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CHARACTERISATION AND ANTIOXIDANT EVALUTAION OF GARLIC EXTRACT AS A NATURAL ANTIOXIDANT FOR JATROPHA CURCAS BIODIESEL STABILITY

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ABSTRACT

The need for environmentally friendly source of energy gives biodiesel lead over fossil fuels, Oxidation is one of the impediments to the biodiesel quality, the greater the oxidation the lesser the quality of the biodiesel and vice versa. Synthetic antioxidants are commonly used to improve biodiesel stability regrettably they have damaging effect on the environment. This study explores the effectiveness of garlic extract as natural antioxidants for Jatropha curcas biodiesel stability. The garlic extract was characterized using FTIR and GC-MS and the fuel parameters of the produced biodiesel were determined. The garlic extracts were added were added in 1%, 3% and 5% respectively to the biodiesel samples and the oxidation stability test of the biodiesel samples were carried out using Rancimat method. The FTIR and GC-MS result of the extract confirmed the existence of phenolic and sulphur compounds. The fuel parameters of the biodiesel produced were in agreement with ASTM standard values. A rise in Induction period of the biodiesel was observed in samples BG3 and BG5 having 3% and 5% antioxidants respectively. The results demonstrates that the antioxidant (garlic extract) can improve induction period of the biodiesel hence can act as natural antioxidant on biodiesel samples.

Keywords
Garlic extract, Jatropha curcas, Oxidation stability, Biodiesel, Fossil fuel, FTIR and GC-MS.

1.0 Introduction

Energy is an essential driving factor for socioeconomic development in our present society. Its impact touches all aspect of human endeavors (Sokoto *et al.,* 2013). The global need to conserve energy, reduce cost and to employ environmentally friendly fuel remains a challenge to researchers in the industries and the academics (Mamuda *et al.,* 2016). Nowadays, biomass has been focused as an alternative energy source since it maintains the level of carbon dioxide in the atmosphere constant through the process of photosynthesis. The carbon dioxide emitted during the combustion of biomass would be absorbed during the process of photosynthesis (Hossain *et al.,* 2008).

Biodiesel Oxidation stability is an essential quality criterion for biodiesel commercial possibilities. When biodiesel is stored for a long time, the fuel may degrade before it can be used and the by- products of biodiesel oxidation are harmful to the engine (Knothe, 2007; Devi *et al*., 2018). Oxidation stability is used to describe the ageing behavior of fuel during transport and storage, the slower the rate of oxidation the higher the quality of the fuel and vice versa.

The oxidation process can be slowed by eliminating materials and conditions that initiate oxidation or by adding various antioxidants to inhibit the initiation and propagation of free radicals, thus, minimizing the formation of degradation compounds(e.g., peroxides, aldehydes, ketones, dimers, and polymers (Kreivaitis *et al.,* 2013). The antioxidants are used in many industries, including food, pharmaceuticals, fuels, lubricants, and petrochemicals (Dantas *et al.,* 2011; Rodrigues *et al.,* 2009).

Antioxidant compounds in food are found to have a health-protecting factor. Primary sources of naturally occurring antioxidants are whole grains, fruits and vegetables. Garlic *(Allium sativum)* has been used in world cuisines as well as in herbal medicine for thousands of years and, at times, has been claimed to help prevent everything from high cholesterol to cancer (Rahman, 2012). This gives an insight of the tendency of using garlic as antioxidant for biodiesel.This work investigates the effect of garlic extract as a natural antioxidant in improving oxidation stability of biodiesel produced from jatropha curcas seed oil.

2.0 Materials and Methods

2.1 Materials

The garlic was procured from Ramin Kura Market in Sokoto State Nigeria, while the jatropha curcas seed sample was procured from the National Research Institute for Chemical Technology (NARICT) Zaria, Kaduna State Nigeria. The Jathropha oil was extracted using cold pressing machine. Reagents used in this study were Ethanol, Methanol, Potassium Hydroxide, Isopropyl Alcohol, Phenolphthalein, Hydrochloric acid, Carbon tetrachloride, Potassium Iodide and Sodium thiosulphate.

2.2 Method of Biodiesel Production

This work adopted the method of biodiesel production reported by Barnawal and Sharma, 2005. In this process the crude jatropha oil (100 cm^3) was measured in a beaker and kept aside, 1g of KOH was weighed and 20 cm^3 of methanol was measured in a measuring cylinder and poured into a round bottom flask.1g KOH was put into the round bottom flask containing the methanol, the mixture (methanol and KOH, i.e methoxide) was covered and shaken until the KOH dissolved. The mixture was added to the oil in the beaker and the oil with the methoxide in the beaker was placed in a water bath at 60^0C and was covered for 20 minutes. After heating the oil and the methoxide in the water bath for 20 minutes, the mixture of oil and methoxide has been transesterified to biodiesel and glycerol. A separation funnel was used to separate the biodiesel from glycerol, the glycerol was amber colored and the biodiesel was light yellow in colour, the glycerol was at the bottom of the separation funnel and the bodiesel was at the top. The percentage yield of biodiesel was calculated using equation 1.

$$\% \text{ Biodiesel Yield} = \frac{\text{Weight of Biodiesel}}{\text{Weight of Oil}} \times 100 \ldots\ldots\ldots\ldots\ldots 1$$

The fuel properties of the produced biodiesel were also determine, which Includes acid value, iodine value, specific gravity, viscosity, flash point and sulphate ash content.

2.3 Characterization Garlic Extract

The garlic was sliced and dried in an open oven at 50^0C and then grinded into powder. The powered garlic were extracted with the aid of a soxhlet extractor using ethanol as solvent according to the method reported by Hossain *et.,al (2008)* and were characterised using FT-IR and GC-MS.

The FTIR analysis was carried out at the Central Science Laboratory Usmanu Danfodiyo University Sokoto using Cary 630 model spectrophotometer. The transmission rate was set at the range of 4000 - 650 Cm^{-1}. The samples were placed in the sample compartment of the spectrometer and spectral data was obtained.

The GC-MS analysis was carried out using GC 7890B, MSD 5977A, Agilent Technology at the Central Science Laboratory Usmanu Danfodiyo University Sokoto. 0.5 mL of the samples was transferred into a 15mL plastic centrifuge tube and to it 10mL of ethanol were added and then votex mixed for 10 minutes. The mixture was centrifuged at 3500 rpm for 10 minutes. The supernatant (1.0 µL) was injected in to the GC machine.

2.4 Biodiesel Preparation for Oxidation Stability Determination

Four biodiesel samples in replicates were used in the experiment one with no antioxidant (B00) and three samples each containing 1%, 3% and 5% (BG1, BG3, BG5) garlic extract solution respectively, the oxidation stability was measured as per EN14112. Experimental setup for Automatic Biodiesel Stability Tester KD-R2223 was used. According to this method, the oxidation was induced by passing a stream of purified air at a rate of 10 l/h through the biodiesel sample ($30cm^3$) kept at 102^0C. The vapours released during the oxidation process together with the air were passed into the flask which contained $60cm^3$ of demineralized water and contained an electrode for measuring the conductivity. The electrode was connected to a measuring and recording device. The end of the induction period was indicated when the conductivity starts to increase rapidly. This accelerated increase was caused by the dissociation of volatile carboxylic acids produced during the oxidation process and absorbed in the water. When the conductivity of this measuring solution was recorded continuously, an oxidation curve was obtained. The point of the inflection of that curve is known as the induction period which gives the quantitative measurement of oxidation stability.

3.0 Results and Discussions

3.1 Percentage Yield Fuel Properties of the Produced Biodiesel

Fuel properties gives an insight on the quality and usability of biodiesel, the more fuel properties are within the approved limit the higher the fuel acceptability and vice versa. The acid value of the biodiesel (0.47±0.13 mgKOH/g) as presented in Table 1 is within the acceptable limit specified by ASTM, this was in contrary to 0.31 mgKOH/g reported by Ved and Padam (2013). This indicates that the biodiesel may not cause wear in fuel systems and storage tanks, free fatty acids can lead to corrosion and may be as a result of water in the fuel (Gerpen *et al*., 2004). Iodine value is a measure of unsaturation level of fats and oils (Knothe, 2006). Esterification process reduces the iodine value to a small extent (Asmare and Gabbiye, 2014). The results of iodine value (8.7±0.02 gI_2/g) as presented in Table 1 are within the ASTM limit. It is also below 13.30 gI_2/g reported Okoronkwo *et al.,* (2014) for African bush mango. The value shows that the biodiesel can exist in liquid form at room temperature.

Specific gravity is an important parameter that affects the mass of fuel injected into the combustion chamber. The value (0.87 ± 0.01) as reported in Table 1 is within the ASTM limit and was in agreement with 0.870 reported for *mangifera indica* oil biodiesel (Ogunsuyi, 2012).

Viscosity is one of the required parameters regarding fuel atomization, combustion as well as fuel distribution (Solomon *et al*., 2010). The Kinematic viscosities of the produced biodiesel (3.7± 0.00 cst) as seen in Table 1 is within the ASTM limit and lower than 9.1cSt for algae oil biodiesel reported by Indhumathi *et al.* (2014). Higher viscosity fuels can cause poor fuel combustion that leads to deposit formation.

Flash point is the lowest temperature at which a volatile products gives sufficient flammable vapours to ignite or momentarily flash. The results obtained (120±0.00 ^{0}C) as shown in Table 1 is within the ASTM limit, lower than 135^{0}C reported for *Lagenaria vulgaris* oil biodiesel (Sokoto *et al*.,2013) and higher than 90^{o}C reported by Muhammad *et al*,. (2015) for *Lageneria siceraria* oil biodiesel. This shows that the produced biodiesel is safe for handling, storage and transportation.

The ash content of the biodiesel (0.01±0.00) as presented in Table 1 is within the ASTM limit and lower than 0.04 reported for *Mangifera indica* biodiesel (Ogunsuyi,2012). Therefor, the residue remaining after complete combustion of the biodiesel will not be a problem to the fuel injector system.

Table 1: Percentage Yield and Fuel Properties of the Biodiesel

Properties	Value	ASTM
Yield (%)	82.5±1.20	
Acid Value (mgKOH/g)	0.47±0.13	0.5 Max
Iodine Value (gI_2/100g)	8.7±0.02	130 max
Specific Gravity	0.87 ± 0.01	0.86-0.90
Viscosity @ 40 (cst)	3.7± 0.00	1.9-6.0
Flash Point (^{0}C)	120±0.00	100-170
Sulphated Ash	0.01±0.00	0.03 Max

3.2 Characterisation of Garlic Extract

3.2.1 FT- IR Analysis Results

The FT-IR spectra of garlic extracts as shown in Table 2 indicated the presence of some functional groups such as hydroxyl, carbonyl, carboxylic, organosulphur and some aromatics. The extract was having a broad absorption at about 3300 cm^{-1} which was due to OH bend for hydroxyl group (Devi *et al.,* 2018), it is also having an absorption around 2910 - 2900 cm^{-1} due to asymmetric stretching of C-H groups of aromatic compound (Divya *et al.,* 2017), these two absorptions might give the two extract an antioxidant activity. The peaks at around 1650 - 1620 cm^{-1} was due to C=O while the peaks at around 1410 -1400 cm^{-1} and the other at 1000 cm^{-1} were due to O-H bend of carboxylic acids and S=O presence of organosulphur (Divya *et al.,* 2017) respectively.

Table 2 FT-IR Absorption Band of Garlic Extracts

Wave number cm^{-1}	Functional Groups
3300	O-H bend for hydroxyl group
2910	C-H stretching for aromatic compound
1650	C=O stretching
1400	O-H bend of carboxylic acids
1010	S=O stretching

3.2.2 GC-MS Analysis Results

the results obtained as shown in tables 3 revealed that garlic extract were found to have reasonable amount of phenolic compounds. phenolic compounds such as butylated hydroxyanisole, butylated hydroxytoluene, propyl gallate and tertiary butylhydroquinone were used as synthetic antioxidants in liquid fuels (das *et al.*, 2009). This gave an insight that the extract can have an antioxidants activity due to the presence of phenolic compounds. it is also in agreement with the ft-ir result presented earlier.

so also the extract was found to have some sulphur compounds which were reported to have antioxidant activity (tsai *etal*.., 2005). the garlic extracts were also found to have octadecenoic acid which was reported to have antioxidant property (gnanvel and sarah, 2013).the result is comparable to that of tsai *et al*., (2005) that reported 22.5, 19.7, 10.2, 11.6 and 20.5 (mg gae/g) as total phenolic contents of ginger, red paper, garlic, green onion and leek extracts respectively and confirmed that all the extract have antioxidant activities. the result was in conformity to chive *et al*. (1992) that reported sulphur compunds as one of the components of onion, odo, *et a,l*. (2017) and saravanakumar *et al*., (2016) that reported octadecanoic acid in root bark extracts of *brenania brieyi* and leaves extract of *pleiospermium alatum* respectively.

Table 3. Percentage Composition of Compounds with Antioxidant Activity in Garlic Extracts

Compound	Percentage Peak Area (%)
Benzene, 1,1 -oxybis[3-phenoxy	5.48
Acetic acid, (4-chlorophenoxy)-, dodecyl ester	5.10
1-(2-Hydroxy-5-methylphenyl)-1-p ropanone (E)-oxime	2.03
4-Chloro-2-methoxyphenol	2.01
Benzene, 1-propenyl	1.65
1-(4-chlorophenyl)-4-phenyl-3-(2-thienyl)-	1.62
4-(4-methylphenyl)-5-phenoxy-6-phenyl	1.09

Dimethyl(2-fluorophenyloxy)dodecyloxy-	1.04
7-Hydroxy-4-methyl-3-(2-thiophenyl)coumarin	0.93
2-oxo-2- phenoxy-4-iodomethyl	0.62
1-[4-(chlorodifluoromethoxy) phenyl]	0.30
9-Octadecenoic acid (Z)	0.26
3-[(4-Ethoxy-2-nitro-phenyl)-hydra zono]	0.22
3-(2-hydroxyphenyl)	0.22
Total	22.57
Other compounds	77.43

3.3 Effect of Garlic Extract on Jatropha Biodiesel Stability

Biodiesel oxidation stability is the ability of biodiesel to resist change in its physicochemical properties cause by interaction with light, oxygen or water. The biodiesel instability is inherent of it chemical composition, biodiesel undergoes autoxidation with time. Oxidation can alter the physical and chemical properties of fuel, this result to distinct instability in the auto ignition engine. This disadvantage makes fuel unsuitable for use in engines because the resulting oxidation products can damage the motors of vehicles (Marilena, *et al., 2011*). Antioxidants are mostly employed to improve the stability of a biodiesel. Induction Period which is the time propagation starts, this is used to assess the efficiency of an antioxidant on biodiesel stability.

The effect of garlic extract as biodiesel antioxidant is shown in figure 1. The result shows that neat biodiesel have an induction period of 60 minutes. Addition of 1% garlic extract have not affected the induction period of the produced biodiesel. Induction period (IP) increases with increase in percentage of garlic extract (3% and 5%); 15 minutes increase in induction period was observed with addition of 3% garlic extract and 30 minutes rise in induction period was observed for 5% garlic extract. This infers that garlic extract can be used as antioxidant in jatropha curcas biodiesel. The result is lower than 0.58 hours increase as reported by Devi *et al* (2018) for potato peel extract and 3 hours ASTM required standard.

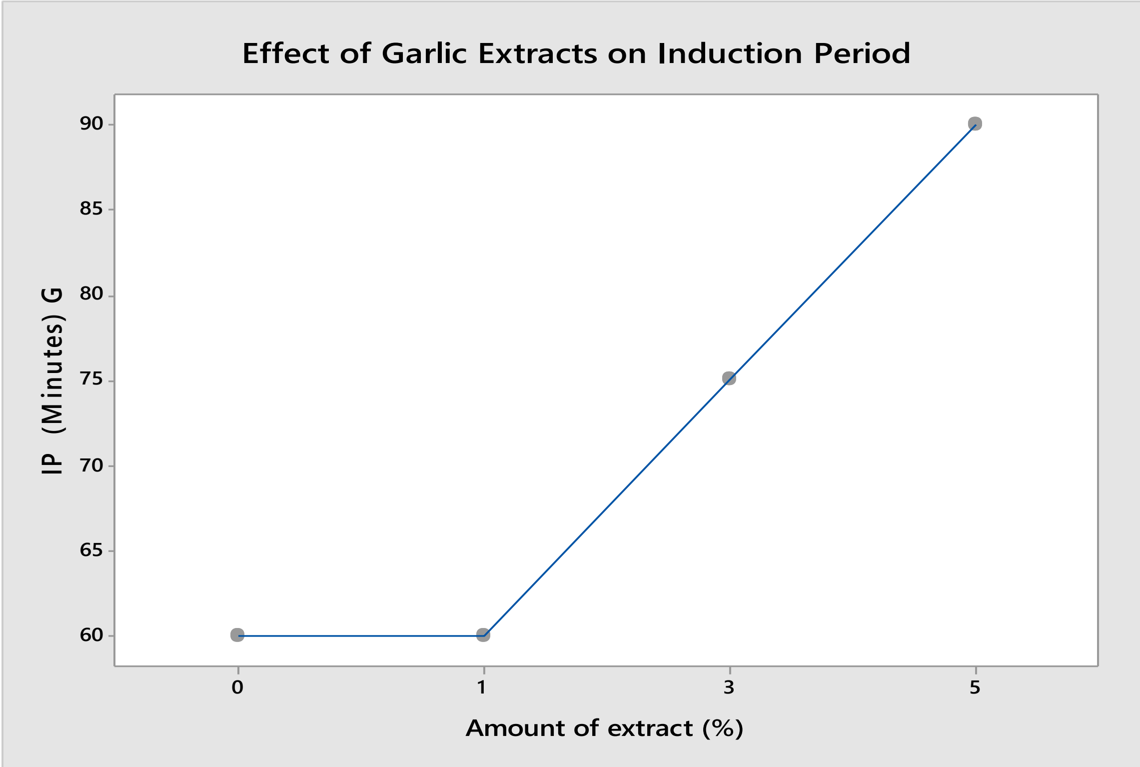

Figure 1: Effect of Garlic Extract on Induction Period.

4.0 Conclusion

This work qualitatively demonstrates that garlic extract can serve as natural antioxidants for biodiesel due to its antioxidant properties. The Induction Period of the biodiesel tends to increase with increasing amount of antioxidant. Though none of the samples meet the required standard specification of 3 hours but it shows that garlic can act as natural antioxidants for biodiesel stability. Therefore, this study recommends the usage of natural materials as biodiesel antioxidants.

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