

Binary Blends of Biodiesel from Macauba (*Acromia aculeata*) Kernel Oil with Other Biodiesels

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Macauba is a palm tree which provides large amount of oil. Particularly its oil from the kernel presents excellent stability to oxidation as it is mainly constituted by saturated organic chains. This stability is inherited by the biodiesel prepared with this oil. Paradoxically, contrarily to the expectation as it is mainly constituted by saturated esters, the biodiesel prepared from the macauba kernel oil presents low cold filter plugging point (CFPP). This can be understood on the basis of the high level of content of saturated esters with relatively short carbon chain. Considering these two properties of the biodiesel prepared from the macauba kernel oil, i.e., excellent oxidation stability and low CFPP, it was studied if such characteristics could be transferred to blends constituted by it and another vegetable oil. Blends with biodiesels from soy, corn, macauba pulp and fry oil were studied and it was observed that, indeed, partial transference occurs, meaning that the inconvenient characteristics of such biodiesels were favorably ameliorated, allowing the use, as fuels, of the biodiesels prepared from other oils which original properties do not attain the quality specified by the regulatory agencies.

Keywords: biodiesel, macauba, *Acromia aculeata*, oxidative stability, properties

Introduction

Macauba (*Acromia aculeata*) is a palm tree native to American tropical forests from Mexico to South America.¹ In Brazil, it is found mainly in the Cerrado, which is localized in the central region of the country.² However, it is also well adapted to the Brazilian subtropical and semiarid regions, also being cultivated in Minas Gerais and São Paulo states.^{2,3} It is an extremely productive palm tree that can produce more than 30 tons of fruits *per* hectare *per* year, with a lipid content between 23 and 34% m/m in the dry matter.² Therefore, macauba is a promising source for the extraction of oil for the production of biodiesel. It can produce up to 6000 kg of oil *per* hectare compared with about 400 to 700 kg soy oil *per* hectare *per* year.¹ It should be also noted that the macauba palm tree reaches its maximum productivity in four years, and that this is maintained for more than 100 years.⁴

Another advantage of macauba oil compared with other oils that can be used in cooking is that its oil is not commonly used for food purposes due to its high acid index. Because of this and also because of its large productivity, the cultivation of this palm does not result in competition with food sources. Also, the exploration of native palm trees can favor poor Brazilian people in rural areas, with consequent social benefits.^{4,5}

Beyond the environmental, social and technical aspects of biodiesel, economic viability is an important factor that must be taken into account, as about 70 to 88% of its final cost is a consequence of the price of the feedstock.⁵ Among eight possible combinations of biodiesel production using different kinds of catalyst (alkaline or enzymatic), alcohol (methanol or ethanol) and macauba oil (oil from pulp or kernel), there were two that presented competitive biodiesel selling prices with petrodiesel.² Therefore, macauba can be considered a favorable source for the production of biodiesel due to its high yield of fruits, its ease of adaptation to a variety of ecosystems and the good quality of its oil. However, the actual exploitation of the macauba is mainly

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by gathering derived from native trees, indicating that it is necessary to improve the method of production in order to assure the availability of the fruit and oil.^{2,6}

Indeed, some research has been performed with the aim of improving macauba crops and processing, in order to reduce costs and increase the competitiveness of macauba biodiesel in fuel market.⁷⁻⁹

Biodiesel is environmentally safe and a renewable resource, which makes it more viable alternative fuel. Biofuels are interesting alternatives to fossil fuels because they can be a substitute for them, either totally or partially. Biodiesels can be directly used in diesel engines in the pure form or mixed with common diesel without the necessity of modifying the machine. Presently, in Brazil, the law forces the use of 8% of biodiesel in the diesel used in motors with a staggered increase up to 10% by 2019.¹⁰ This has created a strong demand for the product in the market, causing Brazil to be one of the biggest producers and consumers in the world. Currently, about 80% of the biodiesel produced in Brazil is prepared from soybean oil.¹¹

Biodiesel must present high quality parameters, meeting official standards, in order for commercialization to be allowed. One of these parameters is oxidative stability. Due to their chemical composition, biodiesels suffer oxidative degradation and hydrolysis during storage and are a target of microbial activity, affecting their physical and chemical properties.¹² The higher the presence of unsaturated carbon to carbon bonds in a biodiesel, the more susceptible it is to oxidative processes.^{12,13} Biodiesel is oxidized in the localized unsaturated fatty acids and particularly the double bonds present high reactivity towards oxygen. Biodiesel oxidation stability is one of the problems in this biofuel. Polymers can be formed in the oxidation process and bring some problems to the engine such as clogging in filters and combustion lines as well as increasing engine wear. A very effective procedure to solve this problem is the addition of antioxidants to the biofuel.¹⁴

Another important biodiesel parameter, which is decisive for its commercialization and use, is the cold flow behavior specially when used at low temperatures. The cold flow behavior of biodiesel is normally assessed using PP (pour point), CP (cloud point) and CFPP (cold filter clogging point). PP is defined as the least temperature at which fuels may become pourable. CP refers to the temperature at which crystals begin to appear. CFPP indicates the temperature where the flow of the fuel passing through a filter is interrupted. This phenomenon occurs because of the decrease in the fluidity of the fuel with the decrease in temperature. High CFPP values make the interruption of the fuel flow towards the motor more likely, preventing it from functioning.¹⁵ Transesterification

of highly saturated oils is expected to result in high CFPP values.¹⁶ Many studies have been published to solve the issues of engine operation during low temperatures, mainly problems such as clogging of fuel filters, inadequate burning, fuel flow interruption and start-up.¹⁴

The necessity of meeting official standards for the quality of the final product, leads to the use of additives in order to improve the physical and chemical properties of biodiesels. In the present work blends of biodiesel from macauba kernel oil with biodiesel obtained from other raw materials such as soybean, corn, palm kernel, macauba pulp and frying waste oils, were studied. The objective was to obtain mixtures with adequate oxidative stability and CFPP, as these two properties are very important for the commercialization of the biodiesel. An additional objective was to contribute to the increase of the use of macauba oil as a source for biodiesel, favoring the social development of poor Brazilian rural areas.

Experimental

Materials

For the synthesis of methyl biodiesel, soybean and corn oils purchased in the local market were used. Macauba oils from kernel and pulp (mesocarp) were acquired from the Association of Small Scale Producers in the city of Riacho Dantas de Montes Claros, Minas Gerais, Brazil. Waste frying oil was generously donated by the Environment Division of Campinas University. Palm kernel oil was acquired from the Agropalma company (Belém, PA, Brazil). Methanol 99.8% purity and analytical grade sulfuric acid were supplied by Synth (Diadema, SP, Brazil). 30% m/m sodium methoxide in methanol (Vetec, Rio de Janeiro, RJ, Brazil) was used as catalyst. For the final purification of the produced biodiesel the Amberlite BD 10 Dry, a sulfonic acid resin from Dow Chemical Company (Shanghai, China), was used. Absolute ethanol (Dinâmica, Diadema, SP, Brazil), Wijs' solution (Dinâmica, Diadema, SP, Brazil), sodium thiosulfate pentahydrate (Synth, Diadema, SP, Brazil) and potassium iodide (Synth, Diadema, SP, Brazil) were used for the determination of the iodine value. A mix of 37 fatty acid methyl esters standards, C4 to C24, was purchased from Supelco (Bellefonte, PA, USA). It was used for the determination of the retention time of each fatty acid methyl ester in the chromatograms.

Equipments

The oxidative stability determinations were performed with a Metrohm Biodiesel Rancimat model 873 device. A

Stanhope-Seta apparatus model 99000-2 was used for the determination of the CFPP. The temperature of the bath of ethanol at $-34\text{ }^{\circ}\text{C}$, for CFPP measurements, was measured using an Instruterm thermometer THR080 with a PT100 sensor. The chromatographic analyses were performed in a PerkinElmer Clarus 600 instrument. The iodine value and acid number value were obtained using a Metrohm automatic titrator Titrand 808, equipped with TIAMO software and glass electrode Metrohm Pt Titrode and Metrohm Solvotrode electrode (electrolyte: saturated LiCl in ethanol). To perform Karl Fischer titration a coulometric Metrohm model 831 device was used.

Biodiesel synthesis

For the soybean, corn, palm kernel and macauba pulp oils the methyl synthesis route was performed in two steps. Initially, about 155 g of methanol and 5.5 g of 30% m/m sodium methoxide solution in methanol was added to 980 g of the oil. The quantities of methanol and catalyst solution relative to the weight of oil were about 16% and 0.58% m/m, respectively.

The mixture was stirred at 900 rpm at $60\text{ }^{\circ}\text{C}$ under reflux for 1 h. The final mixture was transferred to a separatory funnel. Quickly, in some seconds, spontaneous phase separation occurred and the inferior phase was removed. The superior phase was transferred back to the reaction flask. 39 g of methanol was added along with 1.4 g of the catalyst solution. This second step of the reaction was performed in the same manner as the first. The percentages of the additional methanol and catalyst solution relative to the initial weight of the oil were 4 and 0.15% m/m, respectively.

The biodiesel was sequentially washed five times with 50 mL of water at $60\text{ }^{\circ}\text{C}$, followed by decantation after each wash to remove the water and impurities. The biodiesel was dried at $100\text{ }^{\circ}\text{C}$ for 1 h in an oven and then purified by percolation in a column with the cation exchange resin Amberlite BD 10 Dry. Approximately 180 g of the resin *per* liter of biodiesel was used, and the flow rate was approximately 4 mL min^{-1} .

For the macauba and the waste frying oils a prior esterification of the free fatty acids was necessary, as they are present in relatively high concentrations in these oils, as is evident by their high acid numbers. This step was performed adding 24% m/m of methanol and 1% m/m of concentrated sulfuric acid, with respect to the initial mass of oil. The reaction mixture was maintained under reflux at $50\text{ }^{\circ}\text{C}$ with stirring at 900 rpm for one hour.

The obtained mixture was transferred to a separatory funnel where the decantation rapidly occurred. The inferior

phase, containing the oil together with the esterified fatty acids was separated from the superior that contained the excess of methanol. The two-step transesterification alkaline reaction was performed on the oily phase as described above.

The fatty acid composition and the physical and chemical properties of the synthesized biodiesels were analyzed according to the procedures described below to verify their quality, and then mixed in different proportions in order to obtain blends with different properties. Mixtures of biodiesel in the proportions 20:80, 50:50 and 80:20% m/m were prepared and the respective IPs and CFPPs were determined. Blends were stored at room temperature (about $25\text{ }^{\circ}\text{C}$) in sealed amber glass flasks, sheltered from light. Their oxidative stability and cold flow properties were determined.

Analytical methods

Oxidative stability

The induction period (IP), which indicates the oxidative stability, was determined using the EN 14112:2003¹⁷ standard. All measurements were done in triplicate. This method is performed passing a constant air flow at 10 L h^{-1} through 3 g of biodiesel heated up to $110\text{ }^{\circ}\text{C}$. The formed volatile acids are transported by the air flow and collected in another flask containing water where the conductivity is continuously monitored.

Cold filter plugging point

The CFPP was determined using the ASTM D6371¹⁸ procedure. CFPP test calls for cooling a FAME sample at a specified rate and drawing it under vacuum through a wire mesh filter screen. CFPP is then defined as the lowest temperature at which 20 mL of sample safely passes through the filter within 60 s.

Iodine value¹⁹

A mass between 0.13-0.15 g of the biodiesel sample was dissolved in a 500 mL Erlenmeyer flask using 20 mL of chloroform and 25.0 mL of Wijs' solution. The Erlenmeyer was covered with a plastic film. This solution was allowed to rest for sixty minutes in the dark together with the blank sample prepared in the same manner. Then 20 mL of the 10% m/v potassium iodide solution and 150 mL of deionized water were added. The solution was stirred magnetically during one minute and then titrated with standard 0.1 mol L^{-1} sodium thiosulfate solution.

Ester content²⁰

The fatty acid composition of the macauba kernel and pulp oils used for the experiments and for the produced

biodiesels were determined using gas chromatography (GC) under the following conditions: flame ionization detector (FID); Agilent column (“crossbond”, 50% cyanopropylphenyl and 50% dimethylpolysiloxane) 30 m length, 0.25 mm internal diameter, 0.25 mm film thickness; helium (gas carrier) flow rate 1 mL min⁻¹; split injection 1:40; injection volume 0.4 µL; injector temperature 250 °C; detector temperature 250 °C; initial temperature of the oven 100 °C; and 5 °C min⁻¹ heating rate up to 230 °C, with a 20 min hold at 230 °C. The identification of the esters was performed according to the retention times of previously analyzed standard substances. The quantitation was obtained through the normalization of the area of each chromatographic peak, according to the recommended by the AOCS Ce 1-62 method.²⁰

Total water content

The total water content in the biodiesel was determined according to EN ISO 12937²¹ using Karl Fischer coulometric titration (Metrohm model 831). All measurements were done in triplicate.

Acid number²²

The acid number was determined following the method proposed by Aricetti and Tubino.²² All measurements were done in triplicate.

Density

Slightly less than 5 mL of the sample of biodiesel was added to a calibrated volumetric flask of 5 mL of known weight. The sample flask was thermostated in a water bath at 20.0 ± 0.1 °C for 10 min. Thereafter, biodiesel was added until the mark of the volumetric flask. The flask was dried externally with absorbent paper towels. The density was calculated based on the mass/volume ratio. All measurements were made in triplicate.

Kinematic viscosity

The kinematic viscosity was determined according to EN ISO 3104²³ using a thermostatic bath Quimis at 40.0 ± 0.1 °C. All measurements were done in triplicate.

Results and Discussion

Properties of pure biodiesels

The induction periods (IP), the iodine values (IV) and the cold filter plugging points (CFPP) of pure methyl esters obtained from oils of soybean, corn, macauba kernel, macauba pulp and palm kernel were determined and the results are shown in Table 1.

Table 1. Induction periods (IP), cold filter plugging points (CFPP) and iodine values (IV) of methyl esters obtained from macauba kernel, soybean, corn, waste frying, macauba pulp and palm kernel oils

Biodiesel from oil of	IP / h	CFPP / °C	IV / (g I ₂ /100 g)
Macauba kernel	64.3 ± 0.3	-3.0 ± 0.5	32 ± 6
Soybean	4.4 ± 0.1	-6.3 ± 0.6	136 ± 16
Corn	7.10 ± 0.03	-1.7 ± 0.6	115 ± 14
Waste frying	1.61 ± 0.02	-4.3 ± 0.6	116 ± 12
Macauba pulp	4.0 ± 0.2	-0.3 ± 0.6	73 ± 4
Palm kernel	54 ± 3	17 ± 1	48 ± 8

The oxidative stability of biodiesel expressed by the IP is mainly related to the content of unsaturated and especially polyunsaturated esters, following the correlation expressed by equation 1,²⁴ where POLYUNSAT expresses the wt.% concentration of polyunsaturated esters. This equation is valid for the concentration range between 1.2 and 61.3 wt.% of polyunsaturated esters.

$$IP = 49.0(\text{POLYUNSAT})^{-0.50} \quad (1)$$

Other factors, such as the presence of antioxidant substances and metal ions, influence the oxidative stability of the biodiesel. However, the synthesis and purification of biodiesel remove antioxidants that are naturally present in oils.^{13,25,26}

The saturated methyl esters obtained from palm kernel and from macauba kernel oils present low iodine values (less than 50 g I₂ / 100 g sample), indicating a low level of unsaturation. Consequently, they have high oxidative stability, beyond 50 h, as can be seen in Table 1.

High oxidative stability is a desirable quality for biodiesel because it allows storage for long periods of time without the formation of degradation products, which can damage storage tanks and motors.²⁷

Methyl esters obtained from soybean, corn and macauba pulp oils present low oxidative stability with IP values below 8 h, the minimum specified by the standard EN 14214.²⁸ They present low CFPP values as a consequence of their high content of unsaturated molecules (iodine values higher than 100 g I₂ / 100 g sample).

Oxidative stability and CFPP are properties that depend of the saturated/unsaturated esters content of the biodiesel. In principle, higher contents of saturated molecules will lead to higher IP and CFPP.¹⁶ High IP values are desirable because this means better oxidative stability. However, high CFPP values are unwelcome because saturated biodiesels would suffer reduced fluidity even at relatively high temperatures, sometimes at mild environmental

temperatures, e.g. at 18 °C, compromising the operation of motors.

As shown in Table 1, the biodiesel from oil of the macauba kernel is saturated, presenting a low iodine value (IV = 32 g I₂ / 100 g) and a high oxidative stability (IP = 64.3 h). However, contrary to the expectation for saturated methyl esters, its CFPP is low (−3 °C). By comparison, the biodiesel obtained from palm kernel oil, which is very saturated (IV = 48 g I₂ / 100 g), presents a high CFPP value of 17 °C.

Studies presented by Serrano *et al.*¹⁶ demonstrated that not only the degree of saturation of the biodiesel influences the CFPP but also the size of the carbon chain. As can be seen in equation 2, the chains from C4:0 to C14:0 contribute to the lowering of the CFPP values. The chains from C16:0 to C24:0 increase the CFPP. It can be supposed that esters with longer carbon chains present greater surface areas and consequently increased Van der Waals interactions.²⁹ For a homologous series, similar to the temperatures of fusion and boiling, the CFPP must follow the same tendency, i.e. it will increase with the increase of the size of the carbon chain.²⁹

$$\text{CFPP} = -0.12(\text{SAT}_{\text{C4-C14}}) + 0.47(\text{SAT}_{\text{C16-C24}}) - 0.14(\text{UNSAT}) \quad (2)$$

where (SAT_{C4-C14}), (SAT_{C16-C24}) and (UNSAT) are the concentration of the esters, saturated (SAT) and unsaturated (UNSAT) in wt.%. Equation 2 is applicable in the ranges: 0 < (SAT_{C4-C14}) ≤ 81.1 wt.%; 7.4 ≤ (SAT_{C16-C24}) ≤ 44.4 wt.% and 7.1 ≤ (UNSAT) ≤ 92.2 wt.%.

The composition of the esters in the methyl biodiesel of macauba kernel oil was determined by gas chromatography. The results are shown in Table 2. It can be observed that about 65 wt.% of its composition is of short length carbon chains, from C8:0 to C14:0, leading, because of this, to a low CFPP (−3 °C).

Biodiesel blends

To enhance the IP values of biodiesel constituted mainly of unsaturated esters, such as those from soybean, corn, macauba pulp and waste frying oils, blends can be prepared by mixing with other, mainly saturated, biodiesels in appropriate proportions.

Figure 1 shows the variation in the IP and CFPP as a function of the composition of blends prepared from soybean oil and palm kernel oil. The IP value reaches 8 h (the minimum value established by the norm EN 14214²⁸ when the palm kernel oil content is 56% m/m. However, the CFPP of this blend is 6 °C, preventing its use in regions

Table 2. Percentage composition of methyl esters in biodiesel from macauba kernel oil

Fatty acid chain	Methyl ester / %
C8:0	2.15 ± 0.01
C10:0	2.43 ± 0.01
C12:0	43.92 ± 0.03
C14:0	16.88 ± 0.02
C16:0	10.14 ± 0.02
C16:1	0.02 ± 0.01
C18:0	2.26 ± 0.01
C18:1	19.35 ± 0.02
C18:2	2.65 ± 0.01
C20:0	0.12 ± 0.01
C20:1	0.08 ± 0.01
Total saturated	77.90 ± 0.05
Saturated ≤ 14 C	65.38 ± 0.04
Saturated >14 C	12.52 ± 0.03
Total unsaturated	22.10 ± 0.03

where the environmental temperature can reach this level. In Brazil, such blends could be used without restriction in almost all territories, except for some days during winter in the south.

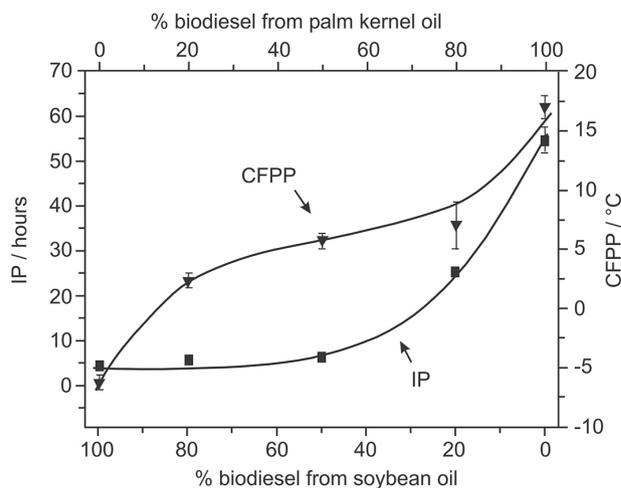


Figure 1. The variation in IP (induction period) and CFPP (cold filter plugging point) as a function of the composition of blends of biodiesels prepared from soybean oil and from palm kernel oil.

The maximum normalized value of CFPP changes according to the country. In Brazil, according to resolution ANP No. 45 (Agência Nacional de Petróleo, Gás Natural e Biocombustíveis),³⁰ the maximum CFPP value varies between 5 and 19 °C depending on the region and the time of year. In Europe these values are more restricted. For example, in Spain the maximum allowed CFPP is 0 °C during summer and −10 °C during winter.

As observed, the methyl esters obtained from macauba kernel oil are predominantly composed of short saturated carbon chains containing a maximum of 14 carbons. This composition leads to relatively low CFPP values despite the high degree of saturation. Therefore, macauba kernel oil biodiesel has an interesting potential use in blends with other biodiesels of low oxidative stability, to increase the IP without causing a large increase in the CFPP.

Figure 2 shows the variation in IP and CFPP as a function of the composition of blends of biodiesels from soybean oil and macauba kernel oil. In this case the IP attains a value of 8 h at the 50% m/m composition and the CFPP is -5°C , i.e. the oxidative stability was significantly increased and the CFPP remained at very good level, only 1°C above the value of the pure soybean oil biodiesel.

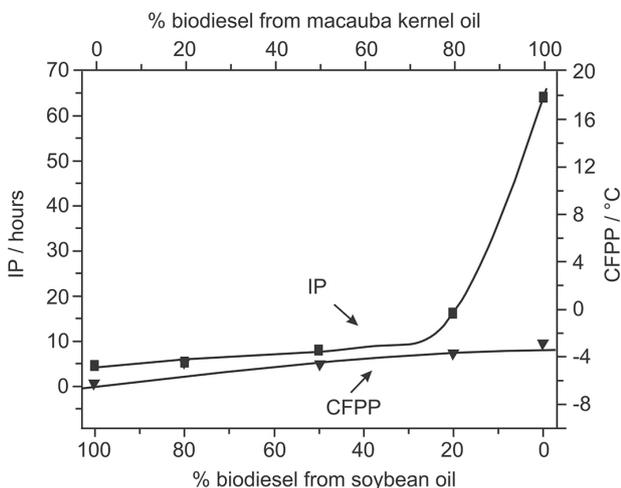


Figure 2. Variation in IP (induction period) and CFPP (cold filter plugging point) as a function of the composition of blends of biodiesels from soybean oil and from macauba kernel oil.

The addition of biodiesel prepared from macauba kernel oil to the biodiesel from corn oil also causes an increase in the oxidative stability, reaching the minimum required value of 8 h at a proportion of 15% m/m of macauba kernel oil biodiesel. In this case, the CFPP value of the blend is -3.5°C , i.e. a decrease of 2°C is observed leading to a more favorable value. Figure 3 shows the variation in IP and CFPP as a function of the proportion of these two biodiesels.

It is also possible to obtain another kind of oil from the pulp (mesocarp) of the macauba fruit. Chromatographic analysis of the biodiesel prepared from this oil shows a composition mainly constituted of unsaturated methyl esters. These results are shown in Table 3.

The biodiesel prepared from macauba pulp oil presents low oxidative stability due to its highly unsaturated character. The determined IP is 4.0 hours. Figure 4 shows the variation in IP and CFPP of blends of biodiesels from macauba kernel oil and macauba pulp oil.

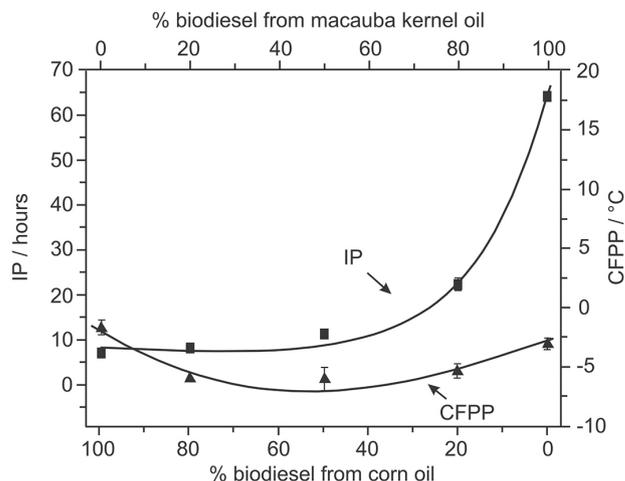


Figure 3. Variation in IP (induction period) and CFPP (cold filter plugging point) as a function of the composition of blends of biodiesels from corn oil and macauba kernel oil.

Table 3. Fatty acid composition of biodiesel prepared from macauba pulp oil. Results obtained by gas chromatography

Fatty acid chain	Methyl ester / %
C12:0	0.22 ± 0.01
C14:0	0.20 ± 0.01
C16:0	18.08 ± 0.02
C16:1	2.98 ± 0.02
C17:0	0.06 ± 0.01
C17:1	0.10 ± 0.01
C18:0	1.86 ± 0.01
C18:1	61.59 ± 0.03
C18:2	14.10 ± 0.02
C18:3	0.82 ± 0.01
C20:1	0.08 ± 0.01
Total saturated	20.42 ± 0.03
Saturated ≤ 14 C	0.42 ± 0.01
Saturated > 14 C	20.00 ± 0.01
Total unsaturated	79.67 ± 0.05

The blend constituted by 50% m/m of each biodiesel from the two different parts of macauba shows an IP of 8 hours and a CFPP of -5°C , meaning that this mixture presents good quality with respect to these parameters.

The use of waste frying oil is another environmentally favorable option for the production of biodiesel. However, low quality biodiesel is obtained from this oil source, mainly with respect to its oxidative stability, with an IP of 1.6 h. Figure 5 shows the variation in IP and CFPP for biodiesel blends obtained by mixing biodiesels from frying and macauba kernel oils.

For these blends an IP of 8 h was obtained with the composition containing about 85% m/m of biodiesel from

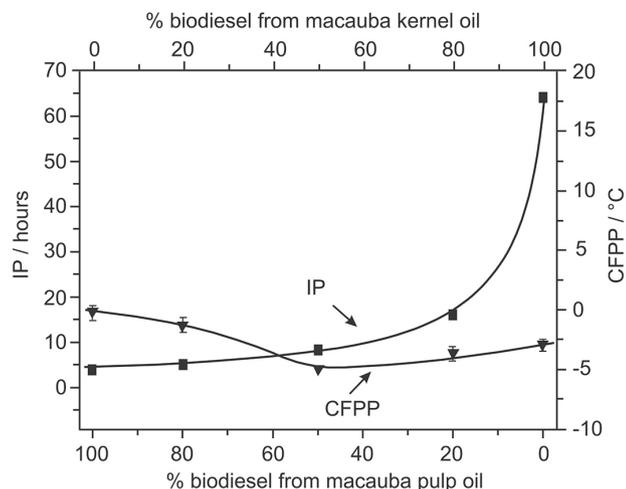


Figure 4. Variation in IP (induction period) and CFPP (cold filter plugging point) versus composition of blends of biodiesels from macauba kernel oil and macauba pulp oil.

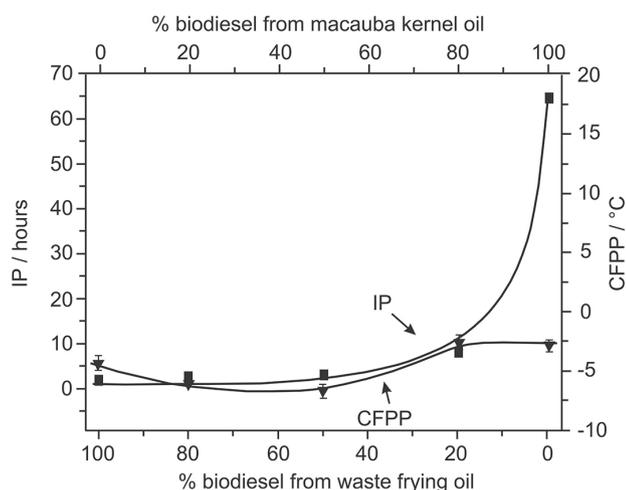


Figure 5. Variation in IP (induction period) and CFPP (cold filter plugging point) versus composition of blends of biodiesels from frying and macauba kernel oils.

macauba kernel oil. In this case the CFPP was $-3\text{ }^{\circ}\text{C}$, considered a good value. These results suggest that it is possible to use biodiesel obtained from residual frying oil in motors if it is mixed with biodiesel prepared from a feedstock like macauba kernel oil.

Table 4. Water content, acid number, kinematic viscosity and density at $20\text{ }^{\circ}\text{C}$ of blends of biodiesel from macauba kernel oil with soy, corn, macauba pulp and fry oils

Property	Unit	Method	Limit ²⁸	Blends of biodiesels from various oils:biodiesel from macauba kernel oil, % v/v			
				Soy (50:50)	Corn (85:15)	Macauba pulp (50:50)	Fry oil (15:85)
Water content	mg kg^{-1}	EN ISO 12937	≤ 500	249 ± 4	518 ± 13	187 ± 16	384 ± 11
Acid number	mg KOH g^{-1}	reference 22	≤ 0.5	0.34 ± 0.01	0.284 ± 0.001	0.312 ± 0.008	0.394 ± 0.005
Kinematic viscosity	$\text{mm}^2 \text{ s}^{-1}$	EN ISO 3104	3.5-5.0	3.67 ± 0.05	3.32 ± 0.04	3.81 ± 0.05	3.38 ± 0.05
Density at $20\text{ }^{\circ}\text{C}$	kg m^{-3}	described in Analytical methods section	860-900	877 ± 3	864 ± 4	873.0 ± 0.9	873.7 ± 0.8

Table 4 shows the water content, acid number, kinematic viscosity and density at $20\text{ }^{\circ}\text{C}$ of blends of biodiesel from macauba kernel oil with soy, corn, macauba pulp and fry oils. All the measured properties of macauba biodiesel blends meet satisfactorily current regulations, including acid number, kinematic viscosity, density, water content, induction period and CFPP.

Conclusions

The results obtained in the present work show that blends of biodiesels with low oxidative stability with macauba kernel oil can achieve good IP values while maintaining low values of CFPP. The characteristics of the macauba biodiesel prepared from kernel oil can be attributed to its composition, which contains high levels of saturated esters of short carbon chains up to 14 atoms, constituting about 65% of the total. Due to the particular characteristics of the biodiesel obtained from macauba kernel oil it was possible to obtain blends with biodiesels from soy, corn and macauba pulp oils which present adequate oxidative stabilities, with IP of 8 h. The CFPPs of such blends were all below $0\text{ }^{\circ}\text{C}$. The blends that presented the best results for IP and CFPP were in the following proportions: soy:macauba kernel, 50:50% m/m; corn:macauba kernel, 85:15% m/m; macauba pulp:macauba kernel 50:50% m/m; frying oil:macauba kernel, 15:85% m/m. In addition, all physical and chemical properties of macauba biodiesel blends studied in the present work were meeting current regulations. These results contribute to the insertion of biodiesel from macauba kernel oil into the Brazilian energy matrix in association with biodiesels from other sources.

Acknowledgments

The authors thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico, CNPq (404808/2013-1) for the financial support. The authors

would also like to thank Gustavo Giraldi Shimamoto for monitoring the biodiesel synthesis reaction.

References

1. Michelin, S.; Penha, F. M.; Sychoski, M. M.; Scherer, R. P.; Treichel H.; Valério, A.; Di Luccio, M.; Oliveira, D.; Oliveira, J. V.; *Renewable Energy* **2015**, *76*, 388.
2. Lopes, D. C.; Steidle Neto, A. J.; Mendes, A. A.; Pereira, D. T. V.; *Energy Econ.* **2013**, *40*, 819.
3. Ferrari, R. A.; Azevedo Filho, J. A.; *J. Agric. Sci. Technol.* **2012**, *2*, 1119.
4. Navarro-Díaz, H. J.; Gonzales, S. L.; Irigaray, B.; Vieitez, I.; Jachmanián I.; Hense, H.; Oliveira, J. V.; *J. Supercrit. Fluids* **2014**, *93*, 130.
5. Dabdoub, M. J.; Bronzel, J. L.; *Quim. Nova* **2009**, *32*, 776.
6. Souza, G. K.; Scheufele, F. B.; Pasa, T. L. B.; Arroyo, P. A.; Pereira, N. C.; *Fuel* **2016**, *165*, 360.
7. Path, M.; Moser, C.; Bailis, R.; Brandt, P.; Hirsch, H.; Klein, A.; Walmsley, D.; Wehrden, H.; *Biomass Bioenergy* **2016**, *91*, 186.
8. Nascimento, A. D. P.; Soares, L. A. L.; Stragevitch, L.; Danielski, L.; *J. Supercrit. Fluids* **2016**, *111*, 1.
9. Santos, B. C. P.; Carvalho, D. B.; Sousa, J. S.; Carvalhinho, M. T. J. E.; Castro, A. M.; Freire, D. M. G.; *Ind. Crops Prod.* **2015**, *77*, 703.
10. <http://www.mme.gov.br/documents/1138769/1732805/Boletim+DCR+n%C2%BA+96+-+fevereiro+de+2016.pdf/9db5f193-af66-4124-80c1-0abc74ed63f7>, accessed in July 2017.
11. César, A. S.; Almeida, F. A.; Souza, R. P.; Silva, G. C.; Atabani, A. E.; *Renewable Sustainable Energy Rev.* **2015**, *49*, 1213.
12. Borsato, D.; Cini, J. R. M.; Silva, H. C.; Coppo, R. L.; Angilelli, K. G.; Moreira, I.; Maia, E. C. R.; *Fuel Proc. Technol.* **2014**, *127*, 111.
13. Knothe, G.; *Fuel Proc. Technol.* **2007**, *88*, 669.
14. Monirul, I. M.; Masjuki, H. H.; Kalam, M. A.; Zulkifli, N. W. M.; Rashedul, M. M.; Imdadul, H. K.; Mosarof, M. H.; *RSC Adv.* **2015**, *5*, 86631.
15. Lôbo, I. P.; Ferreira, S. L. C.; *Quim. Nova* **2009**, *32*, 1596.
16. Serrano, M.; Oliveros, R.; Sánchez, M.; Moraschini, A.; Martínez, M.; Aracil, J.; *Energy* **2014**, *65*, 109.
17. EN ISO 14112:2003: *Fat and Oil Derivatives-Fatty Acid Methyl Esters (FAME) - Determination of Oxidation Stability (Accelerated Oxidation Test)*; European Committee for Standardization, Brussels, 2003.
18. ASTM Standard D6371: *Standard Test Method for Cold Filter Plugging Point of Diesel and Heating Fuels*; ASTM, West Conshohocken, PA, 1999.
19. Tubino, M.; Aricetti, J. A.; *Fuel* **2013**, *103*, 1158.
20. American Oil Chemists' Society, AOCS Official Method Ce 1-62 In *Fatty Acid Composition by Packed Column Gas Chromatography*, 6th ed.; Champaign, 2009.
21. EN ISO 12937:2000: *Petroleum Products-Determination of Water-Coulometric Karl Fischer Titration Method*; European Committee for Standardization, Brussels, Belgium, 2000.
22. Aricetti, J. A.; Tubino, M.; *Fuel* **2012**, *95*, 659.
23. EN ISO 3104:1994: *Petroleum Products - Transparent and Opaque Liquids - Determination of Kinematic Viscosity and Calculation of Dynamic Viscosity*, International Organization for Standardization, Geneva, Switzerland, 1994.
24. Park, J. Y.; Kim, D. K.; Lee, J. P.; Park, S. C.; Kim, Y. J.; Lee, J. S.; *Bioresour. Technol.* **2008**, *99*, 1196.
25. Galvan, D.; Orives, J. R.; Coppo, R. L.; Silva, E. T.; Angilelli, K. G.; Borsato, D.; *Energy Fuels* **2013**, *27*, 6866.
26. Souza, F. H. N.; Maia, F. J. N.; Mazzetto, S. E.; Nascimento, T. L.; Andrade, N. C.; Oliveira, A. L. N. F.; Rios, M. A. S.; *Chem. Biochem. Eng. Q.* **2013**, *27*, 327.
27. Joshi, G.; Lamba, B. Y.; Rawat, D. S.; Mallick, S.; Murthy, K. S. R.; *Ind. Eng. Chem. Res.* **2013**, *52*, 7586.
28. EN 14214:2012+A1:2014: *Liquid Petroleum Products - Fatty Acid Methyl Esters (FAME) for Use in Diesel Engines and Heating Applications - Requirements and Test Methods*, European Committee for Standardization, Brussels, Belgium, 2014.
29. Solomons, T. W. G.; Fryhle, C. B.; *Química Orgânica*, 8^o ed.; LTC: Rio de Janeiro, 2005-2006.
30. Agência Nacional do Petróleo, Gás Natural e Biocombustíveis; Resolução ANP No. 45, available at <https://www.legisweb.com.br/legislacao/?id=274064>, accessed on July 10, 2017.

Submitted: April 25, 2017

Published online: July 13, 2017