Chapter One

Introduction

1.0 Introduction

The worldwide worry about the protection of environment and the dependence on fossil fuel has given rise to development of alternative energy sources as substitute for traditional fossil fuels. Fossil fuel sources are non-renewable, and will be exhausted in the near future. According to Alekett, (2003) the world's oil reserves are up to 80 percent less than predicted, this calls for alternative sources of energy Biodiesel can be a wonderful replacement to conventional petro-diesel fuel, which can be produced from a renewable domestic resource. It is simply produced by transesterification process whereby the vegetable oil or animal fat (Triglyceride) react in presence of a catalyst with a primary alcohol to give the corresponding alkyl esters of the fatty acid mixture that is found in the parent vegetable oil or animal fat.

The oil used in the process can come from many sources including soybeans, corn, canola, and used frying oil. Because it comes from renewable resource, it is referred to as a biofuel. The process involves taking the oil, a triglyceride, combining it with an alcohol, to form biodiesel, which is either an ethyl ester or a methyl ester. The uses a base, either potassium hydroxide or sodium hydroxide can be used as a catalyst to help in the process

Biodiesel is gaining increasing acceptance in the market as an environmental friendly alternative diesel fuel . It is non-toxic, biodegradable, and free of sulphur or any carcinogenic compounds . The demand and cost of edible oils prevents its use in the production of biodiesel. So, a large variety of plants that produce non-edible oils are considered for biodiesel production. In Sudan, there are several non-edible oil seed species such as Jatropha curcas (Jatropha), Pongamia pinnata

(Karanja), Azadirachta indica (Neem), Madhuca indica (Mahua) etc., which could be utilized as a source for production of oil and can be grown in large scale on non-cropped marginal lands and waste lands. Fatty acid profiles of seed oils of 75 plant species having 30% or more fixed oil in their seed/kernel were examined , in which Azadirachta indica, Calophyllum inophyllum, Jatropha curcas and Pongamia pinnata were found to be most suitable for use as biodiesel and they meet the major specification of biodiesel standards of USA, Germany and European Standard Organization.

Neem or Margosa is a botanical cousin of mahogany , it is a tropical evergreen tree native to Indian sub-continent (Roxburgh, 1874). It has been used in Ayurvedic medicine for more than 4000 years due to its medicinal properties. Most of the plant parts such as fruits, seeds, leaves, bark and roots contain compounds with proven antiseptic, antiviral, antipyretic, anti-inflammatory, antiulcer and antifungal uses. It has great potential in the fields of pest management, environment protection and medicine. Neem is a natural source of eco-friendly insecticides, pesticides and agrochemicals (Brahmachari, 2004). It is the most researched tree in the world and is said to be the most promising tree of 21st century. The tree has adaptability to a wide range of climatic, topographic and edaphic factors. It thrives well in dry, stony shallow soils and even on soils having hard clay pan, at a shallow depth. Neem tree requires little water and plenty of sunlight (Sateesh, 1998). The tree grows naturally in areas where the rainfall is in the range of 450 to 1200 mm. However, it has been introduced successfully even in areas where the rainfall is as low as 150 to 250 mm. Neem grows on altitudes up to 1500 m (Jattan et al., 1995; Chari, 1996). It can grow well in wide temperature range of 0 to 49°C (Hegde, 1995). It cannot withstand water-logged areas and poorly drained soils. The pH range for the growth of Neem tree lies in between 4 to 10. Neem trees have the ability to neutralize acidic soils by a unique property of calcium mining (Hegde, 1995).

Biologically active principles isolated from different parts of the plant include: azadirachtin, meliacin, gedunin, salanin, nimbin, valassin and many other derivatives of these principles. Meliacin forms the bitter principles of Neem seed oil; the seed also contain tignic acid (5-methyl-2-butanic acid) responsible for the distincitive odour of the oil (Schmutterer, 1990; Uko and Kamalu, 2001). These compounds belong to natural products called triterpenoids (Limonoids). The active principles are slightly hydrophilic, but freely lipophilic and highly soluble in organic solvents like, hydrocarbon, alcohols, ketones and esters (Schmutterer and Singh, 1995).

1.1 Taxonomical Classification of Neem

Neem is a member of the Mahogany family. It has similar properties to its close relative, Melia azederach. The word Azadirachta is derived from the Persian azaddhirakt . The taxonomic positions of Neem are as follows:

Order: Rutales

Suborder: Rutinae

Family: Meliaceae

Subfamily: Melioideae

Tribe - Melieae

Genus: Azadirachta

Specie: Indica

Latin: Azadirachta indica

Indian: Holy tree, Indian lilac tree

Hindi: Neem, Nim

Sanskrit: Nimba

Hausa: Dogon yaro

Igbo: Ogwu akuma

1.2 Origin and Distribution of Neem

Two species of Azadirachta have been reported, Azadirachta indica A. Juss-native to Indian subcontinent and Azadirachta excelsa Kack. confined to Philippines and Indonesia (Jattan et al., 1995; Hegde, 1995). The former grows as a wild tree in India, Bangladesh, Burma, Pakistan, Sri Lanka, Malaysia, Thailand and Indonesia. Presently neem trees can be seen growing successfully in about 72 countries worldwide, in Asia, Africa, Australia, North, Central and South America (Ahmed et al., 1989; Sidhu, 1995; Sateesh, 1998; Fathima, 2004).

The neem (Azadirachta indica A. Juss) trees have been grown successfully in all parts of Sudan. Neem has become a naturalized species in various parts of the Sudan. In the Sudan, Neem which was introduced in 1921 is frequent in Kassala, in threats in towns and village along the blue and the White Nile irrigated areas of central Sudan and rain fed regions in Kordofan and Darfur (Schmutterer, 1995). Neem tree occurs throughout Sudan; its performance is quite good even in the harshest conditions. Most of the original plantations were carried out by the colonial officers along the railway and the Nile banks. Then they spread all over the country .

1.3 Botanical Description of Neem

It is a hardy, fast-growing evergreen tree with a straight trunk, long spreading branches and moderately thick, rough, longitudinally fissured bark. Mature trees attain a height of 7-15 m (23-50 feet) (Ogbuewu, 2008). The tree starts producing the yellowish ellipsoidal drupes (fruits) in about 4 years, becomes fully productive in 10 years and may live for more than 200 years. The leaves are compound, imparipinnate, comprising up to 15 leaflets arranged in alternate pairs with terminal leaflets (Ogbuewu, 2008). The leaflets are narrow, lanceolate, up to 6 cm long. The flowers are abundant, sweet-smelling white panicles in the leaf axils. Seed propagation in nurseries followed by direct planting in the field is the accepted method to produce plantation stands (Ogbuewu, 2008). The one seed Neem fruit is yellow when ripe and is about one inch long (Ogbuewu, 2008).

1.4 The Uses of Neem

1.4.1 Neem and Environmental Protection

Afforestation: The large scale plantation of Neem trees help to combat desertification, deforestation, soil erosion and to reduce excessive global warming (Sateesh, 1998). Neem has high rate of photosynthesis and liberates more oxygen than many other tree species, thus purifying the atmosphere (Nigam et al., 1994). Neem products have water purifying activity. Neem leaf powder could be used as biosorbent for the removal of dyes like Congo red from water (Bhattacharyya and Sharma, 2004). In agro-forestry, Neem product benefits extended to providing shade, firewood, timber, wind breaks, shelter belt and check against desertification in the semi-arid zone of northern Nigeria.

Neem has the ability to re-sprout after cutting and to re-grow its canopy after pollarding. Thus it is highly suited for pole production. In Saudi Arabia neem plantation when full grown is expected to provide shade to about two million pilgrims (Ahmed et al., 1989). In Chad, Neem constitutes about 17% of the tree cover (Ohabuike, 1995). Neem plantations have been used for halting the spread of Sahara desert in the countries from Somalia to Mauritania.

1.4.2 Pest Management Prospects

The dependency on synthetic chemicals during early and middle twentieth century has prompted the large scale synthesis of newer chemicals (pesticides). Many a times, the side effects of the synthetic pesticides are more serious than problems themselves. They are also known to cause health problems in farmers of both developed and developing countries. According to World Health Organization estimation, annually 220,000 deaths occur due to acute poisoning caused by synthetic pesticides (Sateesh, 1998).

Neem based pesticides are found to be much safer in this regard. Today, Neem has gained importance internationally as all communities have inclined towards green technology. Neem products have no ill effects on humans and animals and have no residual effect on agricultural produce. This makes neem the best, reliable substitute to hazardous pesticides. The demand for chemical pesticides will be reduced by large scale use of Neem based pesticides that will in turn reduce the load of synthetic chemicals in environment.

Neem based pesticides are easy to prepare, cheap and highly effective and thus constitute an important source of pesticide for economically poor third world country farmers (Brahmachari, 2004). Neem bio-pesticides are systemic in nature and provide long term protection to plants against pests. Pollinator insects, bees and other useful organisms are not affected by Neem based pesticides (Tanzubil, 1996).

1.4.3 Neem and Agriculture

Animal feeds: The livestock industry in developing countries has been plagued by numerous problems, which include scarce feed ingredients that are in strict competition with main dietary need.

An effort to develop new feedstuff for animal rearing, a number of researchers in recent times has investigated the proximate composition of Neem seed cake (Bawa et al., 2006; Uko and Kamalu, 2001) and leaf meal (Oforjindu, 2006; Esonu et al., 2006; Ogbuewu et al., 2010a, b) and its use as feedstuff in poultry (Esonu et al., 2006; Oforjindu, 2006; Uko and Kamalu, 2001) and rabbits (Sokunbi and Egbunike, 2000a; Ogbuewu, 2008). Result of proximate analysis of Neem showed that neem leaf meal had of 92.42% dry matter, 7.58% moisture, 20.68% crude protein, 16.60% crude fibre, 4.13% ether extract, 7.10% ash and 43.91% nitrogen free extract (Esonu et al., 2005; Oforjindu, 2006; Ogbuewu, 2008).

Neem cake has also been very widely used as animal feed (Bawa et al., 2006; Uko and kamalu 2001). Despite the bitter components, livestock consume diets containing varied percentage of Neem cake. Alkali treatment of Neem cake with caustic soda yields palatable product, by removing the toxicant triterpenoids (Devakumar and Dev, 1993). Nagalakshmi et al. (1996) and Verma et al. (1998) reported beneficial effect of alkali treated (10-20 g NaOH) Neem kernel cake incorporated into poultry feeds. It resulted to an increased feeding value and protein utilization with spectacular growth. However, no significant difference was observed among the different dietary groups in feed intake, egg production, egg quality, fertility, hatchability and chick weight (Nagalakshmi et al., 1996; Verma et al. 1998).

Neem oil and de-oiled Neem seed cake are used as animal feed. Neem oil which is rich in long chain fatty acids is used in poultry feed. Deoiled neem seed cake is rich in essential amino acids, crude proteins, fiber contents, sulphur and nitrogen (Uko and Kamalu, 2001).

1.4.4 Pharmaceutical Uses

Neem tops the list of 2,400 plant species that are reported to have antimicrobial properties and is regarded as the most reliable source of eco-friendly agrochemical property.Neem products are effective against more than 350 species of arthropods, 12 species of nematodes, 15 species of fungi, 4 strains of viruses, 2 species of snails and 1 crustacean species (Saxena et al., 1989; Nigam et al., 1994; Singh and Raheja, 1996; Mehta, 1997). Two tetracyclic triterpenoids - meliantetyraolenone and odoratone isolated from neem exhibited insecticidal activity against Anopheles stephensi (Siddiqui et al., 2003). Over 195 species of insects are affected by neem extracts and insects that have become resistant to synthetic pesticides are also controlled with these extracts.

1.4.5 Industrial Uses

During the past five decades intensive investigations on the diverse properties of Neem have been carried out. As a result large numbers of research publications and books have been published. Many conferences have been conducted at international level. Hundreds of active compounds that are isolated from various parts of Neem find their applications in pesticide, medicine, health care and cosmetic industry all over the world. World over the Neem tree has been recognized as a commercial opportunity.

Many Neem related processes and products have been patented in Japan, USA and European countries, since 1980s. In 1983, Temuro Corporation obtained the first US patent for its therapeutic preparation from Neem bark. USA with 54 patents on Neem and Neem based products stands first followed by Japan , Australia (Chakraborthy and Konger, 1995) and India (Fathima, 2004). Majority of patents that have been granted are for crop protection application (63%) followed by health care (13%), industrial (5%), veterinary care (5%), cosmetics (6%) and others (8%).

A mature neem tree produces 30 to 50 kg fruit every year and has a productive life span of 150 to 200 years , and its high oil content of 39.7 to 60% (Ragit et al., 2011).

In recent years there are growing concerns about the utility of Neem oil as a source for biodiesel production in order to generate alternate source of energy. This is mainly due to the suitability of oil derived from Neem seeds for biofuel purposes. Neem comprises mainly of triglycerides and large amounts of triterpenoid compounds. It contains four significant saturated fatty acids, of which two are palmitic acid and two are stearic acid. It also contains polyunsaturated fatty acids such as oleic acid and linoleic acids (Muthu V et al., 2010). The current studies on the fatty acids distribution of Neem oil and physicochemical properties of oil viz., oil content, biodiesel yield, density, viscosity, iodine value, free fatty acid and saponification value indirectly influence the quality of oil for biodiesel production. However, such studies are limited in Neem oil which thus warrants systematic investigation.

Transesterifcation reactions can be without a catalyst, alkali-catalyzed, acid-catalyzed or enzyme-catalyzed. Alkali-catalyzed transesterification is much faster and most often used commercially . Alkali-catalyzed transesterification is the most economical process requiring low temperatures and pressures to achieve a 98% conversion yield (Singh et al., 2007). However, one limitation to the alkali-catalyzed process is its sensitivity to the purity of reactants. It is very sensitive to both water and free fatty acids content (Zhang et al., 2003).

The use of edible grade oils as feedstock compete with food supply in the long-term and accounts for the higher price of biodiesel, since the cost of raw materials accounts for 60 to 75% of the total cost of biodiesel fuel (Krawczyk, 1996). One way of reducing the biodiesel production costs is to use the less expensive feedstock mostly containing fatty acids such as inedible oils, animal fats, waste food oil and byproducts of the reÞning vegetable oils (Berchmans and Hirata, 2008). However, feedstocks high in free fatty acid (> 1%), are not easily converted by alkali transesteriÞcation because of concurrent soap formation of the free fatty acids with the catalyst. Excessive amounts of soap significantly interfere with the washing process by forming emulsions, thus leading to substantial yield losses (Freedman et al., 1984). Acid-catalyzed transesterification could have been the best option for high FFA feedstock but the harsh reaction conditions and long reaction times required favor the base-catalyzed reaction . Therefore pre-treatments of non edible oils for lowering the FFA in feedstock for alkali transesterification are inevitable.

Neutralization and acid esterification are among the pre-treatment methods to lower FFA for alkali catalyzed transesterification. Neutralization of vegetable oil (caustic refining) is the most commonly used method for lowering the FFA in oils. It lowers the FFA, along with substantial quantities of mucilaginous substances, phospholipids and color pigments (Bhosle and Subramanian, 2005). An alkali is added to the oil and thereby precipitating the FFA as soap stock; the latter is then removed by mechanical separation from the neutral oil. However, for oils with more than 5% of FFA, neutralization causes high losses of neutral oil due to saponification and emulsification (Bhosle and Subramanian, 2005). Acid esterification as pre treatment before alkali transesterification is thought to be the best route which converts the FFA into esters and therefore reduce the losses which could have produced from caustic refining .

In Tanzania, Jatropha plant (Jatropha curcas) has a good potential to be used as feedstock for biodiesel production. It gives a relatively large oil yield; it does not require a lot of water and nutrients. It can grow in very poor soils, thereby reclaiming land (and preventing soil erosion) (Van Eijck and Romijn, 2008). However , Jatropha oil is one of such non-edible oils which contains high free fatty acid (FFA), which is far beyond the limit of 1% (Kumar et al., 2007). Hence, lowering FFA for converting Jatropha oil, which contains high FFA% into biodiesel, is very much required.

Generally the fuel quality of biodiesel can be influenced by several factors: the quality of the feedstock(minor components i.e. FFA, water, gums, etc), the fatty acid composition of the parent vegetable oil or animal fat (major components i.e. triglycerides), production process and post-production parameters(biodiesel refining and drying) (Van Gerpen, 2003). The information on the quality comparison of biodiesel produced from the neutralized and acid pretreatment processes are hard to find. The present study compares the yield and quality of both feedstock and biodiesel manufactured by the alkali transesterification of neutralized and acid pretreated feedstock.

In today's lab, we will be making biodiesel on a small batch scale. The usual biodiesel process is a continuous process that involves large tanks and pumps. This lab will give we an idea of what happens inside the vessels and pipes as biodiesel is being made.

1.5 Objectives

1. Extraction of Neem seeds oil .
2. Analysis of extracted oil .
3. Transformation of the oil for biodiesel .
4. Analysis of prodused biodiesel .

Chapter Two

Materials and Methods

2.0 Experiments

2.1 Collection and Purification of Neem Seeds

Neem seeds were brought from National Center of Seeds Khartoum ,Sudan , seeds were inspected and manually cleaned to a void foreign matterThe cleaned seeds were sun dried in the open for 2days , and further drying by roasting for few minutes in order to reduse the moiture content . The separation of the shell from the kernel was carried out manually using a dish to blow away the cover and achieve very high yield. Morter and pestle were used to crush the seeds and preparation them for oil extraction.

2.2 Neem Oil Extraction

1liter of normal hexane was poured into round bottom flask. 400 g of the sample was placed in the thimble and was inserted in the centre of the extractor. The Soxhlet was heated at 60^{o}C. When the solvent was boiling, the vapour rises through the vertical tube into the condenser at the top. The liquid condensate drips into the filter paper thimble in the centre, which contains the solid sample to be extracted. The extract seeps through the pores of the thimble and fills the siphon tube, where it flows back down into the round bottom flask. This was allowed to continue for 1hr. It was then removed from the tube, and cooled in the desiccators and weighed . The experiment was repeated for 420g. At the end of the extraction, the resulting mixture of oil was heated to recover solvent from the oil, finally the oil was weighed and the percentage was calculated.

Yield of oil = (grams of oil extracted)/(grams of sample) * 100%

2.3 Biodiesel Production:

2.3.1 : Acid Pretreatment

The crude Neem oil was heated to 60°C while stirred mechanically at 600 rpm under atmospheric conditions to homogenize the oil and avoid moisture . A concentrated sulfuric acid (2% based on oil weight) in 0.60 w/w methanol was heated to 60 °C and added to the pre heated oil (Zullaikah et al., 2005). This mixture was stirred (600rpm) for 2 hours. The reaction product mixture was then poured into a separating funnel and allowed to settle for several hours. The top layer comprised unreacted methanol, whereas the middle layer was oil and fatty acid methylester (FAME) (small amount obtained by conversion of free fatty acids to esters), and water at the bottom layer. The amount of FFA remaining was determined before alkali transesterification. The product was then used for the alkaline transesterification. The acid pretreatment loss was calculated by Equation (1).

Acid pretreatment loss = (weight of crude oil-weight of pretreated oil)/(weight of crude oil) *100% … (1)

2.3.2 Alkaline Transesterification

The pre treated or neutralized Neem oil with low percentage free fatty acid was heated to 60°C and stirred at 600rpm with mechanical stirrer in a hot plate. The catalyst sodium hydroxide (NaOH) 0.5% based on oil weight was dissolved in the required amount of methanol (ratio was methanol: oil = 6:1) and added to the pre treated (Meher et al., 2006). The reaction was conducted for 120min, but it is not complete, hence addition amounts of methanol were added with continues heating and stirring until the end of the reaction. The resulting product was taken into a separating funnel and stand for 4 hours. Two phases were distinct; biodiesel on top and the glycerol at the bottom. The two phases were separated. The biodiesel was then washed twice by using de-ionized water (10% by volume), to wash out impurities like soap and other residues. Finally, the biodiesel was heated to 100°C, for 1 hour to remove the moisture. Based on the initial amount of pre treated been oil, the Biodiesel yields was then evaluated using Equation (2).

Yield=(weight of biodiesel produced)/(weight of oil) *100% …… (2)

2.4 Analysis of Neem Oil and Produced Biodiesel

The following physicochemical parameters were estimated according to (K. C. Verma et al. 2014.)

2.4.1 Density

Density of the sample is directly proportional to unsaturation and inversely to molecular weight. First, the empty . bycnometer was weighed, then filled with water and weighed again, finally weighed after filled with the sample.

2.4.2 Vescosity

Viscosity is a measure of internal friction and resistance of flow.Viscosity of the samples was measured using Ostwald's viscometer in which the sample was allowed to flow from the etched mark X–Y through the capillary of the viscometer. Viscosity was calculated as;

$$\frac{n1}{n2}=\frac{d1t1}{d2t2}$$

where d1 is the density of sample, d2 the density of water, t1 the time of flow for sample, t2 the time of flow for water, n1the viscosity of sample, and n2the viscosity of water.

2.4.3 Free Fatty Acid Content:

It has a significant effect on the transesterfication of glycerides with alcohol using catalyst.For determining free fatty acid one gram of the sample dissolved in 15ml of isopropanol with well shaking , two drops of phenolphthalein was added to the solution. 0.1 N NaOH was used to titrate the mixture with shaking for proper mixing.

FFA [%] = V×0.0282×100/weight of sample

2.4.4 Iodine Value:

The unsaturated fatty acid residues of the glycerides react with iodine, and the iodine value indicates the degree of unsaturation of the fatty acid residues of the glycerides. two gram of the sample was taken in a stoppered bottle and dissolved by 10ml of chloroform , then 25 mL of Wij's solution was added to it. It was mixed properly and allowed to stand for 1 h. A blank was prepared with chloroform. With 50 mL distilled water the stopper and neck of the flask were rinsed thoroughly. 15 milliliters of KI solution was added to it. Then it was titrated with 0.1N sodium thiosulphate (y) till it turned pale yellow. After that few drops of starch solution was added and titrated till blue colour disappears. The steps were repeated with a blank which did not contain any fat sample (x).

2.4.5 Saponification Value:

Saponification value indicates the presence of normal triglycerides, which can be used for production of soap. For determining saponification value, 1 g of oil sample was taken in different conical flasks and 3 mL of fat solvent was added to each flask. Twenty-five millilitres of ethanol potash was added and refluxed for 30 min with frequent shaking. After cooling, two drops of phenolphthalein indicator was added to each flask and titrated with 0.5 M HCl(x) with vigorous shaking without delay to get the end point. The step was repeated for a blank which did not contain oil sample (y).

Saponification value = 28.05×Titre value (x−y)/weight of sample (g)

2.4.6 Color

It's a simple test that indicates oil quality. The dark color is the higher probability of contamination or deterioration of the oil . The colour of Neem oil was tested by using colormeter.

2.4.7 Peroxide Value

This test is commonly used to determine the rancidity of the fat or oil .

Two g of Neem oil were dissolved in a chloroform-acetic mixture and subjected to an excess of iodine as saturated solution of potassium iodide which oxidised with the Peroxide present in the oil to iodine . and the iodine is then titrated to the end point using sodium thiosulphate with starch as indicator . The a mount of iodine produced is directly proportional to the Peroxide .

2.4.8 Flash and Fire Point

Flash point is related to the safety requirement in the handling and storage of fuel; however, biodiesel falls under non-hazardous category. Flash point is the minimum temperature at which the oil vaporises, which when mixed with air forms an ignitable mixture and gives a momentary flash on application of a small pilot flame.

The flash and fire points of the test fuels were measured using Pensky Martens apparatus. The sample was filled in the test cup at the specified level and heated at a slow and constant rate of stirring for proper and uniform heating. The temperature was measured with the help of a thermometer of -10 to 400oC. At every 2C temperature rise, the flame was directed into the cup through the opening provided at the top cover. The temperature at which flash was observed in the form of sound was recorded as the flash point of that sample. An extension of flash point is fire point, reflecting the condition at which vapour burns continuously for at least for 5 sec .

2.4.9 Cetane Index for Biodiesel

Cetane number denotes the ignition delay time. It is ranks the fuel: the higher the cetane number the faster the auto ignition (Cetane $C_{16}H_{34}$ has a cetane number 100). The Cetane number of Biodiesel was calculated by iodine and sabonfication values using the equation:

Cetane number $=46.3 + 5458/(S.V) - 0.225 * I.V$

Where:

I.V =Iodine value for biodiesel.

S.V = Sabonification value for biodiesel.

2.4.10 FT.IR Spectroscopy

A small drop of the sample was placed on one of the KBR plates, the other plate was placed on top to make quarter turn to obtain a nice even film, then the blates were placed into the sample holder and the spectrum was run.

Chapter Three

Results and Discussion

3.0 Results and discussion

3.1 Extracted Neem oil and produced Biodiesel percetages

The extracted Neem oil and Biodiesel percentages during all the processes are explained in table (3) bellow

Table (3.1) Item percentages of oil and Biodiesel :

Item	Percentage %
Neem seeds oil	44.37
Acid pretreatment loss	4.199
Produced biodiesel (based on pretreated oil)	75.5
Produced biodiesel (based on neem Oil)	72.32

The high oil content of neem seeds (44.4%) , indicates it's suitability as nonedible vegetable oil feedstock in oleochemical industries such as biodiesel .this ratio is more than other sites of the world , for example in india it was found 31% in seeds from Bidar and 40.5 in seeds from Zaheerabad . to make biodiesel from neem oil , the base catalysed transesterification is not suitable because it's high FFA value (6.6%) , therefore acid pretreatment method is preferable .

The objective of acid treatment was to reduce the free fatty acid content of crude neem oil before alkali transesterification to avoid sabonification reaction .

Bechamans and Hirata (2008) used similar condition and lowered the high FFA of crude Jatorpha oil from 15% to less than 1% . Based on 100g of crud Neem oil , the loss on acid pretreatment was 4.2% . this loss can be attributed to the difficult process of separating the exess methanol wich contain some dissolved oil from the reaction mixture .

The yield of biodiesel is (75.5%) wich considered relatively high , and the percentage (72.32%) based on crude neem oil is higher than that obtained from neem in india ((seeds from Bidar 60% ,Raichur 65% biodiesel content) . This high value can be explained by the fact that , the lower the FFA in the feedstock for biodiesel the higher the yield (Freedman et al.,1984) . Less FFA limit the catalyst dipletion , soap formation and separstion dificulties due to the saponification reactions .

3.2 Comparison between Neem oil Biodiesl with respect to ASTM standared

Physico-chemical characteristics specifications of Neem oil and produced Biodiesel are shown in table (2) below

Table (3.2) : comparison between properties of Neem oil , produced Biodiesel , and ASTM standards of Biodiesel :

Parameter	Neem oil	Biodiesel	ASTM standards	Unit
Density	0.993	0.987	0.87max	g/ml
API	10.58	11.57	31.1min	Degree
Viscosity	31.25	7.0	1.9 — 6	mm^2/sec
Color	Yellow=2, Red=.43	yellow=1, Red=0.04	–	–
FFA	6.6	1.12	0.5 max	%
Peroxide	1.8	–	–	Meq/O
Iodine	81.1	127.9 3	–	g/100g
Saponification value	187.92	1.403	–	KOHmg/g
Cetane index	_	56.51	47min	_
Flash point		142	93 min	ºC
Fire point	_	178	–	ºC

The density of Neem oil (0.993) was found to be higher than produced biodiesel , wich is heavier than that obtained from indian Neem (Bidar 0.88g\ml , Raichur 0.86g\ml) and that for biodiesel obtained from used vegetable oil (0.98g\ml) .

The higher density means more mass of fuel per unit volume for vegetable oil compared to diesel oil .The higher mass of fuel would give higher energy available for work out put per unit volume .

Viscosity of the oil obtained was (31.25cp) and the Biodiesel produced was found (7.0cp) higher than that produced from used oil and higher than ASTM limit (Max 6.0cp) . Higher viscosity of Biodiesel as fossil oil implies that the Biodiesel has a lubricating effect in imagine which will an added advantage to the users , since it will reduce wear and tear in the ingine .

The FFA content of the crude oil is found (6.6%) which is very high to use as a feedstock to Biodiesel , but after acid treatment it was lowered to (1.8%) . In the obtained Biodiesel the FFA was (1.12%) . It is consider high value which causes corrosion in engine and this is not acceptable in fuel specifications.

The color of crude oil was (yellow=2 ,red =0.43) while the produced Biodiesel has color (yellow=1 , red=0.04) which means that the Biodiesel is lighter than crude oil .

Peroxide value of Neem oil (1.8) is very low which means that it is very stable fixed oil , and very low probability to undergo autoxidation reaction .

High iodine value (80.1%) shows high unsaturation of the oil . The limitation of unsaturation of fatty acid is vital due to the fact that heating of highly unsaturated fatty acid results in polymerization of glycerides which could lead to deposits formation .

High saponification value of Neem oil shows that it is normal triglyceride which is very useful in the production of soap and shampoo .

The results of iodine and saponification value of Biodiesel are use to calculate the ctane index , which is found (56.51) higher than fossil diesel and higher than ASTM required (B100) which means that the Biodiesel is shorter ignition delay period and need very short time for the fuel compusion process to be completed , which reduce engine noise and control legislated emission .

Flash point of Biodiesel produced from neem oil was (142ºC) which is so higher than the minimum limit of ASTM requirements for Biodiesel B100 (93ºC) , that inhanced it's highly safety during handling and storage . and it's fire point was (178ºC) .

3.3 Infra red study

One aspect of control Biodiesel regulation is the FAME (fatty acid methyl ester) content, in the figures (1) and (2) the IR spectra of crude Neem oil and obtained Biodiesel shown in two graphs . The peak Analysis of both spectra shows significant differences which are affected by the ester group. the change for alkyl ester group to methyl ester has the strongest impact in the IR spectra. The inductive effect in carbonyl group need more energy to get it into vibration . The ester group is commonly described as R_1–C(OR)=O in Neem oil , and as R_1–$C(OCH_3)=O$ in Biodiesel .R1 represents long chains of hydrocarbons apears at (3007 , 2928 , 2845)cm^{-1} . additional chains representing palmitic , stearic , and oleic acid are visible in both spectra with the –CH_2 hydrocarbon part .

Noticed that all groups regards CH_2–O are reduced and new signals are visible belonging to CH_3–O vibration in the Biodiesel . The most influence as result of transesterification is to see in the new signal at 1437cm^{-1} which is definitely the methyl ester group with it's deformation vibration. the strong broad signal at 1163cm^{-1} in edible oil is separated in two concrete signals at 1170Cm^{-1} and 1197Cm^{-1}, the averaging of the energy over the trible ester groups of the triglyceride disappeared .

Conclusion

Based on the results obtained from all experiments it was concluded that the transformation of Neem oil to Biodiesel is was carried out successfully . The pretreatment process was been able to lower the FFA content of neem Oil from 6.6% to the acceptable value for alkaline transesterification . The comparison of characteristic fuel properties of the produced Biodiesel with the ASTM standards for diesel fuel indicates that it is comparable . But the level of improvement necessary appears to be attainable.

Based on it's high extraction yield , and physico_chemical properties , this study showed that the Neem oil can be used as raw material to obtain Biodiesel fuel of reasonable quality and could be suitable alternative to petroleum diesel .

Recommendations

*Further research is essential to inhance the knowledge base for improvement in neem oil for quality Biodiesel production .

*Lowering the FFA content of feedstock neem oil is required to increase the yield percentage .

*Blending neem Biodiesel with petroleum improve it's characteristic properties as fuel .

Reference

- Bahuguna, V.K., 1997. Silviculture and management practices for cultivation of *Azadirachta indica* (Neem). Indian For., **123**: 379-386.
- Bandyopadhyay, U., K. Biswas, A. Sengupta, P. Moitra and P. Dutta *et al.*, 2004. Clinical studies on the effect of neem (*Azadirachta indica*) bark extract on gastric secretion and gastroduodenal ulcer. Life Sci., **75**: 2867-2878.
- Bawa, G.S., M. Orumuyin, A.S. Agbaji, Z. Ladan and U.O. Okekeifi, 2006. Effects of different methods of processing Neem seeds on performance of young growing rabbits. Pak. J. Nutr., 6: 212-216.
- Bhattacharyya, K.G. and A. Sharma, 2004. Azadirachta indica leaf powder as an effective biosorbent for dyes: A case study with aqueous Congo red solutions. J. Environ. Manage., **71**: 217-229.
- Chakraborthy, R. and G. Konger, 1995. Root-rot of neem (*Azadirachta indica*) caused by *Ganoderma applanatum*. Indian For., **121**: 1081-1083. Chari, M.S., 1996. Neem and Transfer of Technology. In: Neem and Environment, Sinh, R.P., M.S. Chari, A.K. Raheja and W. Kraus (Eds.). Vol. **I**. Oxford and IBH Publishing Co. Pvt. Ltd., New Delhi, India, pp: 27-38.
- Devakumar, C. and S. Dev, 1993. Chemistry Society, Pest Science. Neem Research Developmant Publication, India, pp: 63-96.
- Esonu, B.O., M.N. Opara, I.C. Okoli, H.O. Obikaonu, C. Udedibie and O.O.M. Iheshiulor, 2006. Physiological responses of laying birds to Neem

(*Azadirachta indica*) leaf meal based diets, body weight, organ characteristics and hematology. Online J. Health Allied Sci., 2: 4-4.

- Fathima, S.K., 2004. Investigations on the biology and management of *Phomopsis azadirachtae* on neem. Ph.D. Thesis, University of Mysore, Mysore, India.
  Hegde, N.G., 1995. Neem and small farmers constraints at grass root level. Indian For., 121: 1040-1048.
- Lale, N.E.S. and A. Mustapha, 2000. Efficacy and acceptability of neem (*Azadirachta indica* A. Juss) seed oil and pirimiphos-methyl applied in three storage devices for the control of *Callosobruchus maculatus* (F.) (Coleoptera: Bruchidae). Zeitschrift Fuer Pflanzenkrankheiten Pflanzenschutz, 107: 399-405.
- Mehta, U.K., 1997. The use of neem products for controlling sugar cane nematodes. Global Neem Update, 2: 10-12.
- Nigam, S.K., G. Misra and A. Sharma, 1994. Neem: A promising natural insecticide. Applied Bot. Abstr., 14: 35-46.
- Oforjindu, O., 2006. The Toxicity of Graded Levels of Graded Levels of Neem (*Azadirachta indica*) Leaf Meal. B. Agric. Tech. Project Report, Federal University of Technology, Owerri, pp: 1-34.
- Ogbuewu, I.P., I.C. Okoli and M.U. Iloeje, 2010. Evaluation of toxicological effects of leaf meal of an ethnomedicinal plant-neem on blood chemistry of puberal Chinchilla Rabbit does. Rep. Opin., 2: 29-34.
- Ohabuike, J.E., 1995. Geographical distribution of neem scale insect in the sub-region. Proceedings of the International Workshop on Neem Scale Insect and Neem Diseases, July 25-27th, LCRI, Maiduguri, Borno State, Nigeria, pp: 354-359.

- Sateesh, M.K., 1998. Microbiological investigations on die-back disease of neem (*Azadirachta indica* A. Juss.). Ph.D. Thesis, University of Mysore. Mysore, India.
- Schmutterer, H. and R.P. Singh, 1995. List of Insects Susceptible to Neem Products. In: The Neem Tree Sources of Unique Natural Products for Integrated Pest Management, Medicine, Industry and Other Purposes,
- Schmutterer, H., 1990. Properties and potential of natural pesticides from the neem tree, *Azadirachta indica*. Annu. Rev. Entomol., 35: 271-297.
- Siddiqui, B.S., F. Afshan, T. Gulzar, R. Sultana, S.N. Naqvi and R.M. Tariq, 2003. Tetracyclic triterpenoids from the leaves of *Azadirachta indica* and their insecticidal activities. Chem. Pharm. Bull. (Tokyo), 51: 415-417.
- Sidhu, D.S., 1995. Neem in agro forestry as a source of plant derived chemicals for pest management. Indian For., 121: 1012-1021.
- Tanzubil, P.B., 1996. Potential for Neem (*Azadirachta indica* A. Juss.) in Armyworm Control in Africa. In: Neem and Environment, Singh, R.P., M.S. Chari, K. Raheja and W. Kraus (Eds.). Vol. I. Oxford and IBH Publishing Co. Pvt. Ltd., New Delhi, India.
- Uko, O.J. and T.N. Kamalu, 2001. The neem tree-uses and potentials. Nig. J. Exptal. Applied Biol. 2: 223-229.
- Verma, S.V.S., S.K. Gowda and A.V. Elangovan, 1998. Responses of single comb white leghorn layers to dietary inclusion of raw or alkali treated neem kernel meal. Anim. Feed Sci. Tech., 76: 169-175.
- Berchmans, H. J.and Hirata, S. (2008), Biodiesel production from crude Jatropha curcas L. seed oil with a high content of free fatty acids. Bioresource Technology, 99, 17161721.
- Canakci, M.and Van Gerpen, J. (1999), Biodiesel production from oils and fats with high freefatty acids .

- S., Budge, S. M., Watts, K. C.and Islam, M. R. .Chhetri, A. B., Tango, M ,(2008)Non-edibleplant oils as new sources for biodiesel production. .International Journal of Molecular Sciences, 9, 169
- Freedman, B., Pryde, E. H.and Mounts, T.L. (1984), Variable effecting the yields of fatty esters from transesterified vegetable oils. Jornal of the American Oil Chemists Society, 61, 1638-1643.
- Singh ,A. K., Fernando, S. .D.and Hernandez, R. (2007) , Base-catalyzed fast transesterification of soybean oil using ultrasonication . Energy Fuels,21,1161-1164.
- Van Gerpen, J. (2005), Biodiesel processing and production. Fuel Processing Technology, 86, 1097-1107.
- Zullaikah, S., Lai, C. C., Vali, S. R.and Ju, Y. H. (2005), A two-step acid-catalyzed process for the production of biodiesel from rice bran oil. Bioresource Technology, 96, 18891896.
- K C Verma and Nisha Juneja Jonija , International Jornal of Sustainable energy , 33(4)2014 946_953
- Pearson,D. (1970). Chemical Analysis of Foods. 6th Edition .
- Nagalakshmi, D., V.R.B. Sastry, D.K. Agrawal, R.C. Katigar and S.V.S. Verma, 1996. Performance of Broiler Chicks Fed alkali-treated neem kernel cake. Br. Poult. Sci., 37: 809-818.
- Ahmed, S., M. Bamofleh and A. Munshi, 1989. Cultivation of neem (*Azadirachta indica*) in Saudi Arabia. Econ. Bot., 43: 35-38. Jattan, S.S., M. Shashikumar and G. Pujar, 1995. Perspectives in intensive management of neem plantations. Indian For., 121: 981-988.
- Roxburgh, W., 1874. Description of Indian Plants. Today and Tomorrows Printers and Publishers, New Delhi, India.

- Saxena, R.C., Z.T. Zhang and M.E.M. Bancodin, 1989. Effects of neem oil on courtship signals and mating behaviour of brown plant hopper. Int. Rice Res. Newslett., 14: 28-29.
- Singh, R.P. and A.K. Raheja, 1996. Strategies in Management of Insect Pests with Neem (*Azadirachta indica* A. Juss). In: Neem and Environment, Singh, R.P., M.S. Chari, K. Raheja and W. Kraus (Eds.). Vol. I. Oxford and IBH Publishing Co. Pvt. Ltd., New Delhi, India.
- Sokunbi, O.A. and G.N. Egbunike, 2000. The performance of growing rabbits fed diets containing sun cured Neem leaf meal. Proceedings of the 5th Annual Conference ASAN, September19-22, 2000, PH, Nigeria, pp: 113-116.

- Sokunbi, O.A. and G.N. Egbunike, 2000. The performance of growing rabbits fed diets containing sun cured Neem leaf meal. Proceedings of the 5th Annual Conference ASAN, September19-22, 2000, PH, Nigeria, pp: 113-116.

- Sokunbi, O.A. and G.N. Egbunike, 2000. Physiological response of growing rabbits to Neem leaf based diets. Haematol. Serum Biochem. Trop. Anim. Prod. Invest., 3: 81-87.
- Ogbuewu, I.P., 2009. Physiological responses of rabbits fed graded levels of neem (*Azadirachta indica*) leaf meal. M.Sc. Thesis, Federal University of Technology, Owerri.