ABOUT JPTAF

The Journal of Petroleum Technology and Alternative Fuels is published bi-monthly (one volume per year) by Academic Journals.

The Journal of Petroleum Technology and Alternative Fuels (JPTAF) is an open access journal that publishes high-quality solicited and unsolicited articles, in all areas of the subject such as alternate fuels on ignition engine, oil recovery from petroleum sludge, Environmental importance of alternate fuel, Fuel extraction and purification, Hydraulic fracturing, Oil shale technology etc. All articles published in JPTAF are peer-reviewed.

Contact Us

Editorial Office: jptaf@academicjournals.org
Help Desk: helpdesk@academicjournals.org
Website: http://www.academicjournals.org/journal/JPTAF
Submit manuscript online: http://ms.academicjournals.me/
Editor

Dr. P. Govindasamy
Dean – Research and Development
Erode Builder Educational Trust’s
Group of Institutions (A Technical
Campus) EBET Knowledge Park; Erode
Road, Kangayam -638 108 Tirupur Dt.,
Tamilnadu, India.
Editorial Board

Dr. Mohamed Younes El-Saghir Selim
Mechanical Engineering Department
Faculty of Engineering
United Arab Emirates University.
UAE.

Dr. N. Saravanan
Mahalakshmi Housing Society,
Plot RH129, BS,
Shahu Nagar, MIDC,
Chinchwad, Pune,
Maharashtra: 411019
India.

Dr. Mohamed N. Lakhoua
22 Rue Hedi Saidi, Marsa
2070, Tunisia.

Dr. Tahar Aifa
Géosciences Rennes, CNRS UMR6118
Bat.15, Campus de Beaulieu
35042 Rennes cedex, France.
Biodiesel potentials of two phenotypes of *Cyperus esculentus* unconventional oils
Assou Sidohounde, Cokou Pascal Agbangnan Dossa, Guevara Nonviho, Sourou Papin Montcho and Dominique Codjo Koko Sohounhloue
Full Length Research Paper

Biodiesel potentials of two phenotypes of *Cyperus esculentus* unconventional oils

Assou Sidohounde, Cokou Pascal Agbangnan Dossa, Guevara Nonviho, Sourou Papin Montcho and Dominique Codjo Koko Sohounhloue*

Laboratory of Study and Research in Applied Chemistry, Polytechnic School of Abomey-Calavi, University of Abomey-Calavi, 01BP2009 Cotonou, Benin.

Received 23 January, 2018; Accepted 23 April, 2018

Two varieties of *Cyperus esculentus*, identified by their phenotype (black or yellow) were collected from Benin. To investigate their biodiesel profiles, the roots were extracted with hexane. Physicochemical properties and fuel profiles of obtained oils (YCE and BCE, respectively *Yellow C. esculentus* and Black *C. esculentus*) were determined by following standards methods. Although the major physicochemical properties (Iodine value: YCE: 72.89 ± 0.00 vs BCE: 79.73 ± 0.00 g I$_2$/100 g-oil and Saponification value: YCE: 178.54 ± 0.6 vs BCE: 178.09 ± 0.13 mg KOH/g-oil) were relatively closed, slight difference were observed with their fatty acids profiles. Major fatty acids were oleic acid (YCE: 63.50 ± 0.15 vs BCE: 63.42 ± 0.11 g / 100 g-oils) and palmitic acid (YCE: 16.50 ± 0.26 vs BCE: 15.94 ± 0.11 g / 100 g-oils). These profiles should be correlated with the density (≈0.89 g.cm$^{-3}$ at 40°C), the viscosity (≈24 mm$^2$s$^{-1}$ at 40°C) and the cetane number (YCE: 60.47 vs BCE: 59.01) of the oils. Their calorific values (YCE: 36361 vs BCE: 37452 KJ/Kg) indicate that they could be used for biodiesel purposes. However, *C. esculentus* oils should be treated before their conversion in biodiesel in order to reduce their high level in minerals.

**Key words:** *Cyperus esculentus*, unconventional oils, fuel profiles, physicochemical properties, phenotype.

INTRODUCTION

The oil shock of the 70 years revealed that an economical growth founded on the fossil energy abundance alone should not be done continually. Besides, the use of fossil energy generates environmental problems (Mecher et al., 2006; Goldemberg, 2008; Balat and Balat, 2009). As alternatives, biofuels are elected today due to their biodegradability, the easy reproducibility of their production techniques and the highest of their lubricating properties (Steenblik, 2006).

In Africa, the use of biofuels is known. In the beginning of the Second World War, to avoid the restocking difficulties in classic fuels, the Society of Construction of the Abidjan’s harbor (Ivory Coast) used close to 100 tons of palm oils in powerful motors (Cirad, 2008). However, the vegetable oil used without a previous refinement could damage the motors. Indeed, in the rooms of

*Corresponding author. Email: cslohoun@gmail.com, ksohoun@bj.refer.org Tel: +229 21 36 09 93. Fax: +229 21 36 01 99 /LERCA.

Author(s) agree that this article remain permanently open access under the terms of the Creative Commons Attribution License 4.0 International License.
combustion, the vegetable oils undergo physicochemical changes which explain the formation of undesirable matters such polymerized fatty acids and carbon (Kulkarni and Dalai, 2006). A better choice of the vegetable oil made by following their physicochemical properties is therefore important.

From the North to the South of Benin, the tubers of *Cyperus esculentus* are harvested. The cakes are used like fuels. The phenotype of this species depends on the zone of culture. So, in the South of Benin (Ouedeme-Adja) the phenotype of *C. esculentus* is yellow dominance while in Mallanville (in the North of Benin), these tubers are valued for their black color.

The fatty acid profile of *C. esculentus* vegetable oils have been described to be highly oleic (65.6%) (Kim et al., 2007). *C. esculentus* vegetable oils present very good biofuel profile for the diesel motors (Zhang et al., 1996; Barminas et al., 2001) in relation to their density closed to diesel oil (in 40°C) (Wauquier, 1994) and their high calorific value, superior to 35000 kJ/kg (CIRAD, 2014).

To our knowledge, no study has been done on the biofuel profile of *C. esculentus* tubers harvested in Benin. So, this work aims to evaluate the physicochemical and the biofuel profiles of two species of *C. esculentus* harvested in Benin.

**MATERIALS AND METHODS**

**Samples collection**

Fruits of black variety of *C. esculentus* were collected in Ouedeme (Southern of Benin) otherwise the yellow variety was collected in Mallanville (Northern of Benin). Once collected fresh, the tubers are manually sorted, washed, sun-dried and stored in a dry place.

**Oil extraction**

Oil extraction from the *C. esculentus* tubers has been done for 6 h with Soxhlet apparatus by using Hexane at 69±1°C under atmospheric pressure.

**Physicochemical properties**

The water content, density and viscosity were determined according to the standardized methods (DIN EN ISO 12937, NF T 60-214, NF ISO 3104).

The acid, peroxide and saponification index of the oils were determined following the French standards T 60-204; T 60-220 and T 60-206. The iodine value was evaluated by the Winkler method. The calorific value was determined by the method of Batel et al. (1980) and the cetane number was calculated from the Klopfenstein equation (1982).

**Mineral elements**

The mineral elements contents of *C. esculentus* oils were dosed according to the dry procedure by Inductive Coupled Plasma (ICP) on a Varian-Vista device equipped with the Coupled Charge Device (CCD) detector.

**Fatty acids contents**

To determine the fatty acid composition, 1 μl of a hexane solution of methyl esters was injected into an Agilent 6890 HP GC series (Agilent, USA) equipped with an Innowax (Agilent, USA) type column, 30 m long, 0.32 mm internal diameter having a film thickness of 0.25 μm. The injector was in split mode, ratio 1/80 at 250°C as temperature. The carrier gas was helium with a flow rate of 1.5 ml.min⁻¹.

**RESULTS AND DISCUSSION**

**Oil extraction yield**

Table 1 shows the moisture and oil content of *C. esculentus* tubers. The black variety contains up to four times more moisture than the yellow one (1.25 ± 0.12%). The oil contents of both varieties are relatively close to 28%. According to the variability observed between oil and moisture contents, it would be interesting to evaluate the impact of roasting on the yield of *C. esculentus* tubers oils. Studies have shown that the yield of seed oil may depend on several parameters, including the edaphic conditions of culture and the morphology of the matrices studied (Abaza et al., 2002). Nevertheless, the oil content of *C. esculentus* from our studies is higher than 15.9% found for *C. esculentus* tubers harvested in Ghana (Yeboah et al., 2012).

**Physicochemical properties**

**Iodine value**

The iodine value reflects the unsaturation of the oil. The more the oil is unsaturated the higher its iodine number is. According to the results recorded in Table 2, the iodine numbers determined are in the order of 72.89 g I₂/100 g-oil for the yellow variety and 79.73 g I₂/100 g-oil for the black variety.

These values are slightly lower than the data (88 - 90 g I₂/100 g-oil) reported by Barminas et al. (2001) on *C. esculentus*, tubers harvested in Nigeria. They are even lower (113 g I₂/100 g-oil) than that of the same species studied in Egypt (Arafat et al., 2009).

However, the iodine values of *C. esculentus* from our work comply with the limit (120 g I₂/100 g-oil) set by EN 14214 standards (CIRAD, 2014) and corroborate the composition of these oils, which are rich in unsaturated fatty acids (studied below). This could justify the fluidity of *C. esculentus* oils (Saillard, 2012).

**Saponification values**

Saponification values (=178 mg KOH/g-oil) indicate that
Table 1. Moisture content and volatile matter (Te) and oil extraction yield of nutgrass tubers (Th).

<table>
<thead>
<tr>
<th>Harvest area</th>
<th>Variety</th>
<th>Te (% g/g)</th>
<th>Th (% g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ouedeme</td>
<td>BCE</td>
<td>5.50±0.76</td>
<td>28.00±0.01</td>
</tr>
<tr>
<td>Malanville</td>
<td>YCE</td>
<td>1.25±0.12</td>
<td>27.49±0.89</td>
</tr>
</tbody>
</table>

*YCE: Yellow Cyperus esculentus; BCE: Black Cyperus esculentus.

Table 2. Physicochemical properties and fatty acids profile of vegetable oils.

<table>
<thead>
<tr>
<th>Physicochemical property</th>
<th>YCE</th>
<th>BCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peroxide value (meq O₂/kg-oil)</td>
<td>8.75 ± 1.63</td>
<td>7.95 ± 0.10</td>
</tr>
<tr>
<td>Iodine value (g I₂/100 g-oil)</td>
<td>72.89 ± 0.00</td>
<td>79.73 ± 0.00</td>
</tr>
<tr>
<td>Saponification value (mg KOH/g-oil)</td>
<td>178.54 ± 0.6</td>
<td>178.09 ± 0.13</td>
</tr>
<tr>
<td>Palmitic acid (C16:0)</td>
<td>16.50 ± 0.26</td>
<td>15.94 ± 0.11</td>
</tr>
<tr>
<td>Stearic acid (C18:0)</td>
<td>06.87± 0.08</td>
<td>09.84 ± 0.05</td>
</tr>
<tr>
<td>Oleic acid (C18:1)</td>
<td>63.50 ± 0.15</td>
<td>63.42 ± 0.11</td>
</tr>
<tr>
<td>Linoleic acid (C18:2)</td>
<td>12.70 ± 0.07</td>
<td>09.01 ± 0.03</td>
</tr>
</tbody>
</table>

*YCE: Yellow Cyperus esculentus; BCE: Black Cyperus esculentus.

there is no significant difference between the two varieties (Table 2). These values are lower than 209 mg KOH/g-oil, of the vegetable oil of C. esculentus harvested in Egypt (Arafat et al., 2009). They are similarly lower than those 196 and 208 mg KOH/g-oil, of vegetable oil of Jatropha curcas conventionally used for biodiesel (Kpòwëssi et al., 2004). This could reflect a low content of our samples in short chain fatty acids (Ferhat et al., 2014).

Peroxide values

The peroxide values determined for the vegetable oils of C. esculentus are 8.75 meq O₂ / kg-oil for the yellow variety and 7.95 meq O₂ / kg-oil for the black variety (Table 2). They are below the limit of 10 meq O₂ / kg-oil, which is the maximum level allowed for most conventional oils (Ferhat et al., 2014). The analysis of these values shows that the oils did not undergo major degradation by oxidation (Abdelaziz and Djamila, 2016).

Fatty acids composition

Fatty acids influence the fuel properties of the oil such as viscosity, oxidation stability, cetane number, exhaust emissions, heat value, cloud point, pour point, etc (Bello et al., 2012). The compositions (in g / 100 g- oils) of fatty acids are presented in Table 2. The unsaturated fatty acids are oleic acid (YCE: 63.50% and BCE: 63.42%) and linoleic acid (YCE: 12.70% and BCE: 09.01%). The particularly high proportions of oleic acid indicate that these oils are stable to oxidation and can be stored for a long time (Lamaisri et al., 2015). However, Gopinath et al. (2010) found that high unsaturation of the oil could reduce the cetane number of its biodiesel. The cetane number is related to the ignition delay. It is high with a decreasing length of the carbon chain (Islam et al., 2013). The proportions of palmitic acid (YCE: 16.50 ± 0.26%, BCE: 15.94 ± 0.11%) and stearic acid (YCE: 06.87 ± 0.08%, BCE: 09.84 ± 0.05%) slightly different from the two varieties, can give a similar view of their cetane number (Table 3).

Fuel properties of vegetable oils

Water content, acid number, density, viscosity, cetane number, phospholipids, Na+K, Ca+Mg and calorific value of the oils were determined. The results are presented in Table 3.

Water content, density and viscosity

The water content (% wt) of both oils (YCE: 0.06 and BCE: 0.05) are lower than those of Terminalia bellerica (0.15%) and J. curcas (0.17%) seed oils reported by Sarin et al. (2010).

It was proved that the richness of oils in monounsaturated fatty acids such as oleic acid increases
Table 3. Fuel properties of two varieties of Cyperus esculentus vegetable oils compared to vegetable oil of rapeseed and biodiesel.

<table>
<thead>
<tr>
<th>Fuel property</th>
<th>Unconventional vegetable oils studied</th>
<th>Pre-Standard DIN 51605 of rapeseed oil</th>
<th>Biodiesel standards</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>YCE(^a)</td>
<td>BCE(^b)</td>
<td></td>
</tr>
<tr>
<td>Water content (%)</td>
<td>0.06</td>
<td>0.05</td>
<td>Max : 0.075</td>
</tr>
<tr>
<td>Acid value (mg KOH.g(^{-1}))</td>
<td>1.77</td>
<td>1.56</td>
<td>Max : 3</td>
</tr>
<tr>
<td>Density (g.cm(^{-3}), 40°C)</td>
<td>0.896</td>
<td>0.898</td>
<td>0.9 – 0.93</td>
</tr>
<tr>
<td>Viscosity (mm(^{2}).s(^{-1}), 40°C)</td>
<td>23.91</td>
<td>24.43</td>
<td>Min : 39</td>
</tr>
<tr>
<td>Cetane number</td>
<td>60.47</td>
<td>59.01</td>
<td>1.9 – 6 / 3.5 - 5</td>
</tr>
<tr>
<td>Phospholipids (ppm)</td>
<td>23.00</td>
<td>25.00</td>
<td>Max : 12</td>
</tr>
<tr>
<td>Na + K (ppm)</td>
<td>110.00</td>
<td>112.30</td>
<td>Max : 10</td>
</tr>
<tr>
<td>Ca + Mg (ppm)</td>
<td>363.61</td>
<td>374.52</td>
<td>Max : 5</td>
</tr>
<tr>
<td>Calorific value (KJ.kg(^{-1}))</td>
<td>361</td>
<td>37452</td>
<td>37400 (^c)</td>
</tr>
</tbody>
</table>

\(^a\)YCE: Yellow Cyperus esculentus; \(^b\)BCE: Black Cyperus esculentus; Min: minimum limit value; Max: maximum limit value; \(^c\). Source: CIRAD (2008).

The two curves (YCE and BCE) juxtapose themselves. This means that YCE and BCE oils have the same behavior when the temperature is increasing.

The viscosity of C. esculentus oils decreases by following an exponential equation: \( y = 86.603e^{-0.031x} \) (where \( y \) is kinematic viscosity and \( x \), the temperature) with increasing temperature.

Figure 2 is the CIRAD standard curves applying for Colza oils, Gasoil half blend, Biodiesel and Gasoil. The green zone represents the zone of normalized viscosity. By following this standard, we identify the minimal heating temperature for C. esculentus oils as 70°C (9.89 cst).

Cetane number and calorific value

The cetane number of our studied oils are 60.47 and...
59.01 respectively for YCE and BCE. Srivastava and Prasad (2000) reported lowest cetane number (< 39) for linseed, rapeseed, soya bean and Babassa seed oils harvested in India (Srivastava and Prasad, 2000).

Vegetable oils studied have a calorific value of 36361 kJ/kg for the yellow variety of C. esculentus and 37452 kJ/kg for the black variety. These values are higher than the minimum predicted by the German pre-standard (35000 kJ/kg) for a biodiesel (CIRAD, 2014) but lower than that of C. esculentus from Nigeria studied by Barminas et al. (2001) which is 40700 kJ/kg.

**Acid value**

The acid value of a vegetable oil is a function of its free fatty acids and characterizes the state of alteration of the oil by hydrolysis (Bettahar et al., 2016). The acid values (mg KOH/g) for the two oils (< 2 mg KOH/g-oil) are below the limit of 3 mg KOH/g-oil for rapeseed and slightly exceed 0.5 mg KOH/g-oil fixed for the reference biodiesel (CIRAD, 2014). These acid numbers, however, remain lower than those of J. curcas oils from eight localities in Benin studied by Kpoviessi et al. (2004).

**Phospholipid, (Na + K) and (Ca + Mg) content**

The phospholipid content (>20 ppm), the Na + K content (>100 ppm) and the Ca + Mg content (>99 ppm) are extremely high for both studied oils. Their values pass the data foreseen by the norms.

The oils should be refined through several processes to decrease these values. Cuvelier and Maillard (2012) proposed chelating agents such as EDTA (Ethylene-Diamine-Tetra-Acetic acid) and citric acid to reduce metallic cations in matrices.

In the same way, in spite of Argemone seed oils having high toxicity and viscosity, Pramanik et al. (2012) revealed that the fuels properties of their oils were closer to those of traditional transesterified biodiesel. They proposed several processes to lower the bothersome parameters of Argemone seed oils.

**Conclusion**

The vegetable oils extracted from the two varieties (yellow and black) of C. esculentus tubers presented quite physicochemical and biodiesel profiles. The properties such as water content, cetane number and calorific value have been seen better than those of which were related for unconventional seed oils such as Argemone, Terminalia belerica, linseed, rapeseed, soy bean and Babassa.

However, by varying the viscosities of the oils depending on the temperature, we reveal that the two species had an identical behavior. These vegetable oils can be used as biofuel if they were preheated to 70°C, at least. In the same way, their use as biofuel requires a pretreatment considering the high level of their mineral compounds. The biofuel potentials of these refined oils and their blend are in progress.

**CONFLICT OF INTERESTS**

The authors have not declared any conflict of interests.