% of weight of the dry seeds. The cake contains carbohydrates, fibers, proteins and the remainder of the oil which may be 9-12% by weight depending on the extraction efficiency and average oil content of the seeds. The high protein content and hence the nitrogen content makes the cake useful as an organic fertilizer. The cake has been found to contain toxic components, but after these are removed, the cake could be used as animal food. Compared to other seeds such as the rape seed, the Jatropha curcas seed, and hence the cake has a high protein content of about 23% (Nayak and Patel, 2010; Montes *et al*., 2011).

Jatropha oil cake has also been found to be useful in the production of biogas (Jingura *et al*., 2010). The major components of press cake are hemicellulose, cellulose and lignin which can be
broken down to produce bio-oils, gas and char. These products are important energy carriers (Jingura et al., 2010). Pyrolysis is also a promising thermochemical conversion technology for recovering energy from biomass (Wannapeera et al., 2008). Fluidized bed flash pyrolysis experiments have been conducted on a sample of Jatropha oil cake to determine particularly the effects of particle size, pyrolysis temperature, and nitrogen gas flow rate on the pyrolysis yields. The particle size of Jatropha oil cake was varied in the range of 0.3–1.18 mm. Reaction temperatures varied from 350°C to 550°C. The nitrogen gas flow rate varied from 1.25 to 2.4 m³/hour. The maximum oil yield of 64.25 wt% was obtained at a nitrogen gas flow rate of 1.75 m³/hour, particle size of 0.7–1.0 mm, and at a pyrolysis temperature of 500°C. Flash pyrolysis experiments of Jatropha oil cake were performed in an electrically heated bubbling fluidized bed reactor under nitrogen atmosphere. The highest yield of oil 64.25 wt% was obtained at a final pyrolysis temperature of 500 °C with a particle size of 0.7–1.0 mm and nitrogen flow rate of 1.75 m³/hour. The pyrolysis oil was identified as a biofuel candidate. The liquid may be used as a source of low-grade fuel directly or it may be upgraded to higher quality liquid fuels. The pyrolysis gas was found to be useful as fuel gas (Raja et al., 2009). Thermogravimetric analysis (TGA) of thermal degradation products showed that the production of hydrogen gas increased with increase in pyrolysis temperature. Thus, hydrogen gas can be produced directly through pyrolysis at high temperature. Hydrogen is a clean energy carrier with a high calorific value (142MJ/ kg).

The cake may also be made into bio-pellets or briquettes (Plistil et al., 2005) and used as fuel for cooking in place of firewood or other sources of energy. In a study by Pambudi (2010), the following results were obtained for the comparison between the heating value of Jatropha curcas
solid waste (cake seed, shell and sludge): for the cake seeds it was 16.97 MJ/Kg, for the shells it was 17.2 MJ/Kg and sludge was 29.7 MJ/Kg. The sludge had the highest heating value, the reason being that it still had a high content of oil. Studies have shown that the oil remaining in the cake influences the gross energy value of press-cake. The oil may be removed by chemical extraction which involves solvent extraction with n-hexane.

The Jatropha cake is renewable and has a high calorific value which makes it useful as an energy source. The calorific value can be compared to that of other common fuels (Table 1) including wood (16MJ/kg) and low temperature coke (26MJ/Kg) (Rose, 1977).

**Table 1: Calorific values of typical fuels**

<table>
<thead>
<tr>
<th>Type of Fuel</th>
<th>Energy Kcal/Kg</th>
<th>MJ/Kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPG</td>
<td>11,100</td>
<td>46.47</td>
</tr>
<tr>
<td>Heating Oil</td>
<td>10,100</td>
<td>42.29</td>
</tr>
<tr>
<td>Natural Gas</td>
<td>9,100</td>
<td>38.10</td>
</tr>
<tr>
<td>Wood Charcoal</td>
<td>7,500</td>
<td>31.40</td>
</tr>
<tr>
<td>Charcoal Fines Briquettes (No Adulteration)</td>
<td>7,400</td>
<td>30.98</td>
</tr>
<tr>
<td>Paper Briquettes</td>
<td>4,800</td>
<td>20.10</td>
</tr>
<tr>
<td>Sawdust Briquettes</td>
<td>4,800</td>
<td>20.10</td>
</tr>
<tr>
<td>Wood Pellets</td>
<td>4,500</td>
<td>18.84</td>
</tr>
<tr>
<td>Wood</td>
<td></td>
<td>16.00</td>
</tr>
</tbody>
</table>
Upgraded biomass fuels, that is, pellets and briquettes have become more common during recent years. The fuel pellets, are well suited for home heating applications and cooking (Rhen, et al., 2006). Briquettes have also been made from the Jatropha cake by mixing appropriate ratios of the cake with coal so as to improve its efficiency and reduce emissions of fossil fuels (Sakamoto et al., 2001). However, although emissions from fossil fuels are reduced, the addition of coal to Jatropha cake increases the heating value of biomass as well as the emissions.

Complete combustion of biofuels results in carbon dioxide emission, but because approximately the same amount of CO$_2$ is used to grow the biomass, it does not result in net increase of CO$_2$ in the earth’s atmosphere. Biofuels are called CO$_2$ neutral because the carbon in these fuels was recently extracted from atmospheric CO$_2$ by growing plants during photosynthesis (EPA, 2002). This is in contrast to fossil fuels that contain carbon that was encaptured millions of years ago. However, complete combustion is almost impossible to achieve. In reality, as actual reactions come to equilibrium, a wide variety of major and minor species such as carbon monoxide (CO) and pure carbon (soot) will be present. Additionally any combustion in atmospheric air will also create several forms of oxides (Endecot et al., 1994). NO$_x$ emissions range from about 303 mg/m$^3$ (95 g/GJ) for wet wood to 674 mg/m$^3$ (211 g/GJ) for dry wood. The hotter burning dry wood can yield higher flame temperatures if not controlled (for example, with overfire air or flue gas recirculation) and therefore, greater NO$_x$ formation. However, NO$_x$ controls are focused on reducing flame temperature without compromising combustion efficiency or heat transfer (Gadi et al., 2003).
Combustion produces ash and smoke which consists of gases and airborne particles. In a report by the EPA (2002), it was pointed out that specific chemicals in smoke depend on the type of fuel used but includes the following: unreacted air, CO₂, CO, H₂O, volatile organic compounds (VOCs), NOₓ, SOₓ, aldehydes (formaldehyde, furfural), polycyclic aromatic hydrocarbons, alkylbenzene (toluene) and hydrogen cyanide. Smoke drastically weakens the lungs’ immune system. Research has found that continual exposure of early man to camp fires used as heat sources in enclosed areas contributed to increased incidences of nasal cancers. Any material undergoing combustion can produce toxic gases (Gaffney and Marley, 2009).

Studies by Gadi et al. (2003) in India have shown that biofuels, among other fuels, contribute to the NOₓ and SOₓ in the atmosphere. Data in Table 2 and Table 3 (Gadi et al., 2003) show results of the contribution to NOₓ and SOₓ of different sources over a number of years. In the study, evaluation of emission factors, based on the laboratory studies carried out on various biofuels, showed that SO₂ emissions are lowest from bagasse and highest from dung cakes, while for NOₓ it is the opposite.
Table 2: NO$_x$ and SO$_2$ emissions from India for several years

<table>
<thead>
<tr>
<th>Source</th>
<th>SO$_2$ (Tg)</th>
<th>NO$_x$ (Tg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthropogenic sources &amp; volcanic eruptions</td>
<td>3.08 in 1987</td>
<td>2.56 in 1987</td>
</tr>
<tr>
<td>Energy sources</td>
<td>1.65 in 1975</td>
<td>1.38 in 1975</td>
</tr>
<tr>
<td></td>
<td>2.01 in 1980</td>
<td>1.67 in 1980</td>
</tr>
<tr>
<td></td>
<td>3.01 in 1987</td>
<td>2.56 in 1987</td>
</tr>
<tr>
<td>Biofuels</td>
<td>0.91 in 1990</td>
<td></td>
</tr>
<tr>
<td>Anthropogenic sources</td>
<td>5.1 in 1990</td>
<td></td>
</tr>
<tr>
<td>Biofuels</td>
<td>0.88</td>
<td>0.46</td>
</tr>
<tr>
<td>Biomass burning</td>
<td></td>
<td>0.109</td>
</tr>
<tr>
<td>Anthropogenic sources</td>
<td>4.83–8.33</td>
<td></td>
</tr>
<tr>
<td>Anthropogenic sources</td>
<td>3.48 in 1990</td>
<td>5.62 in 2000</td>
</tr>
<tr>
<td>Total biomass</td>
<td>0.94 for 1990</td>
<td></td>
</tr>
<tr>
<td>Anthropogenic sources</td>
<td>2.0 for 1990</td>
<td></td>
</tr>
<tr>
<td>All sources</td>
<td>3.4 in 1985</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.44 in 1990</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.04 in 1995</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.28 in 1997</td>
<td></td>
</tr>
<tr>
<td>Biomass burning</td>
<td>0.24</td>
<td>0.65</td>
</tr>
<tr>
<td>All sources</td>
<td>4.64</td>
<td>3.46</td>
</tr>
<tr>
<td>Biofuels</td>
<td>0.4 ± 0.3</td>
<td>1.0 ± 0.4</td>
</tr>
</tbody>
</table>

($Tg$ – teragrams = $10^{12}$ grams)
Table 3: NO\textsubscript{x} and SO\textsubscript{2} emission factors

<table>
<thead>
<tr>
<th>Fuel type</th>
<th>SO\textsubscript{2}</th>
<th>NO\textsubscript{x}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residential heating</td>
<td>0.23 g kg\textsuperscript{-1}</td>
<td>0.77 g kg\textsuperscript{-1}</td>
</tr>
<tr>
<td>Residential cooking</td>
<td>0.6 g kg\textsuperscript{-1}</td>
<td>0.7 g kg\textsuperscript{-1}</td>
</tr>
<tr>
<td>Cowdung</td>
<td>6 g kg\textsuperscript{-1}</td>
<td></td>
</tr>
<tr>
<td>Biomass burning</td>
<td>0.78 g S kg C\textsuperscript{-1} (0.62 g kg\textsuperscript{-1})</td>
<td>-</td>
</tr>
<tr>
<td>Fuel wood</td>
<td></td>
<td>0.5 g N kg\textsuperscript{-1}</td>
</tr>
<tr>
<td>(Savanna plants)</td>
<td></td>
<td>(1.64 g kg\textsuperscript{-1})</td>
</tr>
<tr>
<td>Firewood (Australian Savanna fires)</td>
<td></td>
<td>2.1 g kg\textsuperscript{-1}</td>
</tr>
<tr>
<td>Fuel wood (SAFARI 92 and FOS/DECAPE-91)</td>
<td>0.37-2.09 g N kg\textsuperscript{-1}</td>
<td>(1.22-6.87 g kg\textsuperscript{-1})</td>
</tr>
<tr>
<td>Firewood</td>
<td>0.69 ± 0.18 g N/kg (2.27 ± 0.59 g kg\textsuperscript{-1})</td>
<td>0.02 ± 0.02 g N kg\textsuperscript{-1} (0.07 ± 0.07 g kg\textsuperscript{-1})</td>
</tr>
<tr>
<td>Charcoal production</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Firewood (Savanna fires)</td>
<td>0.6 g kg\textsuperscript{-1}</td>
<td>3.1 g kg\textsuperscript{-1}</td>
</tr>
<tr>
<td>Bagasse</td>
<td>0.23 g kg\textsuperscript{-1}</td>
<td>0.68 g kg\textsuperscript{-1}</td>
</tr>
<tr>
<td>Fuel wood</td>
<td>0.18 g kg\textsuperscript{-1}</td>
<td>1.23 g kg\textsuperscript{-1}</td>
</tr>
<tr>
<td>Fuel wood</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residential cooking</td>
<td>0.6 g kg\textsuperscript{-1}</td>
<td></td>
</tr>
<tr>
<td>Residential heating</td>
<td>0.23 g kg\textsuperscript{-1}</td>
<td></td>
</tr>
<tr>
<td>Dung</td>
<td>6.0 g kg\textsuperscript{-1}</td>
<td></td>
</tr>
<tr>
<td>Agricultural waste</td>
<td>0.52 g kg\textsuperscript{-1}</td>
<td></td>
</tr>
<tr>
<td>Fuel wood</td>
<td>0.58 g kg\textsuperscript{-1}</td>
<td>0.70 g kg\textsuperscript{-1}</td>
</tr>
<tr>
<td>Crop residue</td>
<td>0.52 g kg\textsuperscript{-1}</td>
<td>1.3 g kg\textsuperscript{-1}</td>
</tr>
<tr>
<td>Animal waste</td>
<td>1.24 g kg\textsuperscript{-1}</td>
<td>0.24 g kg\textsuperscript{-1}</td>
</tr>
<tr>
<td>Firewood, vegetable waste and dung</td>
<td></td>
<td>0.10-0.12 G g PJ\textsuperscript{-1} (2-2.4 g kg\textsuperscript{-1})</td>
</tr>
<tr>
<td>Wood</td>
<td>2.25 g kg\textsuperscript{-1}</td>
<td>-</td>
</tr>
<tr>
<td>Cattle dung, agriculture residue, forest biomass, grassland</td>
<td>1.55 g kg\textsuperscript{-1}</td>
<td></td>
</tr>
<tr>
<td>Fuel wood</td>
<td>0.8 g kg\textsuperscript{-1}</td>
<td>2 g kg\textsuperscript{-1}</td>
</tr>
<tr>
<td>Dung</td>
<td>0.6 g kg\textsuperscript{-1}</td>
<td>0.86 g kg\textsuperscript{-1}</td>
</tr>
<tr>
<td>Agriculture residue</td>
<td>0.6 g kg\textsuperscript{-1}</td>
<td>0.86 g kg\textsuperscript{-1}</td>
</tr>
<tr>
<td>Charcoal</td>
<td>-</td>
<td>2.76 g kg\textsuperscript{-1}</td>
</tr>
</tbody>
</table>
The nitrogen and sulphur oxides are a result of oxidation of nitrogen and sulphur in the fuel and to some extent in the air above the flame. The parental compounds \( \text{SO}_2 \) and \( \text{NO}_2 \) themselves in air are established to have direct health effects on humans. Being a mild to strong irritant, \( \text{SO}_2 \) in the air is established to have quick effects on respiratory function. Long term respiratory effects are now also becoming more evident. Under quiet nasal breathing, \( \text{SO}_2 \) has more prominent effect only as far as the nose and throat. A study conducted for Canadian Centre for Occupational Health and Safety in 1997 revealed that short exposure (1-6 hours) with low concentration of 1ppm show reversible decrease in lung function. Shorter duration of higher concentration (5ppm) produces bronchial constriction. Very high concentration in closed spaces causes severe airway obstruction, hypoxemia, and pulmonary oedema. Long term exposure of many years (of even less than 5ppm) is believed to cause pulmonary impairment.

Nitrogen oxides (\( \text{NO}_x \)) is a group of different gases made up of different levels of oxygen and nitrogen, the most common being nitrogen dioxide (\( \text{NO}_2 \)) and nitric oxide (\( \text{NO} \)). The oxides of nitrogen and sulphur can combine with water in the atmosphere and cause acid rain which is harmful to the environment and animals. Oxides of nitrogen like nitrogen dioxide (\( \text{NO}_2 \)) react with water to form nitrous acid (\( \text{HNO}_2 \)) and nitric acid (\( \text{HNO}_3 \)) as shown by the equation:

\[
2\text{NO}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HNO}_2(aq) + \text{HNO}_3(aq)
\]

Sulfur dioxide and water form sulfurous acid (\( \text{H}_2\text{SO}_3 \)) as in the reaction:

\[
\text{SO}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{SO}_3(aq)
\]
In some cases sulfur dioxide (SO$_2$) oxidizes to sulfur trioxide (SO$_3$) which then combines with water to make sulfuric acid (H$_2$SO$_4$) as shown by the following equations:

\[
\begin{align*}
2\text{SO}_2(g) + \text{O}_2(g) & \iff 2\text{SO}_3(g) \\
\text{SO}_3(g) + \text{H}_2\text{O}(l) & \iff \text{H}_2\text{SO}_4(aq)
\end{align*}
\]

The negative impacts of acid rain are mostly direct on vegetation, soil, aquatic-life creatures and buildings. Aquatic life creatures like frogs and fish, have difficult time adapting to and reproducing in an acidic environment. Studies have shown that the small fish are the most affected by the low pH of water, if there are no small fish then this will lead to starvation of the bigger fish and the food chain is affected (Schindler, 1988). The acid in rain water is too dilute to have significant health effects on humans directly. However, acid rain causes leaching of toxic trace metals from soil and this may cause contamination of ground water sources. Lead plumbing exposed to acidified water has a risk of lead entering drinking water (Goyer et al., 1985).

The term volatile organic compounds (VOCs) refers to a wide group of organic compounds (alkanes, alkenes, aromatic compounds, aldehydes and ketones) whose vapor pressure is at least 0.01 kPa at 20 °C (Fernández-Martínez et al., 2001). VOCs are also characterized by their low water solubility. The VOCs are a product of combustion and once they are in the atmosphere participate in photochemical reactions producing photochemical oxidants. Their high vapor pressure results from a low boiling point, which causes large numbers of molecules to evaporate
or sublimate from the liquid or solid form of the compound and enter the surrounding air. Many VOCs are dangerous to human health or cause harm to the environment.

The toxic gases that are emitted during combustion are acidic. There are several methods for the determination of products of combustion in the gaseous form. Endecot et al., (1994) designed a gas chromatographic (GC) method for the determination of toxic gases present in combustion atmosphere. GC with a high sensitivity thermal conductivity detector (TCD) was used and the results showed that the method was effective for individual and simultaneous determination of four toxic gases (CO, H₂S, HCN and SO₂).

Acidic gaseous products can be collected in an alkaline solution such as aqueous ammonia (Resnik et al., 2004). Collection in alkaline solution produces ammonium sulphate and ammonium nitrate which can be determined calorimetrically. The method of collecting in aqueous ammonia was developed as an alternative to the one that used mono-ethanolamine due to its disadvantage of low carbon dioxide loading capacity.

As was noted earlier, combustion of biomass produces ashes which may be put to good use since they contain alkaline metals. Depending on the use of the fuel, the ash may actually be problematic due to deposits on heat transfer surface on the combustion device (Amand et al., 2006), this may cause interference on operation and eventually lead to corrosion or blockage of gas paths.
3.0 Methodology

The cake used in the study was obtained from Mutoko, Zimbabwe by random selection. The cake was crushed and pulverized to obtain a homogeneous sample. Chemical extraction using n-hexane was used to obtain the oil-free cake. The study was carried out as shown in the flow diagram below:

![Flow diagram of the methodology]

**Figure 1: Flow diagram of the methodology**
3.1 The major instruments that were used

An IKA C5003 Bomb calorimeter was used for the determination of the calorific value and percent sulphur. The oxygen pressure was 25 atm, the temperature temperature was $20 \pm 0.2^\circ$C.

A Shimadzu Flame Atomic Absorption (FAA) spectrometer was used in the determination of the metals in the ashes. An air acetylene flame was used.

A UV-Visible spectrophotometer was used for the determination of the oxidized forms of nitrogen and sulphur ($\text{NO}_3^-$ and $\text{SO}_4^{2-}$ respectively).

A double tube sulphur furnace from Leonara Light Industries was used for the combustion of Jatropha cake samples and collection of $\text{NO}_x$ and $\text{SO}_2$.

3.2 Preparation of Standard solutions

1000 ppm of the stock solutions were prepared as follows:

**Calcium stock solution** was prepared by dissolving 0.2497g CaCO$_3$ in 5ml concentrated HCl and solution diluted to 100ml.

**Magnesium stock solution** was prepared by dissolving 0.1g Mg metal in 10ml concentrated HCl, this was then diluted to 100ml.

**Potassium stock solution** was prepared by dissolving 0.2542g KNO$_3$ in 5ml deionized water, 1ml concentrated HCl was added and solution diluted to 100ml.

**Sodium stock solution** was prepared by dissolving 0.1907g NaCl in 5ml deionized water, 1ml concentrated HCl was added and solution diluted to 100ml.
Ammonia 14% solution was prepared by dilution.

Nitrate stock solution was prepared by dissolving 1.629g potassium nitrate in 1 litre deionized water.

Sulphate stock solution was prepared by dissolving 1.5729g sodium sulphate (Na\textsubscript{2}SO\textsubscript{4}) in 1 litre deionized water.

3.3 Analytical procedures

Several analytical methods were used for determination of the various parameters, metals and anions.

3.3.1 Determination of moisture and total volatile organic compounds

Moisture content was determined by heating a 1.0g sample at 110\textdegree{}C in an oven for 24 hours. After drying, the sample was reweighed and total moisture loss determined. The total volatile organic compounds were determined by ignition of a 1.0g sample in a furnace at 550\textdegree{}C. The sample was left in the oven for 12 hours after which it was cooled and weighed to determine the total mass loss (Vogel, 1989).

3.3.2 Determination of ash content of Jatropha cake

Ash content was determined by igniting a 1.0g sample of the cake at 550\textdegree{}C in a furnace, the sample was left at this temperature for 24 hours. The resulting ash was weighed (Misra et al., 1993).
3.3.3 **Determination of oil content of Jatropha cake**

Soxhlet extraction was used for the determination of the oil from 1.0g of the Jatropha cake, the solvent used was n-hexane. After extraction, a rotary evaporator was used to remove the solvent from the oil which was then weighed (Nzikou *et al.*, 2009).

3.3.4 **Determination of nitrogen content of Jatropha cake**

The kjehldahl method was used for the determination of nitrogen. The sample was digested in concentrated sulphuric acid followed by steam distillation and titration of free ammonia which was liberated in the presence of excess alkali. The distillate was collected in a receiver (50ml conical flask) containing excess boric acid with drops of mixed indicator (Nayak and Patel, 2010).

3.3.5 **Determination of sulphur content of the cake**

Combustion of sample was done in a bomb calorimeter. The washings were collected and titrated with standard sodium carbonate followed by neutralization with aqueous ammonia. Solution was boiled, filtered and 10ml of concentrated HCL was added. 10% Barium chloride was added whilst boiling the solution. Solution was then covered and precipitate allowed to settle for an hour after which it was filtered through an ash-less filter paper. After several washings, the filter paper and sample was placed in a weighed crucible and ignited (Mohammed and Adamu, 2009).
3.3.6 Determination of metals

The sample was ignited at 500°C for 24 hours, followed by acid digestion of sample. The concentration of metals in the resulting solution was determined by flame atomic absorption (FAA) (Vogel, 1989). A composite standard solution was prepared for the determination of Na⁺, K⁺, Ca²⁺ and Mg²⁺.

3.3.7 Collection of gases

The simultaneous collection of the NOₓ and SO₂ was done using the sulphur furnace shown in Figure 3. The gases were collected in a mixture of 14% aqueous ammonia solution and 1% hydrogen peroxide. The nitrate and sulphate formed were determined by colorimetric methods (Gadi et al., 2003).

Figure 2: Setup for collection of combustion gases
3.3.8 Determination of NOx collected as nitrate

Nitrate was measured calorimetrically at 410nm by measuring the intensity of the yellow color developed by reaction of phenol-disulfonic acid with nitrates (Jenkins and Medsker, 1964). A blank was also carried out to minimize errors. Nitrate, (NO$_3^-$) was reacted with phenodisulfonic acid to give a yellow color with an absorption maximum at 410nm. Chloride interference was removed by precipitating with silver sulphate.

3.3.9 Determination of SO$_2$ collected as sulphate

Sulphate was measured calorimetrically at 420nm using turbid metric method (APHA, 1980). Sulphate ion was precipitated with barium ion in an acid solution to form barium sulphate crystals of uniform size. Standard sulphuric acid solution was used to prepare sulphate standard solution. A blank was carried out to minimize errors. Both standards and unknowns were treated equally and processed at the same time.
4.0 Results and discussion

Table 4: Characteristics of the Jatropha seed cake

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Jatropha cake</th>
<th>Oil-free Jatropha cake</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calorific Value MJ/kg</td>
<td>17.96 ± 0.29</td>
<td>17.00 ± 0.18</td>
</tr>
<tr>
<td>Oil content %</td>
<td>10.83 ± 0.65</td>
<td>- -</td>
</tr>
<tr>
<td>Moisture content %</td>
<td>6.55 ± 0.58</td>
<td>7.25 ± 0.10</td>
</tr>
<tr>
<td>Volatile matter %</td>
<td>90.90 ± 0.003</td>
<td>90.90 ± 0.00</td>
</tr>
<tr>
<td>Ash %</td>
<td>9.00 ± 0.00</td>
<td>9.00 ± 0.00</td>
</tr>
</tbody>
</table>

Figure 3: Oil content of Jatropha cake samples
Figure 4: Calorific values of Jatropha cake samples

Figure 5: Moisture content of Jatropha cake samples
The oil remaining in the Jatropha seed cake from the mechanical extraction is between 10-12% of the weight of the cake. These values are in agreement with the literature values. The calorific values of the cake imply that it is useful as an energy source for use with, or substitution of wood, sawdust or paper briquettes (Rose, 1977). The calorific values for the Jatropha seed cake and de-oiled Jatropha seed cake are 17.96 ± 0.29MJ/kg and 17.00 ± 0.18 MJ/kg respectively. Figure 4 shows that the calorific value of the Jatropha seed cake is lower for the oil-free cake by about 1.00 MJ/kg compared to that of the cake with oil. It is evident that the remainder of the oil in the cake contributes to the calorific value of the samples (Jingura et al., 2010), this makes the process of oil removal unimportant if the cake is to be used as a source of fuel since the high oil content gives a greater calorific value.

The moisture content of biomass has a great impact on its effectiveness as a fuel source (Wright Tech Systems Inc., 2006). The de-oiled Jatropha seed cake had high percentages of moisture which (Figure 5). The high moisture content may have contributed to the low calorific values in addition to the lowering due to the absence of oil. The absence of oil may have promoted adhering of water molecules from the atmosphere onto the cake samples. This effect was absent in the cake with oil since oil and water do not mix.
Table 5: Elemental content of the Jatropha cake ash

<table>
<thead>
<tr>
<th>Element</th>
<th>Jatropha cake</th>
<th>Oil-free Jatropha cake</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium %</td>
<td>10.87±0.25</td>
<td>5.10±0.11</td>
</tr>
<tr>
<td>Sodium %</td>
<td>2.04±0.07</td>
<td>2.56±0.27</td>
</tr>
<tr>
<td>Calcium %</td>
<td>8.82±0.19</td>
<td>6.80±0.61</td>
</tr>
<tr>
<td>Magnesium %</td>
<td>1.11±0.05</td>
<td>0.45±0.16</td>
</tr>
<tr>
<td>Nitrogen %</td>
<td>2.7</td>
<td>2.8</td>
</tr>
<tr>
<td>Sulphur %</td>
<td>0.6</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The metal content of the Jatropha seed cake ash and the de-oiled Jatropha seed cake ash are comparable as shown in Table 5 and Figures 6 - 9. The slight differences in percentages may be due to loses of elements to the gas phase. Studies have shown that during the complex combustion process, a part of the volatile compounds, including the alkali metals, sulphur, chlorine and heavy metals are released from the fuel to the gas phase and subsequently undergo homogeneous gas phase reactions. High concentrations of Na, K, Pb and Zn may have resulted in high aerosol formation (Brunner et al., 2002).

The current results show that the cake may be useful in soap making since the metal content in the ash is quite significant. The ash is rich in potassium and this will give a soft soap. However, studies have to be done to see the effects of the other metals on the soap quality.
Figure 6: Sodium content in Jatropha cake ash samples

Figure 7: Potassium content of Jatropha cake ash samples
Figure 8: Calcium content of Jatropha cake ash samples

Figure 9: Magnesium content of Jatropha cake ash samples
Table 6: The amount of NO\textsubscript{x} at various furnace temperatures

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>NO\textsubscript{x} ppm (cake with oil)</th>
<th>NO\textsubscript{x} ppm (de-oiled cake)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>8.13</td>
<td>1.83</td>
</tr>
<tr>
<td>600</td>
<td>2.45</td>
<td>2.41</td>
</tr>
<tr>
<td>800</td>
<td>4.05</td>
<td>3.47</td>
</tr>
<tr>
<td>1000</td>
<td>4.58</td>
<td>5.51</td>
</tr>
<tr>
<td>1200</td>
<td>6.81</td>
<td>10.13</td>
</tr>
</tbody>
</table>

Table 7: The amount of SO\textsubscript{2} at various furnace temperatures

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>SO\textsubscript{2} ppm (cake with oil)</th>
<th>SO\textsubscript{2} ppm (de-oiled cake)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.87</td>
<td>0.58</td>
</tr>
<tr>
<td>600</td>
<td>0.58</td>
<td>0.87</td>
</tr>
<tr>
<td>800</td>
<td>1.44</td>
<td>1.74</td>
</tr>
<tr>
<td>1000</td>
<td>0.12</td>
<td>0.12</td>
</tr>
<tr>
<td>1200</td>
<td>0.50</td>
<td>0.30</td>
</tr>
</tbody>
</table>
Figure 10: The effect of temperature on the amount of NO\textsubscript{x} produced during combustion
The apparatus shown in Figure 2 was used for the determination of the nitrogen and sulphur oxides. The fuel was observed to ignite and burn often almost immediately upon entry into the furnace, as has been reported elsewhere during co-combustion with coal and paper, plastic waste (Boavida et al., 2003). Oxides of nitrogen (NO\textsubscript{x}), primarily nitric oxide (NO) and nitrogen dioxide (NO\textsubscript{2}) are formed by the oxidation of nitrogen, both in the fuel and in the air, with the fuel nitrogen being more reactive. The nitrogen oxides and sulphur dioxide that resulted from combustion of Jatropha cake samples were collected in aqueous ammonia as the nitrate and sulphate respectively.
The results show a general increase in the amount of NO\textsubscript{x} with increasing temperature for both the oiled and de-oiled Jatropha cake which agrees with the literature (Khan et al., 2012). The initial high amount of NO\textsubscript{x} in the oiled cake may have been due to some compound that could have been extracted by hexane with the oil or conversion of volatile nitrogen containing species NH\textsubscript{3} and HCN at the lower temperature (Houshfar \textit{et al}, 2012). It has also been found that high amounts of these oxides at high temperatures (>~1600\textdegree{}C) are due to the oxidation of fuel elements and oxidation of elements in the combustion air (Habib \textit{et al.}, 2008). Although such high temperatures were not used, there is a chance that oxidation of elements in the combustion air contributed to NO\textsubscript{x} since it was difficult to lower the temperature of the furnace.

The results also show that the amount of SO\textsubscript{2} increases with temperature for both the oiled and de-oiled Jatropha cake, then decreases from about 800\textdegree{}C. This agrees with literature information although other factors may have influenced the values such as steam (Khan \textit{et al.}, 2012). However, the cause for the increase beyond 1000\textdegree{}C is not known. The initial high amount of the SO\textsubscript{2} in the oiled cake may also have been due to the same or similar compound that caused the initial high amount of NO\textsubscript{x}, which may have been removed during the chemical extraction of the oil. It is possible that the compound may be due to contamination rather than a fuel component.
5.0 Conclusion

In the study, it was found that the calorific value of Jatropha cake is about 18MJ/kg. This value is comparable to that of the wood sources that are currently available (see Table 1). The calorific value for the press cake (oiled) was higher than that of the cake after chemical extraction (de-oiled). It was also found that during combustion of the Jatropha cake, NO$_x$ and SO$_2$ are emitted; the amount of SO$_2$ emitted during the combustion is greater than NO$_x$. Compared to other biomass fuels and fossil fuels (Table 3) the amounts of NO$_x$ and SO$_x$ produced during combustion of Jatropha cake are quite low (Tables 6 and 7). About 0.02mg/kg NOx being produced at the flame temperature of about 1000$^\circ$C and about 0.15mg/kg SO2 at a temperature of 800$^\circ$C. These values makes the Jatropha cake more friendly to the environment when used as a fuel. It was also determined that the ash from combustion of the fuel had significant amounts of the alkaline metals and this makes it useful for soap making. Thus, if the cake is used as a source of energy, then the ash for soap making, the energy of the Jatropha cake would have been maximized.
6.0 Recommendations

There is still need to continue researching on the fuel characteristics of Jatropha cake by:

- Determining characteristics of aerosols and flying ash produced during combustion of Jatropha cake;
- Determining detailed information about formation process of aerosols and flying ash;
- Determining the emission factor of Jatropha cake and also
- Determining the effect of temperature on the amount of ash and its composition.
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