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OILS FROM DIFFERENT VEGETAL SOURCES AS PRECURSOR MATERIALS INFLUENCING ESSENTIAL PHYSICOCHEMICAL CHARACTERISTICS OF THE BIODIESEL OBTAINED *VIA* THE TRANSESTERIFICATION REACTION.

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A set of physicochemical properties, *viz* acidity, color, density, saponification, kinematic viscosity, free glycerol, carbon residue and oxidation stability, were determined for transesterification products from methyl and ethyl alcohol reactions with triacylglycerides of oil-rich natural substrates extracted from fruits of traditionally cultivated plants, namely corn (*Zea mays*), soybean (*Glycine max*), sunflower (*Helianthus annuus*) and rapeseed (*Brassica napus*), and from three other species: physic nut (*Jatropha curcas*), pequi (*Caryocar brasiliense*) and macaúba palm (*Acrocomia aculeate*), which are of potential commercial value for the industrial production of biodiesel. The obtained data were compared with the main officially recommended certification indexes. Oils from the two native species from the Brazilian flora, *Acrocomia aculeate* and *Caryocar brasiliense*, were confirmed to have real commercial potentiality to produce biodiesel.

INDEX TERMS: *Jatropha curcas*, *Caryocar brasiliense*, *Acrocomia aculeate*, pequi, macaúba

INTRODUCTION

Recent scientific and technological efforts devoted to improve the chemical and physical characteristics and the energetic performance of biofuels have been gaining growing attention from academics, industry engineers, government policy makers and environmentalists worldwide [1-5]. This is accompanied by an increasing interest in the search of new oil plant sources, particularly of a given regional native flora, in order to identify starting oil material to produce biofuel, or, more specifically, biodiesel. The priority focus on native plants arises from several strategic reasons, as they (i) prevent investing efforts and money on plant species that are already traditionally cultivated as food crops, being, directly or indirectly, destined to humans [6-9]; (ii) tend to minimize environmental and ecological impacts in large oil plant-based agriculture systems [10-12]; (iii) represent efforts to reduce economic investments on their cropping, by taking advantages of the naturally adapted native plants to soil and climate, as, for instance, those prevailing in tropical regions, to putatively reduce needs to chemically control plagues or diseases [4,8,13]; (iv) allow a continuous supply of oil for the biodiesel industry, by diversifying the biomass yields of crops, in different seasons [4,14] and (v) tend to maximize productivity of the agriculture system for the biodiesel industry, by stimulating the identification of new oil-richer vegetal sources that could be bio-prospected under a chemically-based criterion [15-17].

In this work, some chemically-based assessments of two oil-rich native plants of the Brazilian flora, namely *Caryocar brasiliense* and *Acrocomia aculeate*, were carried out, by probing some physical and chemical characteristics of the products resulting from transesterification reactions in bench-scale, by keeping similar conditions to those used to produce industrial biodiesel. The starch-rich fraction of the pequi cake, a sub-product from pressing the pequi nuts, to extract its oil, may be converted into reducing sugars and fermented to produce bioethanol. This process was reportedly found to convert as much as 60 % of initial amount of starch [18]. These characteristics are conventionally taken as essential criteria to certificate the marketable biofuel [19-21]. The exotic oil-rich plant species *Jatropha curcas* is not yet used to produce directly any human food derivative, but is widely considered to be a strong candidate, and has been representing, though yet sparsely, a primary source, for the industrial production of biodiesel [22,23]. For these reasons, it is included in our comparative study with other four plants, for which seed-oils are traditionally used for both human food consumption and industrial production of biodiesel: corn (*Zea mays*), soybean (*Glycine max*), sunflower (*Helianthus annuus*) and rapeseed (*Brassica napus*) [24-27].

MATERIALS AND METHODS

The raw oil samples from the two native plants were obtained from their ripened fruits collected from trees, in three areas of the state of Minas Gerais, Brazil: (i) *Caryocar brasiliense*, from native plant trees in Paracatu (17^{o} 13’ 21.02’’ S 46^{o} 52’ 32.85’’ W) and (ii) independent oil fractions of *Acrocomia aculeate*, as obtained by pressing two separate parts of the fruits, specifically the nut and the mesocarp, from native trees found in the city of Carmo do Paranaíba (19^{o} 00’ 22.85’’ S 46^{o} 14’ 53.12’’ W). The oil samples from *Jatropha curcas* were obtained from fruits of trees of an experimental parcel installed near the city of Viçosa (20^{o} 45’ 15.60’’ S 42^{o} 52’ 56.10’’ W). The raw oils from fruits of those three species were purified through conventional solvent extraction with n-hexane, followed by solvent removal in a rotary evaporator. The other four oil samples, specifically from corn (*Zea mays*), soybean (*Glycine max*), sunflower (*Helianthus annuus*) and rapeseed (*Brassica napus*) were directly taken as aliquots from commercial products destined to domestic use.

The transesterification was conducted by reacting each oil sample with either analytical-grade ethanol or methanol, according to reported procedures [28]. The essential physicochemical parameters were measured following recommended standard protocols, as listed in Table 1.

RESULTS AND DISCUSSION

The composition profiles in fatty acids (Figure 1) for the oils of all studied plants and for the commercial products were found to be roughly comparable, except for few remarkable differences. For pequi (or “souari nut”; *Caryocar brasiliense*), the content in palmitic acid (16:0; Table 1) of the oil was comparatively higher and so was the content in lauric acid (12:0) of the oil from *Acrocomia aculeate*, particularly in the mesocarp.

These different composition profiles, showing that they are oils richer in relatively lighter fatty acids, may account for the relatively lower viscosity (Figure 2) of the transesterification products from both its nut and the mesocarp oils. However, biodiesel from oils from these hitherto non-cropped plants, *Caryocar brasiliense*, *Acrocomia aculeate* and *Jatropha curcas*, displayed viscosity values well within the recommended limiting values for kinematic viscosity of 3.0 and 6.0 mm^2 s^{-1}, at 40^o C (Table 2).

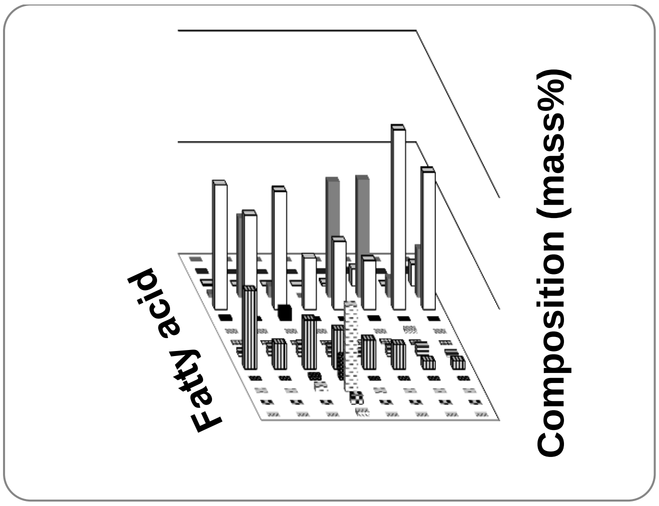

Figure 1. Main characteristics of oils from *Caryocar brasiliense*, *Jatropha curcas*, *Acrocomia aculeate* (N = nut; M = mesocarp), corn (*Zea mays*), soybean (*Glycine max*), sunflower (*Helianthus annuus*) and rapeseed (*Brassica napus*) by their chemical nature by composition in fatty acids (for the used nomenclature, see Table 1).

The combustion of biodiesels rich in methyl esters from oil extracted from grains of *Zea mays* and from both ethylic and methylic transesterification of oil from seeds of *Helianthus annuus* produced relatively higher residual carbon, among all oil sources tested (Figure 2(a)), but the corresponding reaction products present lower saponification index, indicating a high conversion of oils (figure 2(b)). It is also interesting to observe that the ethylic transesterification tended to produce biodiesels with higher viscosity than those obtained through the methylic counterpart (Figure 2(c)). An inverse trend was observed for density, except for the transesterification product starting with triglycerides from the *Jatropha curcas* oil (Figure 2(d)).

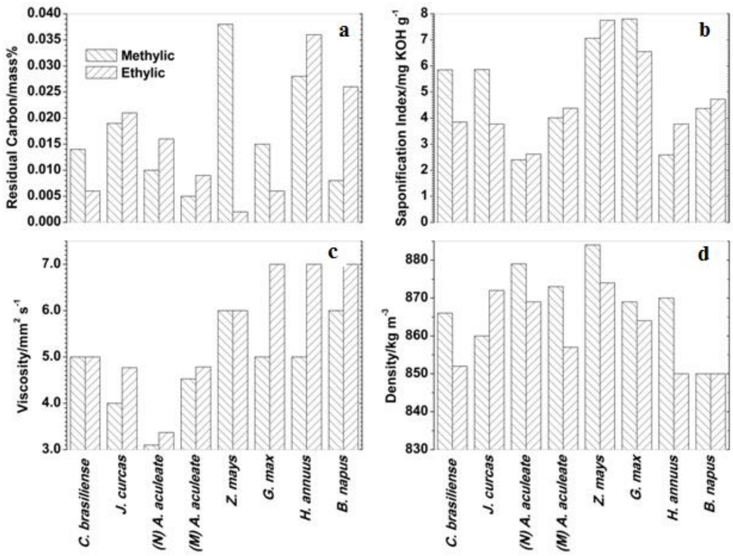

Figure 2. Determined physicochemical parameters of (a) Carbon residue, (b) saponification index, (c) viscosity and (d) density for biodiesel produced *via* methylic or ethylic transesterification of triacylglycerides in oils from *Caryocar brasiliense*, *Jatropha curcas*, *Acrocomia aculeate* (N = nut; M = mesocarp), corn (*Zea mays*), soybean (*Glycine max*), sunflower (*Helianthus annuus*) and rapeseed (*Brassica napus*).

From data in Figure 3(a) and (b), the physical chemical characteristics of transesterification products from all these oils are well comparable, except for the acidity index for the biodiesel from oil of *Acrocomia aculeate*, which is the lowest, comparatively to the products from other oils. From Figure 3(c), the biodiesel derived *Caryocar brasiliense* presents the highest ASTM color index.

The *Caryocar brasiliense* biodiesel presented a noticeable oxidative stability (Figure 3(d)). This behavior cannot be explained only on basis of the chemical nature of the fatty acids, but suggests the occurrence of an extra chemical compositional factor controlling the chemical stability. Ethylic biodiesels from oils of *Acrocomia aculeate* and *Jatropha curcas* showed the lowest oxidative stability (Figure 3(d)).

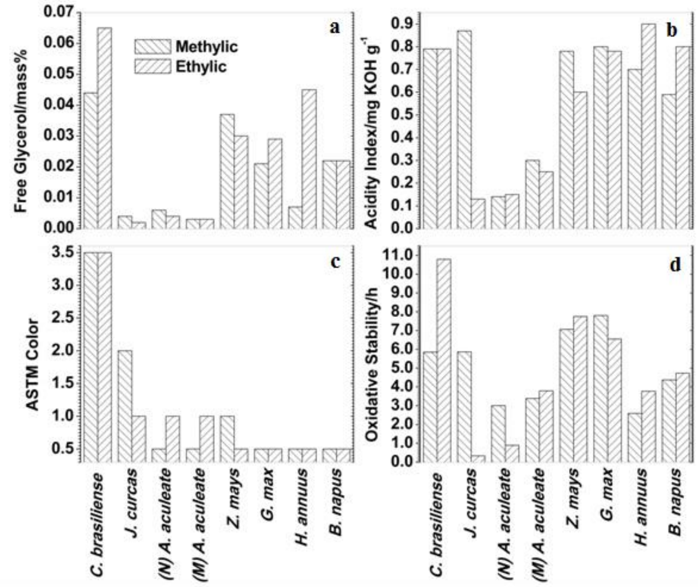

Figure 3. Determined physicochemical parameters of (a) free glycerol, (b) acidity index, (c) ASTM color and (d) oxidative stability for biodiesel produced *via* methylic or ethylic transesterification of triacylglycerides in oils from *Caryocar brasiliense*, *Jatropha curcas*, *Acrocomia aculeate* (N = nut; M = mesocarp), corn (*Zea mays*), soybean (*Glycine max*), sunflower (*Helianthus annuus*) and rapeseed (*Brassica napus*).

For all studied species, except *Caryocar brasiliense*, there was no apparent correlation between oil composition in saturated fatty acids and the oxidative stability of their corresponding transesterification products. Any plausible chemical mechanism for the oxidative processes of the biodiesels requires therefore further investigation.

From Figure 4, oils from the two native plants of the Brazilian flora, *Caryocar brasiliense* and mesocarp of *Acrocomia aculeate,* were richer in total saturated fatty acids than those from the oily grains of traditionally cropped plants (corn, soybean, sunflower and rapeseed). The relative content of saturated fatty acid for the nut of *Acrocomia aculeate* was comparable to that of *Caryocar brasiliense*.

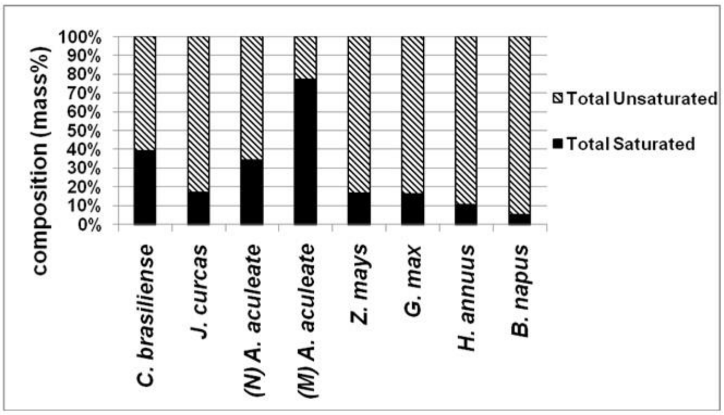

Figure 4. Determined relative contents in unsaturated and saturated fatty acids for oils from *Caryocar brasiliense*, *Jatropha curcas*, *Acrocomia aculeate* (N = nut; M = mesocarp), corn (*Zea mays*), soybean (*Glycine max*), sunflower (*Helianthus annuus*) and rapeseed (*Brassica napus*).

For the *Acrocomia aculeate*-derived biodiesel, the values of free glycerol content and acidity index (nut) were the lowest among all studied samples.

Acrocomia aculeate produces a comparatively remarkable amount of oil per unit of land area [29]. But, in the context of this work, to effectively think of *Acrocomia aculeate* as an oil-source plant in an industrial scale, some biological and agronomical aspects must be seriously taken into account. For instance: (i) the size of an adult palm tree of *Acrocomia aculeate* is too high (the upper part of an adult tree usually reaches to 15 m in height), making it more difficult to harvest its fruits, in any large commercial agriculture systems and (ii) raw oils either from the wild specimen of *Acrocomia aculeate* [33] and *Caryocar brasiliense* [34] are reported to contain relatively high amounts of free fatty acids. As a consequence, all efforts of research and development directed to this purpose should include plant genetic breeding and design and optimization of the chemical industrial processes, in order to improve biodiesel yields, by preventing further side saponification reactions.

Possible alternative industrial routes to use highly acid raw oils would be (i) pre-refining the starting oil, in order to remove as much as possible free fatty acids, prior to pump it into the industrial line, or (ii) preserving their original compositions in fatty acids to process directly the raw oils *via* a two-steps catalysis [35-38], involving both esterification through acid catalysis, followed by separation of products, and subsequent transesterification, with an alkaline catalyst. This second alternative would prevent loosing starting material, as it would occur by pre-refining the crude vegetal oil.

Table 1. Limiting values and reference of analytical protocols as recommended by the Brazilian Association for Technical Specifications [29], American Society for Testing and Materials [30] and European Committee for Standardization [31] used to determine characteristic parameters of these plant oils [32] and their corresponding biodiesel.

Parameter	Unit	Recommended limiting values	ABNT	ASTM	CEN
Density at 20º C	kg m^{-3}	850 – 900	NBR 7148 NBR 14065	D-1298 D-4052	EN ISO 3675 EN ISO 12185
Kinematic viscosity at 40º C	mm^2 s^{-1}	3.0 - 6.0	NBR 10441	D-445	EN ISO 3104
Maximum acidity index	mg KOH g^{-1}	≤0.50	NBR 14448	D-664	EN 14104
Minimum stability to oxidation at 110ºC	h	≥6			EN 14112
Residue carbon	Mass%	≤0.050		D-4530	
Free glycerol	Mass%	≤0.02	15341	D-6584	EN 14105 EN 14106
ASTM Color				D-1500	
Saponification index			MB-75		

Table 2. Molecular chain size (number of carbon atoms:double bond position) and chemical nomenclature for selected fatty acids.

Molecular chain	Fatty acid	Chemical nomenclature
8:0	Caprylic	Octanoic
10:0	Capric	Decanoic
12:0	Lauric	Dodecanoic
14:0	Myristic	Tetradecanoic
16:0	Palmitic	Hexadecanoic
16:1	Palmitoleic	Cis-9-hexadecenoic
18:0	Stearic	Octadecanoic
18:1	Oleic	Cis-9 octadecenoic
18:2	Linoleic	Cis-9, cis-12 octadecadienoic
18:3	Linolenic	Cis-9,cis-12,cis-15-octadecatrienoic
20:0	Arachidic	Eicosanoic

CONCLUSIONS

The present work was focused on a primary chemical characterization of biodiesel produced *via* transesterification reaction of triacylglycerides of oils from fruits of traditional grains, namely corn (*Zea mays*), soybean (*Glycine max*), sunflower (*Helianthus annuus*) and rapeseed (*Brassica napus*), and from two native plants, pequi (*Caryocar brasiliense*) and macaúba palm (*Acrocomia aculeate*) of the Brazilian flora. Oil from fruits of a third non-traditionally cropped plant for food production was also studied: physic nut (*Jatropha curcas*), which is an exotic plant that is becoming more and more an important commercial source of oil, to industrially produce biodiesel, in Brazil.

These results recommend looking for future viable alternatives to the currently dominant use of oil-rich grains from traditionally cropped plants (soybean, sunflower and rapeseed). The regular and massive use of food-grains would tend to deepen the threatening competition between the biofuel production, based on traditional agriculture crops, to respond to the increasing demand of energy, and the global food availability to a growing human population.

From these data, *Acrocomia aculeate* is a native plant with the best potentiality of the two studied, to serve as an oil source for biodiesel, but the *Caryocar brasiliense* biodiesel also presents good chemical characteristics. In general, it follows that they constitute native plants that should be genetically bred, in the coming future, in an effort to improve their agronomic characteristics and the chemical quality of their oil for this purpose.

From a broader view at the present stage and as far as the officially recommended chemical standards are concerned, the *Jatropha curcas* oil itself is a source of a high quality biodiesel, particularly through methylic transesterification, even though its acidity is relatively high and the oxidative stability is low.

Raw oils with high acidity may alternatively be processed *via* a specific route involving two-steps catalysis [35,37,38], meaning direct esterification through acid catalysis, separation of products and subsequent transesterification, with an alkaline catalyst [36].

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NOMENCLATURE

ANP – National agency of petroleum, natural gás e biofuels

ASTM – American Society for testing and materials

CEN – European Committee for Standardization

ABNT – Brazilian association for technical specifications

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