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Gas Chromatography Mass Spectrometry of *Quassia undulata* Seed Oil

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Abstract
The use of gas chromatography mass spectrometry (GC MS) as a sensitive and specific technique for the separation and identification of fatty acids has drawn the interest of many biodiesel producers as a means of identifying the fatty acid profiles of oil seeds, monitoring the reaction process and determining the relative amount of each component. In this research, the GC MS of *Quassia undulata* seed oil revealed the following major fatty acids with their percentage occurrences: 6-octadecanoic acid (46.36%), octadecanoic acid (33.44%), hexadecanoic acid (10.45%) and 11-nonadecanoic acid (5.70%). The other fatty acids occurred as minor components. The result indicates that 6-octadecanoic, a monounsaturated fatty acid is the most abundant component in *Quassia undulata* seed oil. Secondly, the unique combination of saturated and unsaturated fatty acids will have a positive influence on both the cold flow properties and stability of the fuel to oxidation, peroxidation and polymerization reactions. The revealed fatty acids and their percentage occurrences, therefore, affirm the suitability of *Quassia undulata* seed oil as a potential non-edible feedstock for the production of a high quality biodiesel.

Key words: *Quassia undulata*, GC MS, Biodiesel, Gbur, seed oil, Gas Chromatography, Mass Spectrometry

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Introduction

The search for a suitable alternative to petroleum derived fuel has been more rewarding with triglycerides (Pazoukiet *al*., 2010; Knothe, 2005). The properties of these triglycerides and their applications depend on the fatty acid constituents (Botinesteanet *al*., 2012; Moser, 2009). A large variety of fatty acids from algae (Sarsekeyeva *et al*., 2014; Elumalai and Sakthivel, 2013), animals (Young *etal*., 2012), edible (Kailet *al*., 2012) and non-edible (Gashaw and Lakachew, 2014; Ahmad *et al*., 2011) plants have been investigated for the production of biodiesel.

Due to the large variety of fatty acids that can be used for biodiesel production and the change in fuel characteristics that can occur for each feedstock used, various analytical techniques are often employed to identify the fatty acid composition and to monitor the quality of biodiesel (Pinto *et al*., 2005). These include the use of Gas chromatography-Mass spectrometry (Panchal *et al*., 2014), Near-Infrared Spectroscopy (Liu *et al*., 2015), Fourier Transform Infrared (Hariram and Shangar, 2014), Gas chromatography-flameionizationdetector (Young *et al*., 2012) in fatty acid and fatty acid methyl ester analysis.

Gas chromatography (GC) and mass spectrometry (MS) has proved an effective combination for fatty acid and biodiesel analysis, for the capacity of this technique to simultaneously identify and quantify the various components of the sample mixture (Soomro and Sherazi, 2013; Monteiro *et al*., 2008; Yayli *et al*., 2001; Pauls, 2011; Knothe, 2001). There are numerous scientific affirmations that the hyphenation of GC to MS is a good marriage. This is due to the high sensitivity and high specific detection of this technique (Eberlin, 2009), which allows for a much finer degree of substance identification than either unit used separately (Sahil *et al*., 2011).

The ability of GC MS to separate and confirm identity by mass spectral structure elucidation has enabled researchers to study the influence of fatty acids on the quality of biodiesel fuel. For example, several reports have stated the good fuel properties of biodiesel due to the occurrence of high levels of monounsaturated fatty acids and low levels of saturated and polyunsaturated fatty acids (Koria and Nathya, 2011; Knothe, 2008; Pinto *et al*., 2005). In this connection, Refaat (2009) and Knothe (2008) proposed methyl oleate as a suitable major biodiesel component. Knothe also noted methyl palmitoleic acid as an alternative to methyl oleate with comparable advantages, especially with regards to low-temperature properties.The determination of components by GC MS has continued to gain prominence not only in establishing the oil composition but also in quality (Aluyor *et al*., 2009). This, in addition, finds importance when choosing vegetable oils and fats that will give the desired biodiesel quality.

One of the key features (hallmarks) of countries that have a breakthrough in biodiesel production and utilization is the extensive qualitative and quantitative research on the fatty acid profiles of suitable oil producing seeds amenable to their regions. The objective of this study is to analyze *Quassia undulata* seed oil so that the revealed fatty acid profile can serve as a guide to the possible transesterification of the oil to fatty acid methyl or ethyl esters. Secondly, the type and percentage occurrence of the fatty acids with respect to their saturation or unsaturation can give an idea of the quality of biodiesel that can be produced from this feedstock. Many non-edible plants in Nigeria have been investigated but the need still remains for the unstudied plants. In this research, the fatty acids of *Quassia undulata* were investigated.

Quassia undulata is a perennial shrub distributed in tropical and subtropical Africa, America, Asia and Australia (Louppe*et al.,* 2008). *Quassia undulata* is a fast growing member of simaroubaceae family that has rich quassinoids (seco-triterpernoid compounds), including quassin responsible for the bitter taste (50 times more bitter than quinine) [Louppe *et al.,* 2008]. Various quassinoids isolated from the plant have shown antimalarial (Ajaiyeoba *et al.,* 1999), antimicrobial and cytotoxic activity (Adesanwo*et al., 2009*). Because of the strong political and social pressures to avoid the use of edible oils as a biodiesel source, the non edible seeds of *Quassiaundulata* therefore occupies a special place among the oil plants that grow in Nigeria.

Materials and Methods

Collection, processing and Extraction of oil from Quassia undulata seed: The sample preparatory process and subsequent extraction of the oil were previously reported (Iko and Eze, 2012).

Gas chromatography mass spectrometry (GC MS) analysis of QUSO: The GC MS analysis was performed with Shimadzu, GCMS-QP2010 gas chromatography mass spectrometer employing the following conditions; the injection temperature was 250°C. The column oven temperature was initially held at 70°C and then increased to 280°C at 10°C/min with a hold time of 5min. The carrier gas was helium at a column flow rate of 1.80mL/min and the total flow rate of 40.8mL/min at the pressure of about 116.9kPa. The analysis was performed at injector temperature of 250°C and ion source temperature of 200°C and a split ratio of 20:0. An electron ionization system with ionization energy of 70eV was used for GC MS detection while scanning mass range from 30.00 to 350.00 m/z with a total scan time of 24 min. Identification of the unknown QUSO profiles was performed by comparing the MS spectra of QUSOs with those from the National Institute of Standards and Technology (NIST) mass spectral library of the GC MS system while quantification was done by Shimadzu data handling software and the QUSOs composition was reported as relative percentage of the total peak area.

Results and Discussion

The Gas chromatographic analysis of the fatty acids showed several peaks in form of total ion current (TIC) chromatogram (Fig 1). These peaks represent an important tool for the identification of individual components (Montalbino, 2012). The area percentage covered by individual peaks, their retention times, molecular formula, molecular weight and compositions are presented in table 1. The fatty acid profile was dominated by 6-octadecanoic acid with a percentage of 46.36. The percentage composition of 6-octadecanoic acid in QUSO is similar to the monounsaturated fatty acids of many fuels adjudge to have suitable properties such as *Tabernaemontana divaricata* seed oil which has 56.23% of oleic acid (Basumatary *et al*., 2013), rape seed oil methyl ester has 46.12% (Milina and Mustafa, 2013), *Pistacia chinensis* seed oil methyl ester has 52.32% (Quin *et al*., 2012). Generally, monounsaturated fatty acids have been reported to strike the best balance between cold flow properties and the oxidative stability of biodiesel. Fuels with one major component have also been suggested to have more favourable properties (Knothe, 2008). Similar amounts of monounsaturated fatty acids and saturated fatty acids were found (table 1). Octadecanoic acid, heptadecanoic acid and 11-nonadecanoic acid were also present in reasonable amounts. A number of minor components and the presence of other derivatives were also confirmed.

The identity and distribution of fatty acids have been amply documented as the determinants of both the physical and chemical properties of biodiesel and other derivatives of fatty acids. The fatty acid profile of QUSO indicates that when transesterified to methyl or ethyl esters, the percentage occurrence of the unsaturated fatty acid components will have a positive influence on the kinematic viscosity, cloud point of the fuel and other cold flow properties while the saturated fatty acids will impact on the stability of the fuel to oxidation, polymerization and peroxidation reactions. The unique percentage occurrence of monosaturated (52.06) and saturated (47.94) fatty acids has affirmed the eligibility of QUSO as a good candidate for the tranesterification reaction into biodiesel with suitable fuel properties.

GC MS Analysis of QUSO

Table 1: Result of *Quassiaundulata* Seed Oil by GC-MS Analysis

Name of compound	Mol. Formula	Mol. Weight (g/mol.)	Ret. Time (min)	Composition (%)
Heptadecanoic acid	$C_{17}H_{34}O_2$	270	15.592	0.66
Heptadecanoic acid	$C_{17}H_{34}O_2$	256	16.150	10.45
11-Nonadecenoic acid	$C_{19}H_{36}O_2$	296	17.292	5.70
Nonadecanoic acid	$C_{19}H_{38}O_2$	298	17.492	1.63
6-Octadecenoic acid	$C_{18}H_{34}O_2$	282	17.882	46.36
Octadecanoic acid	$C_{18}H_{36}O_2$	284	18.025	33.44
Heneicosanoic acid	$C_{21}H_{42}O_2$	326	19.225	0.26
9,12-octadecadienoyl chloride	$C_{18}H_{31}O\,Cl$	298	20.542	1.50

Chromatogram of QUSO

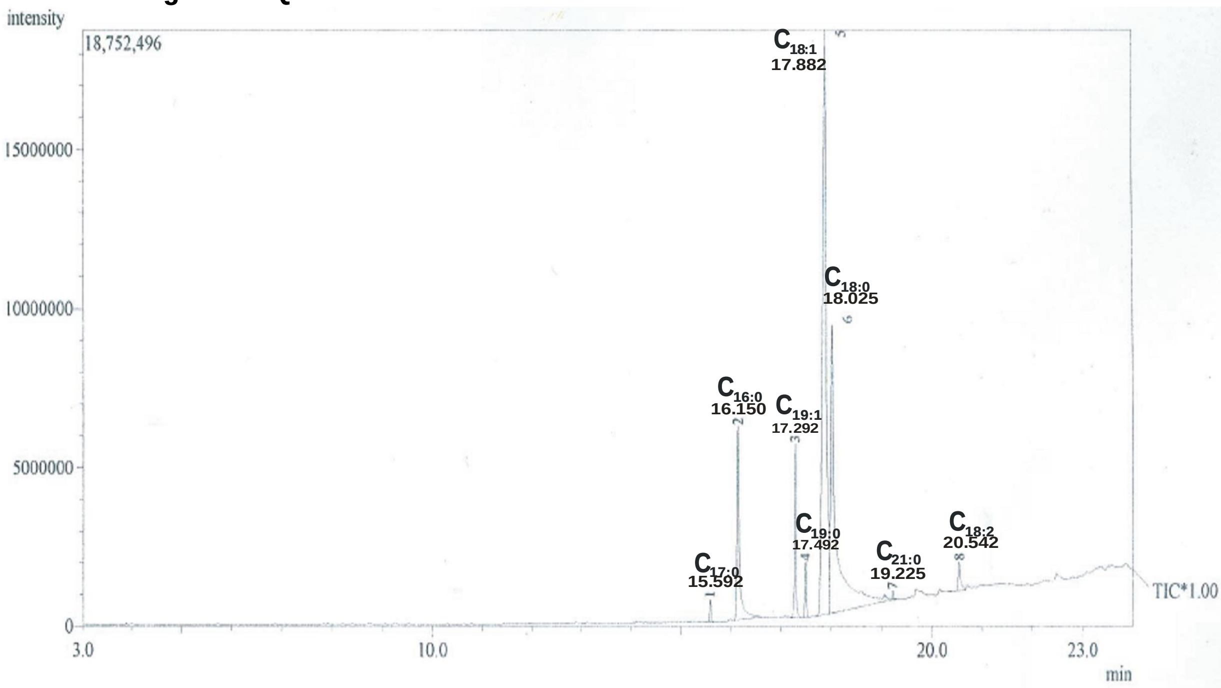

Figure 1: Total Ion Chromatogram of QUSO
The meaning of the legends in Fig 1are: C17:0 = Heptadecanoic acid, C16:0 = Hexadecanoic acid, C19:1 = 11-Nonadecenoic acid, C19:0 Nonadecanoic acid, C18:1 = 6-Octadecenoic acid, C18:0 = Octadecanoic acid, C21:0 = Heneicosanoic acid, C18:2 = 9,12-octadecadienoyl chloride

Conclusion

QUSOis a promising non-edible seed oil for the production of biodiesel going by the balance between the saturated and unsaturated fatty acids profile as revealed by GC-MS. The suitability of this seed oil as a biofuel resource was earlier forecasted with respect to its physicochemical properties (Iko and Eze, 2012). Therefore, the fatty acid profile further confirms the potential fuel properties of *Quassia undulata* seed oil and its suitability for biodiesel production.

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