African Journal of Biotechnology Vol. 11(42), pp. 10003-10007, 24 May, 2012
Available online at http://www.academicjournals.org/AJB
DOI: 10.5897/AJB11.1659
ISSN 1684–5315 © 2012 Academic Journals

Full Length Research Paper

Physico-chemical properties of oil from some selected underutilized oil seeds available for biodiesel preparation

Sabinus Oscar O. EZE

Department of Biochemistry, University of Nigeria Nsukka, Enugu State, Nigeria. E-mail: sabinus.eze@unn.edu.ng or ezeaug22@yahoo.com. Tel: +2347066090552.

Accepted 8 May, 2012

In the past few decades, there has been increasing demand for reduction on the reliance on fossil fuels. As a result, there is an increasing search for renewable resources for biodiesel production. In this study, the feasibility of using some selected tropical seeds: palm kernel, breadfruit, groundnut, bambara groundnut, pumpkin, African oil bean, melon, sesame, coconut, soybean, *Cucumeropsis manii*, and *Dacryodes edulis* as sources of biodiesel production were investigated. These results suggest that these seeds (with the exception of breadfruit, African oil bean, coconut and dacryodes edulis), could be used as sources of biodiesel production, going by their yield. Physico-chemical analysis revealed that tested parameters were within the **American Society for Testing and Materials (ASTM) standard specifications for biodiesel production. In actual fact, the iodine values of palm kernel, groundnut, bambara groundnut, pumpkin, African oil bean and sesame, show that they could be used as lubricants and hydraulic brake fluid.**

Key words: Oil seeds, biodiesel, properties, extraction.

INTRODUCTION

About 36% of the world's energy comes from petroleum oil and 22% from gas (Rodriguez-Acosta et al., 2010). This dependency on fossil fuel has also led to increasing pollution and cost, yet it is non-renewable. Consumer nations have become dependent on foreign suppliers and their economies have become hostage to international events such as wars, coup d'états, and terrorism. The desire to move away from dependency on fossil fuels created an interest in alternatives (Kalam and Masjuki, 2002) as reliance on imported petroleum and fluctuating prices is creating apprehension among users. Biodiesel (Singh and Singh, 2010), is a promising alternative which is already in use in some countries.

Due to the need to achieve this, crops or other similar agricultural sources would have to be considered as potential source of biodiesel (Lea, 2003; Kheang and May, 2006a). Consequently, there is an increasing need to search for oils from vegetative sources to augment the available ones and also to meet specific applications (Kyari, 2008). Hence, neglected and underutilized plant species readily comes to mind, as exploitation of this will greatly reduce poverty in developing countries. In Nigeria, there are some native oil seed plants (Afolabi, 2008) which grow well in fallow lands and could be used as source of alternative to fossil fuel. There are strong political and social pressures to avoid the use of edible oils as a biodiesel source (Singh and Singh, 2010). The plants selected for study in this research are: palm kernel, pumpkin, *Dacryodes edulis*, breadfruit, groundnut, African oil bean seed, melon, coconut, sesame, and *Cucumeropsis manii*. Though they are edible, but are highly neglected and underutilized. Akubugwo et al, (2008) observed that attention had been focused on under-utilized local seeds for possible development and use for biodiesel production.

They can grow well in tropical and sub-tropical countries. Most of these oils (Encinar et al., 2007) used for biodiesel production have problems of stability as evidenced in their peroxide value. Also, the viscosity, iodine value, saponification value and density are of importance (Tomasevic and Siler-Marinkovic, 2003), while considering oils for biodiesel production.

Hence, the main thrust of this work was to evaluate the properties of these selected oils available for biodiesel production, with a view to contribute to the knowledge of biodiesel potentials of these seed oils.

MATERIALS AND METHODS

The seeds were purchased from Orba Modern Market in Enugu State Nigeria. They were identified according to the flora of West Africa at the Botany Department of the University of Nigeria.

Extraction and physico-chemical properties

Seeds from each sample (500 g) were crushed, using commercial grinder and fed to a soxhlet extractor fitted with a 2 L round bottomed flask (Rashid et al., 2008). The extraction was executed on a water bath for 6 h, with n-hexane. The solvent was removed under vacuum, using a rotary evaporator. The amount of oil extracted was determined using the equation below:

Oil content (%) = weight of oil extracted / weight of seed × 100

The extracted oil was immediately analyzed for chemical properties, such as: iodine, peroxide, acid and saponification value, while specific gravity, viscosity refractive index and colour were examined for the physical properties. Estimation of the percentage free fatty acids as oleic acid was done, following the method of Cocks and Rede (1998). The refractive indices of the oil (at room temperature) were determined with Abbe refractometer (Alamu et al., 2008) and the specific gravity measurement (also carried out at room temperature), using specific gravity bottle (Oderinde et al., 2004). The state and colour of the oil were noted, using visual inspection at room temperature (Oderinde et al., 2009). Viscosity and yield were determined, following the method described by the Association of Official Analytical Chemists (AOAC) (1984). Results are expressed as the means of two separate determinations.

RESULTS AND DISCUSSION

Physical properties

Results of the physical properties of the selected oils examined were shown in Table 1.

Yield

Oil yield from pumpkin, ground nut, sesame, melon, *Cucumeropsis manii*, palm kernel, *Dacryodes edulis* and coconut were considered economical for commercial production of oil in Nigeria. That of breadfruit, African oil bean, soybean, and Bambara groundnut oil which were between 9.71 to 19.2%, is however low to be considered an oilseed for commercial purposes, but their use may not be discouraged, as they are important nutritionally. Ene-Bong and Carnovale (1992) observed 18 and 43% yield for soybean and groundnut, respectively. Kyari Kheang and May (2006b) also recorded a yield of 7.42% for *Detarium microcarpum*. The oil yield (35.76%) from groundnuts (*Arachis hypogaea*) in this study is less than that reported for fully matured groundnut (40 to 50%) by Afolabi (2008). This might be due to the level of maturity of the seeds before oil extraction. An oil yield of 26 to 42% was considered to be at reasonable yield levels (Kyari, 2008). It should be noted that the mode of extraction is a very important parameter affecting the yield of oil. Singh and Saroj (2009) reported that the best available method for extraction, especially for castor oil at present, is by the use of hydraulic press.

Viscosity

Viscosity is a measure of the resistance of a fluid to deform under shear stress. It is commonly perceived as thickness, or resistance to pouring. Viscosity describes a fluid's internal resistance to flow and may be thought of as a measure of fluid friction (Nzikou et al., 2010). The value of the viscosity of the various oils extracted fell outside the recommended standard range of 6.3 to 8.8 St, with the exception of melon oil with a value of 15.14.

Refractive index

The refractive index which is the ratio of the velocity of light in vacuum to the velocity of light in a medium is an indication of the level of saturation of the oil (Oderinde et al., 2009). The refractive index analysis shows that only palm kernel, pumpkin, breadfruit, bambra ground nut and African bean oils, with the values between 1.459 and 1.476, met the ASTM values that ranges from 1.476 to 1.479 (ASTM International, 2002). Others could be attributed to the presence of some impurities and other components of the crude oil mixture. The refractive index values were similar to those by (Izuagie et al., 2008), for *Cucumeropsis edulis*, *Colocynthis citrillus* and *Prunus amygdalus*.

Chemical properties

The chemical properties of the oils analyzed are shown on Table 2.

Peroxide values

The peroxide values (PV) are in all cases very low, especially in pumpkin and African bean, where it is zero. The low values of PV are indicative of low levels of oxidative rancidity of the oils and also suggest strong presence or high levels of antioxidant. Certain antioxidants may however be used to reduce rancidity,

Table 1. Physical properties of the oils.

Physical properties of the oils	Palm kernel oil	Breadfruit oil	Groundnut seed oil	Bambara G/nut oil	Pumpkin seed oil	African bean oil	Mellon seed oil	Coconut seed oil	Sesame oil	Soybean oil	Cucumeropsis	Dacryodes
Yield (%)	45.6	9.71	35.76	19.2	33.72	12.23	48	22.4	48	36	38.70	20.92
Specific gravity	0.9956	0.917	0.913	0.9563	0.945	0.915	0.874	8.2312	0.95	0.95	1.0657	1.0556
Viscosity at 28°C [St]	1.023 cprus	1.097	0.276	2.317 cprus	7.21×10^{-2}	2.72×10^{-2}	15.14	8.23	1.35	1.02	0.919	2.862
Refractive Index at 28°C	1.40	1.367	1.233	1.433	1.469	1.476	1.333	1.30	1.33	1.30	1.30	ND
Colour	Light yellow	Clear light yellow	Clear yellow	Clear yellow	Brown-yellow	Light yellow	Pale yellow	Pale yellow	Pale yellow	Pale yellow	Light yellow	Dark green

Table 2. Chemical properties of the oils.

Chemical properties of the oils	Palmkernel oil	Breadfruit oil	Groundnut seed oil	Bambara G/nut oil	Pumkin seed oil	African bean oil	Mellon seed oil	Coconut seed oil	Sesame oil	Soybean oil	*Cucumeropsis manii*	*Dacryodes*
Acid Value (mg NaOH/g of oil)	19.035	12.903	8.976	24.071	5.54	1.20	4.710	3.927	5.049	2.805	2.244	44.88
Saponification Value (mg KOH/g of oil)	214.71	221.59	198.63	157.4	44.88	28.05	187.0	218.429	98.56	195.63	152.7	126.8
Iodine value (g I_2 /100 g of oil)	3.927	164.97	77.210	12.903	84.1	86.3	126.90	129.48	21.51	123.42	98.62	110.427
Peroxide Value (Meq/kg)	7.96	6.38	1.03	4.3421	0.00	0.00	8.386	10.562	10.32	16.32	6.2	8.3

such as propyl gallate. The peroxide values are low and are pointers to the fact that the oils may not be easily susceptible to deterioration. Izuagie et al. (2008) observed a PV of 1.72 ± 0.01 and 1.42 ± 0.01 m Eq/kg for *C. citrullus* and *C. edulis*, respectively.

Acid values

Acid value represents free fatty acid content due to enzymatic activity, and is usually indicative of spoilage. Its maximum acceptable level is 4 mg KOH/g oil (CODEX Alimentarius Commission, 1982), for recommended international standards for edible Arachis oil. Results obtained from this work indicate that the acid value of the oils as determined range from 1.20 mg KOH/oil for African oil bean to 44.88 mg KOH/oil for *Dacryodes* (Table 2). Higher acid value is due to free fatty acid present in the oil. It is least for the African bean oil. In addition, all the values fall within the range specified in literature. Thus, in all cases there are corresponding low levels of free fatty acids in the oils, which also suggests low levels of hydrolytic and lipolytic activities in the oils.

The acid value is on the high side for *Dacryodes* (44.88), palm kernel (19.04 ± 0.41 mg KOH/g oil), and breadfruit (12.903 mg KOH/g oil).

This can be used to check the level of oxidative deterioration of the oil by enzymatic or chemical oxidation. The acid value is expected to range from 0.00 to 3.00 mg KOH/g oil before it can find application in cooking. But on the contrary, the value is high for the oil under study. This acid value can be made fit by subjecting the oil to refining and this may also improve its quality for industrial purposes (Oderinde et al., 2009).

Saponification values

Table 2 shows the results for the saponification value of the various oils and were found to be high. These shows that more alkali would be required to enable it neutralize the available free fatty acid librated by the oil, except for the African bean oil, whose value is comparatively low. The saponification values of all the oils are highly comparable with the result specified for quality oil. The saponification value (SV) shows palm kernel, breadfruit, groundnut, coconut, soybean, and dacryodes to be in the range of 195 to 261 (mg

KOH/g sample). Kyari (2008) reported that SV for palm oil is 200 (mg KOH/g sample), for groundnut is 193 (mg KOH/g sample) and for coconut oil is 257 (mg KOH/g sample). The differences observed might be as a result of the differences in the method of extraction. Thus, the oils with SV in the range reported above may be used for soap making, shampoos and lather shaving creams (Oderinde et al., 2009). Saponification values had been reported to be inversely related to the average molecular weight of the fatty acids in the oil fractions. Oil fractions with saponification values of 200 mg KOH/g and above, had been reported to possess low molecular weight fatty acids (Abayeh et al., 1998).

Iodine values

The result obtained for the Iodine value for the different oils were shown in Table 2. Higher values show increase in the average degree of un-saturation of the oil, as such, the amount of iodine which can be absorbed by unsaturated acids would be higher. As a result of their agreement with standard, all the oils could be classified as non-drying oils; since their iodine values are lower than 100 (gI_2/100 g sample) except for *Dacryodes*. Certainly, those oils whose values are less than 100 (g I_2/100 g sample) could be used extensively as lubricants and hydraulic brake fluids. The iodine values obtained here are comparable to the literature value of castor oils and olive oils, both of which are non-drying oils.

A good drying oil should have iodine value of 180 (Abayeh et al., 1998). Thus, all the oils in Table 2 are not suitable as alky resins for paint formulation or use as varnishes; they may, however find uses in conjunction with amino resins as finishes for certain appliances, and in this case, the oils can also act as plasticizers (Abayeh et al., 1998). Iodine value is a measure of the degree of unsaturation in an oil, and it is an identity characteristic of native oil. This value could be used to quantify the amount of double bonds present in the oil, which reflects the susceptibility of oil to oxidation. The iodine value obtained places the oil in the non-drying groups. This oil may find application as a raw material in industries for the manufacture of vegetable oil-based ice cream (Oderinde et al., 2009).

Conclusion

The percentage oil content of most of the seeds selected: melon, sesame, palm kernel, groundnut, pumpkin, coconut, and *Dacryodes* show them as high oil yielding. But for others: *Cucumeropsis*, soybean, African oil bean, bambara ground nut, and breadfruit, whose yield are low, satisfactory result could not be achieved by solvent extraction process, using laboratory soxhlet apparatus. The oil produced in this research was analyzed for physical and chemical properties. Most of the values obtained complied with the standard specified by ASTM (ASTM International, 2002). The oil is of good quality and could be recommended as suitable for industrial usage especially, in biofuel production. Some of the oils need to be refined before use.

Seeds examined in this work have been shown to contain oils in reasonable levels in terms of yield (20.92 to 48%) except breadfruit, bambara groundnut, African bean seed and soybean, which contain 9.71, 19.2%, 12.23 and 16% oil (w/w), respectively. Most of them (breadfruit, melon seed, coconut seed, soybean and *Dacryodes*), contain mainly unsaturated fatty acids judging by their high iodine value which exceeded 100, and therefore are suitable for use in biofuel production. Palm kernel, breadfruit, groundnut, bambara, melon, coconut, soybean, *Cucumeropsis* and *Dacryodes* may however be useful for other purposes such as soap making, due to their high saponification values in the range of 126.8 to 221.

ACKNOWLEDGEMENTS

The author greatly appreciates the role played by Fransisca O. EZE of Dean's office, Faculty of Biological Sciences in typing this manuscript.

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