Review of the stability of biodiesel produced from less common vegetable oils of African origin

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The stability of biodiesel is dependent on storage conditions such as contact with ambient air and metals, exposure to sunlight and high temperature conditions which accelerate oxidation reactions. In addition, biodiesels are more susceptible to degradation when compared to fossil diesel because of the presence of unsaturated fatty acid chains which are prone to oxidation. The stability of biodiesel is categorised according to oxidation stability, storage stability and thermal stability. Oxidation instability can led to the formation of oxidation products such as aldehydes, alcohols, shorter chain carboxylic acids, insolubles, gums and sediments in the biodiesel. Thermal instability is concerned with the increased rate of oxidation at higher temperature, which in turn increases the weight of oil and fat due to the formation of insolubles. Storage stability is the ability of liquid fuel to resist change to its physical and chemical characteristics brought about by its interaction with its storage environment, such as contamination with metals. These fuel instabilities give rise to the formation of undesirable substances in biodiesel beyond acceptable limits as per global biodiesel standards such as those of the American Society for Testing and Materials (ASTM D6751) and European Standards (EN 14214). When such fuel is used in the engine, it impairs engine performance through fuel filter plugging, injector fouling, and deposit formation in the engine combustion chamber and various components of the fuel system. We review the stability of biodiesel made from less common vegetable oils of African origin and synthetic antioxidants used in improving the stability of produced biodiesels.

Introduction

Diesel fuel has been widely used in industry and in automobiles for over a century.[1] However, as the petroleum prices continue to rise, the diesel supply is becoming scarce and unreliable.[2,3] Also, because of environmental issues concerning the use of petro-diesel, the search for cleaner environmental fuels has increased in the past few decades.[4] Thus, the mono-alkyl esters of long chain fatty acids derived from renewable lipid feedstock, such as vegetable oils, animal fats and used cooking oils, also known as biodiesel, are well positioned to replace mineral diesel.[5-8] Biodiesel is a biodegradable, non-toxic biofuel, which possesses inherent lubricity. It reduces most regulated exhaust emissions and has a relatively high flash point in comparison to petroleum based diesel, making it safer than other fuels during transportation, storage and handling. In addition, the use of biodiesel reduces dependence on imported fossil fuels, which continue to decrease in availability and affordability.[1,9]

However, despite the advantages, biodiesel's chemical nature makes it more susceptible to oxidation in comparison to mineral diesel during long-term storage.[10] The sensitivity to oxidation varies depending on the fatty acid composition of the raw materials or feedstocks used for production of biodiesel; the presence of naturally occurring antioxidants; and the storage conditions, such as exposure to atmospheric oxygen, daylight, high temperatures and metals that have a catalytic effect and expedite the oxidation reaction. Poor oxidation stability of biodiesel is the central problem associated with its commercial acceptance.[10,11] Therefore, to enhance the practical feasibility of biodiesel, antioxidants are added to increase its storage stability. However, it is quite possible that these additives may also affect other basic fuel related properties of biodiesel.[12]

We therefore review the work done on the oxidation, thermal and storage stability of biodiesel produced from less common vegetable oils of African origin such as those from *Croton megalocarpus*, *Moringa oleifera*, *Jatropha*, manketti seeds, marula nuts and rubber seeds as well as neem oils. In addition, we provide the background and chemistry of various synthetic antioxidants used in improving the stability of biodiesel made from these vegetable oils.

Stability of biodiesel

The stability of biodiesel depends on the fatty acid profile of the parent feedstock, with the biodiesels with high unsaturated fatty acids content such as linoleic and linolenic acids being unstable compared to the ones containing saturated fatty acids.[11,13] The oxidative degradation of biodiesel affects some basic properties such as kinetic viscosity, cetane number and acid value. This fuel instability through oxidation can give rise to sediments and gum formation and fuel darkening.[10] As previously reported in the literature, the neat biodiesels are more prone to oxidation than the feedstocks or straight vegetable oils. The oxidised biodiesels can develop a wide variety of alcohols, aldehydes, peroxide, insolubles, gums and sediments which are formed during transport and long-term storage, causing acidity in the biodiesel.[10,14,15] The use of such oxidised biodiesel in engines can impair the performance of the engine because of possible fuel filter plugging, injector fouling and deposit formation in the engine combustion chamber and various components of the fuel system.[8,14] The decrease in stability of biodiesel is recognised by the increased iodine value, peroxide value and total acid number of either straight vegetable oils or methyl esters/biodiesels.[8,10] The lower stability of biodiesel when compared to that of straight vegetable oils is possibly because the antioxidants naturally present in the vegetable oils are either deactivated during the transesterification process or removed during the subsequent purification or separation procedures. Therefore, addition of synthetic antioxidants is imperative to increase oxidation stability of biodiesels for longer storage.[11] Generally, the stability of biodiesel is categorised according to oxidation, thermal and storage stability.[10] The specifications related to oxidation stability of biodiesels in the global biodiesel standards such as ASTM D6751 and EN14214 are summarised in Table 1.

Table 1: Specifications related to oxidative stability in biodiesel standards[16]

Specification	Method	ASTM† D6751	EN‡ 14213	EN‡ 14214
Oxidative stability (110 °C)	EN 14112	3 h (minimum)	4 h (minimum)	6 h (minimum)
Content of FAME≥ 4 double bonds (%m/m)		–	1 (maximum)	1 (maximum)
Linolenic acid content (%m/m)	EN 14103	–	–	12 (maximum)
Iodine value (g iodine/100 g)	EN 14111	–	130 (maximum)	120 (maximum)
Kinematic viscosity (mm^2/s)	D445; ISO 3104/3105	1.9–6.0	3.5–5.0	3.5–5.0
Acid value	D664; EN 14104	0.50 (maximum)	0.50 (maximum)	0.50 (maximum)

†American Society for Testing and Materials; ‡European Standard

Measurement of oxidation stability

The oxidation stability of biodiesels without and with different dosages of antioxidants and its blends with mineral diesel are measured using Rancimat equipment as per EN 14112 specification of biodiesel oxidation stability. The working principle of the Rancimat instrument is illustrated in Figures 1 and 2. The biodiesel sample (10 mL) kept at constant temperature (110 °C) in the Rancimat is induced by passing a stream of purified air at a flow rate of 10 L/h over it. The vapours released during the oxidation process together with the air are passed through the flask containing distilled water, which contains an electrode for measuring the conductivity. The electrode is connected to a measuring and recording device which indicates the end of the induction period, when the conductivity of water begins to increase rapidly. The acceleration of conductivity is caused by the dissociation of volatile carboxylic acids produced during the oxidation process of biodiesel. These volatile organic acids are absorbed by the water. When the conductivity of this solution is recorded continuously, an oxidation curve is obtained (Figure 2) whose point of inflection is known as the induction period. This provides a good parametric value for oxidation stability.

Oxidative degradation chemistry

Figure 3 depicts the typical oxidation reactions of biodiesel.[10,17] Oxidation of biodiesel starts with the removal of hydrogen from a carbon atom to produce a carbon free radical. If diatomic oxygen is present, the subsequent reaction to form a peroxy radical is extremely fast. The peroxy free radical is not as reactive as the carbon free radical, but is sufficiently reactive to quickly abstract hydrogen from a carbon to form another carbon radical and a hydroperoxide (ROOH). The new carbon free radical can then react with diatomic oxygen to continue the propagation cycle. This chain reaction terminates when two free radicals react with each other to yield stable products like aldehydes, shorter chain carboxylic acids, insolubles, gum and sediments. As previously discussed, when biodiesel containing these oxidation products is used in the engine, it impairs engine performance.[10]

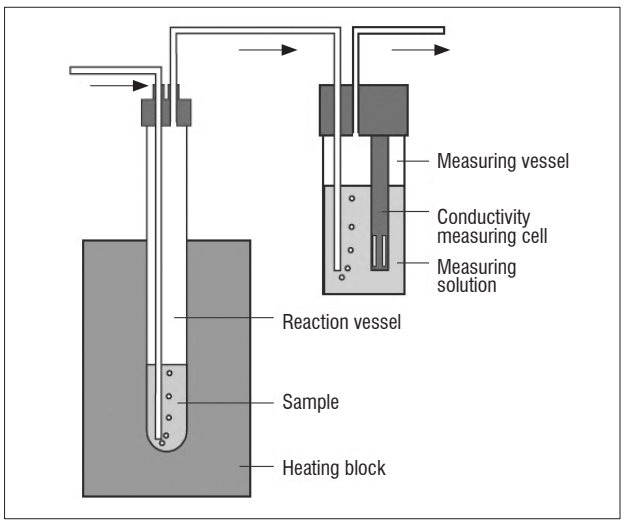


Figure 1: Principle of the Rancimat instrument.[11]

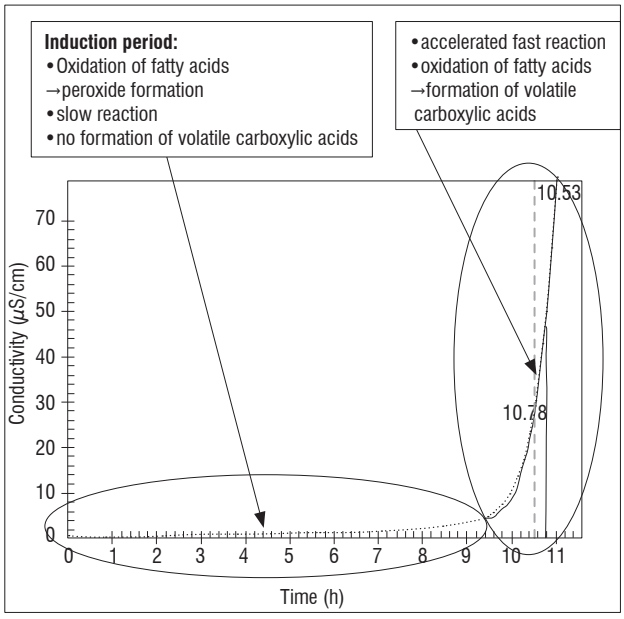


Figure 2: Typical curve obtained with a Rancimat instrument.

Initiation:	$RH + I \rightarrow R^- + IH$
Propagation:	$R^- + O_2 \rightarrow ROO^-$
	$ROO^- + RH \rightarrow ROOH + R^-$
Termination:	$R^- + R^- \rightarrow R\text{-}R$
	$ROO^- + ROO^- \rightarrow$ stable products

Figure 3: Typical oxidation reaction of biodiesel.[10,11]

Thermal stability

Thermal stability of biodiesel fuel refers to the resistance of biodiesel fuel to oxidation when exposed to high temperatures. The increase in temperature significantly increases biodiesel oxidation, which consequently increases the oil weight due to the formation of insolubles.[18-20] Sarin et al.[21] measured the induction period of various biodiesels, including jatropha, by using Rancimat equipment at 100, 110 and 120 °C. They found that the oxidation stability of biodiesel from all sources decreased as the temperature increased, but no difference in relative stability was noticed. However, the oxidation stability of biodiesel from the oil which contained only a small fraction of unsaturated fatty acids and a large fraction of saturated fatty acids was found to be even better than that of the biodiesel from oil sources which contained a large fraction of unsaturated fatty acids, for example, jatropha and Karanja oils, which showed less oxidation stability.

Freire et al.[22] conducted a thermal investigation of oil and biodiesel produced from *Jatropha curcas* L. The jatropha biodiesel was synthesised by the transesterification reaction with ethanol, using oils from seeds of different crops and a homogeneous catalyst (KOH). Samples were named 2005/2006, 2006/2007, 2007/A and 2007/B, terms which were related to the harvest period and storage conditions. The results indicated that physic nut oil and ethyl biodiesel produced from different crops were thermally stable until 203 °C (2007/B) and 108.9 °C (2007A). The higher volatility of biodiesel, indicated by a lower initial decomposition temperature, certifies the quality of physic nut biodiesel as biofuel. The oil and biodiesel produced from the 2005/2006 harvest were less stable than the others because of the higher water content in the seeds. In general, the oxidative induction time values were 13 min for both oils and biodiesels, except for the 2007/B sample, which was 33 min. The quality of *Jatropha curcas* oils was dependent on how the seeds were dried, treated and stored.[23]

Measurement of thermal stability using thermogravimetric analysis

Thermogravimetric analysis is a test that is performed on a sample to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature and temperature change. Analysis is carried out by raising the temperature gradually and plotting the weight against the temperature. A derivative weight loss curve can be used to infer the point at which weight loss is most apparent (Figure 4). For example, a sample of biodiesel with or without antioxidant of approximately 5 mg is placed on a partially sealed pan and positioned into a platinum pan beam attached to the instrument. The air is purged at a rate of 130 mL/min. The temperature can be programmed to increase from 30 °C to 500 °C at a ramp rate of 10 °C/min. When oxidation takes place, the removal of secondary oxidation products causes a sudden weight loss in the sample. The onset temperature of oxidation can be obtained by the intersection of the extrapolated baseline and the tangent line of the curve, as shown in Figure 4 for the thermogravimetric measurement of croton oil methyl ester, which was found to be thermally stable up to 211.40 °C. It should be noted that, practically, a biodiesel which maintains its stability up to 150 °C can be regarded as thermally stable.[11]

Storage stability

Storage stability is defined as the relative resistance of a liquid fuel to physical and chemical changes brought about by interaction with its environment.[10,24] Storage instability occurs when liquid fuel or biodiesels interact with contaminants, light, factors causing sediment formation and other stress factors that accelerate the oxidation degradability of the fuel and reduce the cleanliness of the fuel.[10] The resistance of biodiesel to oxidation degradation during storage is an important issue for the viability and sustainability of an alternative fuel. Several studies related to the storage stability of biodiesel derived from less common tree-borne non-edible oil seeds under different conditions have been reported in the literature.[25-28] Sarin et al.[21] studied the influence of metal contaminants on the oxidation stability of jatropha biodiesel. Different metals were put into contact with jatropha biodiesel for a period of 6 months. The oxidation stability results indicated that copper contamination had the strongest detrimental and catalytic effect on the oxidation stability of biodiesel, where even a small concentration thereof showed nearly the same influence on the oxidation stability as that of the large quantities.

Das et al.[27] investigated the long-term storage stability of biodiesel produced from Karanja oil for 180 days under various conditions and reported that the oxidative stability of Karanja oil methyl ester (KOME) decreased; that is, the peroxide value and viscosity increased with the increase in storage time of the biodiesel. KOME samples were stored in different storage conditions such as dark or sunlight exposure, with air or without air exposure and with or without antioxidant additives, to assess the effect of storage conditions on oxidation stability and the most appropriate conditions for biodiesel storage. The samples stored under the condition of being 'open to air inside the room' had a high peroxide value and viscosity compared to those stored in other conditions, because the presence of air enhanced oxidation degradation. It was concluded that the long-term storage study gave a better understanding of the effect of the different storage conditions on the stability of biodiesel. This suggests that it is necessary to take special precautions during the storage of biodiesel, for example, limiting access to oxygen and exposure to light, metal and moisture.

Antioxidant chemistry

An antioxidant is a chemical that delays the start or slows the rate of the oxidation reaction.[29] It inhibits the formation of free radicals or interrupts the propagation of free radicals and hence contributes to the stabilisation of the biodiesel.[30] The two most common types of antioxidants are chain breakers and hydroperoxide decomposers. The most frequently used antioxidants at present are the chain breakers, which include phenolic types and aminic types.[31,32] The antioxidant contains a highly labile hydrogen that is more easily abstracted by a peroxy radical than fatty oil or ester hydrogen. The resulting antioxidant free radical is either stable or further reacts to form a stable molecule that does not contribute to the chain oxidation process. In this way, the chain breaking antioxidants interrupt the oxidation chain reaction.[11,21,31] Most of the previous studies on the stability of fatty acids and esters investigated applications of the phenolic type of antioxidants.[11,12,17,21] In esters and fatty acids, two common sources of antioxidants are natural antioxidants (α, β, γ and δ tocopherols) and the synthetic antioxidants.[21,30]

Table 2 depicts three widely used effective synthetic antioxidants for improving the oxidation stability of biodiesels derived from non-edible oils, with their chemical structures, as reported in the literature.[8,11,17,26,28] It should be noted that most of the less common vegetable oils of African origin used for biodiesel production are non-edible oils. In most studies, pyrogallol (PY) and propyl gallate (PG) were more effective than butylated hydroxyanisole (BHA) because they possess three hydroxyl (−OH) groups in their aromatic rings as shown in Table 2, while BHA has only one −OH group in its molecular structure. The −OH group of the antioxidant is very active so the hydrogen is abstracted from −OH and donated to the

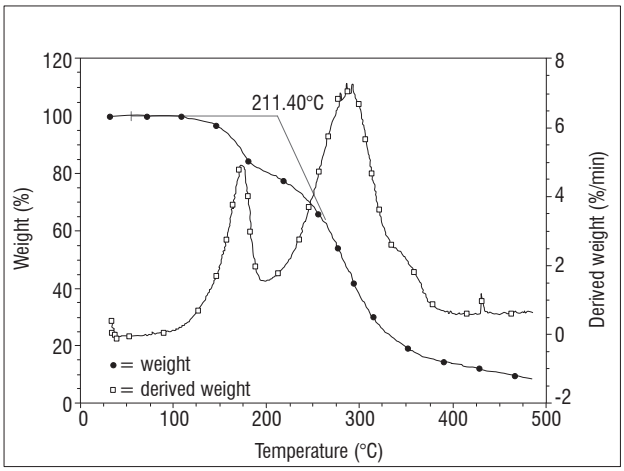
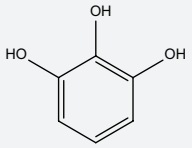
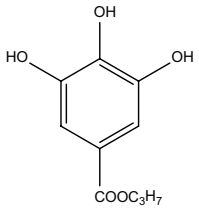
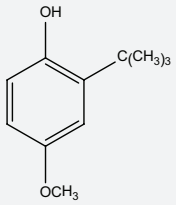


Figure 4: Typical thermogram for croton oil methyl ester.[11]

oxidised free radical to inhibit the rate of oxidation in methyl esters. The resulting antioxidant is a stable radical that can react with other fatty acid free radicals and further contribute to oxidation inhibition.[11]

Table 2: Synthetic antioxidants

Antioxidant name	Molecular structure
Pyrogallol: 1,2,3 tri-hydroxy benzene, 98%	
Propyl gallate: 3,4,5 tri-hydroxy benzoic acid, 99%	
Butylated hydroxyanisole: 2-tert butyl-4-methoxy phenol, 96%	

Stability of biodiesels from vegetable oils of African origin

Most of the less common vegetable oils of African origin are non-edible oils. They are derived from non-food feedstocks such as *Jatropha*, *Croton megalocarpus*, neem, *Moringa oleifera*, and rubber seed oils. Biodiesel produced from these non-edible oils (tree-borne non-edible oil seeds) is more economical compared to that produced from edible oils, which are more expensive than conventional diesel fuel, and eliminates the fuel versus food conflict.[11]

The challenge with regard to most non-edible oils is that they contain a high proportion of free fatty acids (FFAs) which, when they react with alkaline catalysts during the transesterification process, result in foam soap which prohibits the separation of biodiesel and glycerol. The soaps formed by the FFAs cause foaming in aqueous media which results in an increase in biodiesel viscosity.[33] The best method for reducing FFAs in non-edible oils is acid esterification; this is mainly a pre-treatment process for reducing the FFAs. The process converts FFAs to esters using an acid catalyst (H_2SO_4). The acid esterification process reduces the FFA concentration below 2% in the oil which is then recommended for the application of the one step alkaline transesterification method for biodiesel production in which the oil reacts with an alcohol (e.g. methanol) in the presence of a catalyst (e.g. KOH and NaOH).[34] The end products of the reaction are the fatty acid alkyl ester (biodiesel) and glycerine.[11] It should be noted that most of the biodiesel synthesised from non-edible oils of African origin are rich in unsaturated fatty acids which are prone to oxidation. It is therefore imperative that they are doped with antioxidants for longer storage.[21]

There have been several studies related to the production of biodiesel from less common vegetable oils of Africa origin (edible and non-edible oils) and their oxidation stability. The background of these feedstocks, the oil content of the seeds and the oxidation stability of synthesised biodiesels are discussed in the sections to follow.

Jatropha oil

Jatropha oil has been widely used for biodiesel production. It is mostly found in developing countries, especially in Africa and Asia. Jatropha plants have a high seed yield which can be continuously produced for 30–40 years. The oil content in the jatropha seeds is approximately 30–40% by weight.[21,23] Most researchers have found that jatropha oil can be used in biodiesel production as an alternative fuel in diesel engines and does not require major engine modification.[35] Free fatty acid content in jatropha oils is very high (approximately 14%) compared to those of other feedstocks.[34] Therefore, it requires two steps for biodiesel production (esterification followed by transesterification). The concern with biodiesel derived from jatropha is that it is rich in unsaturated fatty acid methyl esters[12,34] which are prone to oxidation.

Kivevele and Huan[12] and Kivevele et. al[17] studied the oxidation stability of biodiesel synthesised from jatropha oil of African origin. The fatty acid composition of produced jatropha oil methyl ester (JOME) was rich in unsaturated fatty acid (77.5%) with only 22.4% saturated fatty acid methyl esters. The neat JOME recorded oxidation stability of 5.85 h, meeting the minimum requirement of ASTM D6751 of 3 h. It is possible that the presence of naturally occurring antioxidants in the produced JOME favoured this reasonable oxidation stability. However, it did not meet the minimum requirement prescribed in the EN 14214 of 6 h as displayed in Table 1. Therefore, it was necessary to add antioxidants to increase oxidation stability for longer storage of JOME.

Amongst the antioxidants investigated were PY, PG and BHA. The overall performance of these antioxidants were in the order of PY>PG>BHA as previously discussed. It required only 200 ppm of PY and PG for JOME to meet the minimum requirement of ASTM D6751 (3 h) and EN 14112 (6 h). The South African standard for minimum requirement of oxidation stability of biodiesel is also 6 h (SANS 1935). Therefore, it can be seen that it is impossible to store JOME without antioxidant additives. JOME was observed to be thermally stable, displaying an onset temperature of 242.30 °C.

Moringa oleifera *oil*

Moringa oleifera is indigenous to the sub-Himalayan regions of northwest India, Africa, Arabia, Southeast Asia, the Pacific and Caribbean Islands and South America. It thrives best in a tropical insular climate and is plentiful near the sandy beds of rivers and streams. Moringa seeds contain between 33% and 41% (w/w) vegetable oil.[5,20] The potential of moringa oil of African origin as a feedstock for preparing biodiesel has been discussed previously in the literature.[36,37] However, few studies have reported on the stability of biodiesel derived from *Moringa oleifera* oil of African origin.

Kivevele and Huan[12] reported on oxidation stability of biodiesel synthesised from *Moringa oleifera* oil of African origin which was obtained from Tanzania and Kenya. Moringa oil methyl ester (MOME) is rich in 68.5% oleic acid methyl esters (C18:1) and 13.5% palmitic acid methyl esters (C16:0) with lower polyunsaturated fatty acid methyl esters (2.5%). Pure MOME recorded oxidation stability of 5.07 h, less than what is recommended in EN 14214 and the South African standard on oxidation stability of biodiesel (SANS 1935) of 6 h. The antioxidants were doped to increase the oxidation stability of MOME. Among the antioxidants investigated, PY and PG were more effective than BHA. Similar findings were previously reported in the literature on the oxidation stability of MOME.[17] It is also important to note that the most conspicuous property of MOME is its high cetane number of about 62.25, which is reported to be amongst the highest cetane numbers for a biodiesel fuel.[5] This is attributed to high saturated fatty acid methyl esters in its composition (26.5%). In addition, MOME was observed to be thermally stable, recording the onset temperature of 237.05 °C.

Rubber seed oil

Rubber trees have been widely used as a natural source of rubber, but now are regarded as one of the perfect biodiesel feedstocks in Nigeria as a result of their oil rich seeds.[38] Although there are variations in the oil

content of the seed from different countries, the average oil yield has been reported to be around 40%. Rubber seed oil (RSO) contains 17–20% saturated fatty acids (myristic, palmitic, stearic, arachidic and behenic) and 77–82% unsaturated fatty acids.[38,39] It can be noted that RSO is rich in unsaturated fatty acids which are prone to oxidation. Therefore, for longer storage of biodiesel derived from RSO, it needs to be doped with antioxidants. Njoku et al.[38] reported that RSO recorded higher oxidation stability than rubber oil methyl ester (ROME). The oxidative stability of ROME was reduced possibly because of the trans-methylation method used in its production in which the natural occurring antioxidants in the RSO were either deactivated during trans-methylation process or removed during separation and purification procedures. However, it was concluded that rubber oils can be used to produce biodiesel fuel with similar properties to those of conventional diesel fuel and can be used directly in a diesel engine without major engine modifications.

Neem seed oil

Neem oil is a non-vegetable oil pressed from the fruits and seeds of neem trees (*Azardirachta indica*). The neem plant is a fast-growing and long-living tree, native to Myanmar and India, but now grown all around the world. In Africa, it is mainly found in West Africa (Nigeria). It is an evergreen tree growing in tropical and semi-tropical regions.[40,41] Neem oil comprises mainly triglycerides and large amounts of triterpenoid compounds, which are responsible for the bitter taste. Neem leaves in the form of powder are used as a herbal supplement in health care and in bio-pesticides in agriculture.[40] A mature neem tree produces 30 to 50 kg of fruits every year and has a productive life span of 150 to 200 years.[40] Neem seed has been reported to have a high oil content of about 39.7–60% by weight, which is a high yield desirable for a potential feedstock for biodiesel production.[40,41] Aransiola et al.[40] investigated biodiesel derived from neem nut oil and observed that neem seed oil exhibits a high FFA content (acid value of 32.538 mg KOH/g) which required two steps for biodiesel production (esterification followed by the transesterification process). The produced neem oil methyl ester (NOME) had a high percentage (44.5%) of monounsaturated fatty acids (C18:1); polyunsaturated acids (C18:2, C18:3) at 18.3% and 0.2%, respectively, which are prone to oxidation; and a controlled amount of saturated fatty acids (C16:0, C18:0) at 18.1% each. Although oxidation stability of NOME was not investigated in their study, the reported fatty acid profile indicates the instability of NOME, especially during long-time storage. Therefore, it is imperative NOME be doped with antioxidants.

Croton megalocarpus oil

Croton megalocarpus plants are indigenous to East Africa, and are widely found in the mountains of Tanzania, Kenya and Uganda.[42-44] They are used to make a good living fence while the leaves are used for mulch and green manure and the oil mostly in medicinal activities.[42] In recent years, it has been discovered that the oil from *Croton megalocarpus* seeds is a potential source for biodiesel production.[42] *Croton megalocarpus* seeds contain approximately 40–45% of oil on mass basis when extracted mechanically using a hydraulic press.[42]

There are several reports of biodiesel production from croton oil in the literature.[43-46] In most of the studies, it has been reported that croton oil methyl ester (COME) is rich in unsaturated fatty acid methyl esters. Kafuku and Mbarawa[44] reported that COME has 72.7% linoleic fatty acids and that because it is rich in unsaturated fatty acids, COME has remarkably cold flow properties. It yielded a cloud and pour point of −4 °C and −9 °C, respectively. These superior cold flow properties displayed by COME indicate that it is viable for use in cold regions.

Kivevele et al.[11] investigated the impact of various antioxidants on the oxidation stability of COME. The neat COME recorded an oxidation stability of 4.04 h, which did not meet the minimum requirement of oxidation stability prescribed in EN 14214 and SANS 1935 of 6 h. The presence of polyunsaturated fatty acid methyl esters of about 78.5% in total was the reason behind COME recording lower oxidation stability. To improve the oxidation stability of COME for longer storage, the effectiveness of various antioxidants was investigated. Among the antioxidants investigated, PY and PG were still the most effective antioxidants in improving the oxidation stability of COME. Only 200 ppm of PY and PG was required to increase the oxidation stability of COME above the minimum requirement prescribed in EN 14214 and SANS 1935. Similar observations on the oxidation stability of COME were reported in other studies.[8,12,13,17]

Manketti seed oils

The manketti tree (*Schinziophyton rautanenii*) occurs naturally in southern and western Zambia, where it is locally known as mungongo and is called manketti in Angola, Namibia, Botswana, western Zimbabwe and northern Mozambique. The edible oil extracted from manketti tree seeds is used locally in cooking, food preparation and personal care products. In addition, the seed oil has applications in modern cosmetic and personal care products, such as a body rub during dry winter months or as a skin cleanser and moisturiser because of its healing and nurturing properties. The land where the manketti trees are indigenous is not suitable for agricultural exploitation and all of the nuts are collected from the wild. The development of additional uses and external markets for this under-recognised oil seed could benefit the rural communities, provide a new export product for Africa, a new ingredient for the global cosmetic industry and an alternative fuel (biodiesel). There are few studies in the literature discussing manketti seeds oil as a possible source for biodiesel production. Juliani et al.[47] studied mungongo cold-pressed oil as a new natural product with potential cosmetic applications. They discovered that this oil is rich in unsaturated fatty acids – 25% linolenic acid (C18:3), 37% linoleic acid (C18:2), 15% oleic acid (C18:1), 8% palmitic acid (C16:0) and 9% stearic (C18:0) acid.

Kivevele and Huan[48] produced biodiesel from manketti seeds oil and evaluated its physical and chemical properties. The FFAs of manketti seeds oil was 1.57% which is below the 2% required for a one step transesterification process to produce manketti seeds oil methyl ester (MAME). Most of the fuel related properties of the produced MAME fulfilled the minimum requirement for biodiesel standards such as ASTM D6751, EN 14214 and SANS 1935. MAME showed slightly higher oxidation stability (4.75 h) which fulfilled the minimum requirement of ASTM D6751 (3 h), but did not meet the minimum requirement of EN 14214 and SANS 1935 of 6 h, due to their high percentage of methyl linoleate (45.6%) and methyl linolenate (20.3%) which are prone to oxidation. To improve the oxidation stability of MAME, the antioxidants were doped at 200, 500 and 1000 ppm dosage and tested in the Rancimat to observe effectiveness. It was found that oxidation stability increased with the increase in dosage of these antioxidants. Amongst the antioxidants used, PY and PG were found to be more effective than BHA at all dosages.

Marula nut oil

The marula tree (*Sclerocarya birrea)* is indigenous to most parts of southern Africa. The tree grows in warm and dry climatic conditions and produces oval fruits that turn pale yellow when ripe. The fruit consists of a hard woody seed covered by pulp and juice that make up the fleshy part of the fruit. The hard seed contains mostly two oil rich nuts (kernel) which can be eaten as a snack. However, small groups of rural communities in some parts of southern Africa are currently using the nut oil to produce cosmetic ointments.[49] There is now a worldwide trend to explore wild plants for oil to supplement the already existing sources of oil. The fact that the marula tree grows in drier parts where common oil seeds cannot thrive has stirred interest in marula nut oil as a valuable renewable source of energy. Studies exploring the potential use of marula nut oil as a potential source for biodiesel production are scarce. Gandure and Ketlogetswe[49] investigated the crude marula nut oil of Botswana's climatic conditions as a possible source of biodiesel. The oil content of the marula nut was reported to be about 59%. This is a relatively high yield desirable as a potential feedstock for biodiesel production. The FFA content of the crude marula oil was 0.7%, which thus required a one step transesterification process during biodiesel production. The oil was rich in oleic fatty acid (about 70%); however, the oxidation stability of marula nut oil was not reported.

Mariod et al.[50] studied the synthesis of alkyl esters from three unconventional Sudanese oils for their use as biodiesel. Amongst the oils investigated was the Sudanese marula oil. It was observed that biodiesel synthesised from marula oil recorded remarkably high oxidation stability (27.1 h), meeting both global biodiesel standards (ASMT D6751 of 3 h and EN 14214 of 6 h). The higher oxidation stability recorded by Sudanese marula methyl ester possibly was because of the presence of naturally occurring antioxidants in crude marula oil and also reasonably high saturated fatty acids (25.2%) and lower polyunsaturated fatty acids (6.1%), which are more prone to oxidation than are monounsaturated fatty acids.

Conclusion

In the present study, we reviewed the stability of biodiesel synthesised from less common vegetable oils of African origin such as *Jatropha*, *Moringa oleifera*, *Croton megalocarpus*, rubber seed, manketti seed, neem and marula nut oils. Most of the biodiesels synthesised from these vegetable oils were observed to meet the minimum requirements prescribed in the global biodiesel standards such as ASTM D6751 and EN 14214. However, the outstanding issue is the oxidation stability. Most of the biodiesels are rich in unsaturated fatty acids which are prone to oxidation. The biodiesels recorded oxidation stabilities below the minimum requirements prescribed in EN 14214 and SANS 1935 of 6 h, except biodiesel made from marula nut oil. Therefore, it can be concluded that for longer storage it is imperative that these biodiesels be doped with antioxidants to increase oxidation stability. Among the antioxidants investigated in various studies on improving the oxidation stability of biodiesel derived from the reviewed vegetable oils of African origin were PY and PG, which were found to be the most effective.

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Authors' contributions

T.K developed the concept, wrote the manuscript and performed the data analysis. Z.H was the project supervisor.

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