

Indian-nut (*Aleurites moluccana*) and tucum (*Astrocaryum vulgare*), non agricultural sources for biodiesel production using ethanol: composition, characterization and optimization of the reactional production conditions

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Abstract: Indian-nut (*Aleurites moluccana*) and tucum (*Astrocaryum vulgare*) are oleaginous non eatable that present excellent oil content (about 60% and 30%, respectively) compared to soy bean grains (20%). Biodiesel production from these oils, using bioethanol as reactant, is an alternative for renewable energy source. In this paper, experimental design was used to determine the influence of these different kinds of oils on the transesterification reaction in order to evaluate the viability of biodiesel production process using ethanol as reactant. The most influential variables on the transesterification reaction yield were: alcohol to oil molar ratio, mass of catalyst, temperature and reaction time. In this paper, the variables was operated using experimental design with central composite. Compositional difference between both tucum and *Aleurites* oil has been verified by ¹H-NMR and GC analysis. Physicochemical properties presented by *Aleurites* biodiesel are in accordance with ANP Regulation n. 07. On the other hand, the same conditions were not adequate to achieve a high transesterification yield from handmade *Astrocaryum* oil. In this case, better conditions were only obtained from refined oil. The reactional conditions optimized based on a kind of oil sometimes can't be suitable for any biodiesel production reaction.

Keywords: Biodiesel, Bioethanol, *Aleurites*, Optimization, Experimental design.

1. Introduction

Vegetable oils are one of the most commonly used biofuels raw materials. The main reason is their great versatility in the industrial transformation and environmental gains of their processing, in relation to petroleum, due to the absence of sulfur and heavy metals in their composition [1]. In this way, vegetable oils enable the production of biodiesel, a biofuel with very similar features as petrodiesel. The biodiesel is obtained from the chemical transformation of the oils (glycerides) by a transesterification process. In this case, the glycerides react with an alcohol of short carbon chain in the presence of a strong acid or alkaline catalyst, to produce a mixture of fatty acid alkyl esters and glycerol [2].

The alcohol generally employed in transesterification reactions to biodiesel production is methanol, however, it presents some disadvantages, such as: mostly of it is obtained from non-renewable sources, presents high toxicity and Brazil do not produces sufficient amount for internal consumption. In other hand, ethanol, even deprecated due some reactional inconveniences, becomes very attractive under economic, strategic and environmental points of view; presents low toxicity and can be produced from sugar-cane, a highly renewable source. Brazil is currently the world's leader in bioethanol production obtained from sugarcane. Because of government subsidies, large sugarcane crops, and high sales taxes on gasoline, Brazil has built a profitable national bioethanol industry. Sugarcane is grown in the

country as the climate presents perfect conditions for its cultivation and production. It is very easily converted to ethanol, and provides Brazil with huge supplies of bioethanol [3,4].

Lima *et al.* (2007; 2008) used bioethanol to prepare biodiesel from glycerides abundant in vegetable sources present in Brazil Midwest, North and Northeast regions, by homogenous catalysis reaching quantitative yield on catalytic process. These results became the motivation for a research aiming to overcome the reactional limitations for bioethanol and to improve its insertion into biodiesel energetic matrix.

Brazil has a lot of oleaginous vegetables with huge potential to produce biodiesel. The *Aleurites moluccana* seeds (so called indian nut or “noz-da-índia” in Brazil or “nogueira-de-iguapé”) has been employed as an oil source for several years. *Aleurites* is original from tropical Asia and pacific islands; In Brazil, it is broadly spread in Atlantic Forest. The species is a tree with 10 meter height, that produces green fruits having one or two seeds. The percentage of oil extracted from *Aleurites* seeds is higher than soy bean grains, for example. It is about 63% composed of oleic glycerides that have excellent properties for biodiesel production. The oil obtained from *Aleurites* seeds is mostly used to make soaps, candles and varnish [6] and was already used to produce methylic biodiesel [7] but, to the best of our knowledge, there are no reports on its use to produce ethylic biodiesel.

There is a great biodiversity of palm trees in Brazil and among them there is a palm tree, *Astrocaryum vulgare*, Mart. (popularly known as “tucum” or “tucumã” in Brazil) not used as a source of oil for biodiesel production. The “tucum” is a palm tree that grows up to 10 m high, in a highly dry soil and those that floods occasionally. The almond supplies eatable white grease used to produce soaps, cosmetics and medicines. The fruits are very appreciated and the fruition occurs between November and May [8]. The “tucum’s” mature fruits are yellow and consist of the pulp and the almond that correspond respectively to about 53.2% and 24.5% of the fruit weight [9]. The pulp produces orange oil (18.18% w/w) in which polyunsaturated fatty acids predominate and the almond produces a white grease (29.59%) rich in lauric and myristic fatty acids. In Brazil it is possible to found the “tucum” tree in the Amazon and Northeast regions. The majority of its fatty acids consist of short chain, mainly lauric (52.51%) and myristic (25.04%). This property facilitates the kinetic of the transesterification reaction for biodiesel production leading to a product with more oxidative and thermal stabilities than biodiesel obtained from other oils, such as soybean [9].

As discussed earlier, nowadays, the optimization of biodiesel production mainly applying ethylic route, is of great relevance. The use of experimental design is a powerful tool to process optimization. The experimental design is a technique able to rationalize the application of experiments, to investigate, simultaneously, all potential variables that affect the results of a process. The advantages of working with experimental design are the achievement of more information using a smaller number of experiments, to perform studies about individual effect of each variable, how these variables interact independently and more than this, to analyze the results with a model that allows previsions of what will happen for any experiment into studied range. The response surface methodology, also, is a statistic tool for optimization based on factorial designs, to denote the response of the system, under study, with alterations in the variables [10].

According to Sarin *et al.* (2010), the properties of a biodiesel are influenced by the structure and amount of the component fatty acid esters, which depends on the oil source. So, the main objective of this work is to discuss the application of experimental design based on a specific

oil to a different oil, for the production of biodiesel. Moreover, we intend to propose “tucum” and indian nut oils as raw materials for biodiesel production using the ethylic route. In such way we intend to improve the reactional conditions, using experimental design, to obtain biodiesel from indian nut seeds oil, by ethylic route (NaOH as catalyst). Then, the best conditions should be applied to prepare biodiesel from almond oil of “tucum”. Ester content, and other physico-chemical properties established by Resolution n. 07/2008, from Brazilian Regulatory Crude Oil, Natural Gas and Biofuels Agency [12], will be the principal reference parameters to verify the efficiency of reactional conditions obtained from experimental design.

2. Methodology

2.1. Experimental design for ethylic biodiesel preparation from *Aleurites* oil.

In order to obtain the response surface, it was applied an experimental design with central composite design. All variables: heating time, temperature, ethanol/oil molar ratio and mass of catalyst, were evaluated under five levels. These variables are shown in Table 1, together with their respective levels. A total of twenty six experiments were predicted. The results were analyzed using the software Statistica 7.0 [13].

Table 1. Variables and studied levels for the preparation of biodiesel from *Aleurites* seeds oil and ethanol (NaOH catalyst).

Variables	Level				
	-1,41	-1	0	+1	+1,41
Heat time /min.	50	70	90	110	130
Molar ratio /ethanol/oil	6:1	7:1	8:1	9:1	10:1
Temperature /°C	40	50	60	70	80
Catalyst /% w/w	0,6	0,7	0,8	0,9	1,0

2.2. Materials, methods and instruments

Ethanol (Synth, lot 118784) and sodium hydroxide (Qhemis, lot Q0011) of analytical grade were used without additional purification. Indian nut seeds were gathered at the city of Araraquara-SP, Brazil. The oil was obtained by milling the seeds and extracting the resulting material with hexane in a Soxhlet system during 10 hours. The yield was calculated dividing the final mass of oil extracted by the mass of the milled seeds. The “tucum” oil was obtained from the municipal district of Altos, PI, Brazil, and extracted by handmade way, in other words, it was extracted by milling and heating in water.

2.3. Preparation of the tucum and Indian-nut biodiesel

The transesterification of oils with ethanol, catalyzed by sodium hydroxide, were made using a three necked flask over a heating plate with magnetic stirrer. A condenser and a thermometer were connected to the flask. The third neck was closed with a rubber septum, through which the catalyst solution in ethanol was introduced using a syringe with a long needle under the heated ethanol/oil mixture surface. The reaction time began to be counted from this moment. The reaction mixture was kept in the flask under magnetic stirring. After the reaction time be completed, the final products were separated by centrifugation and the biodiesel (upper phase) was washed with distilled water. The biodiesel was, then, dried by heating at 60 °C about 40 minutes under argon flow.

2.4. Physicochemical characterization of the tucum and Indian-nut biodiesel

The “tucum and Indian nut biodiesels were characterized by: visual aspect; ^1H NMR spectra; viscosity at 40 °C (ASTM D445), specific gravity at 20 °C (ASTM D4052), copper corrosivity (3h at 50 °C - ASTM D130); cold filter plugging point (ASTM D6371), acidity index (ASTM D664); ester content (EN/ISO 14103); free and total glycerol and glycerides index (EN 14105); iodine index (EN 14111), water content measured by the Karl Fisher method (ASTM D6304), content of sodium, potassium, calcium, magnesium and phosphorus (ICP-OES - NBR 15553) and oxidative stability analysis (Rancimat - EN 14112).

^1H NMR spectra were obtained in a equipment Varian Inova of 500MHz. CDCl_3 was applied as solvent (30 μL of sample and 600 μL of solvent). ^1H NMR spectrum was obtained at 300K temperature using 64000 acquisitions with pulse standard (s2pul), and tetramethylsilane TMS as reference. The spectral profile was used to observe the conversion of oil to biodiesel and to verify the oils composition.

3. Results / Discussion

Aleurites moluccana presented fruits with a high content of oil (60 %), such as found in other researches [7]. Tucum, how presented in the introduction [9], can produce around 30% of oil. This yield is better than soybean that shows an oil content around 25%, for example.

3.1. Experimental design for *Aleurites* biodiesel synthesizes

After all of the twenty six experiments and measure the ester content were done, were built six surface designs where the Y axis represents the percentage of ester content. The best results was obtained employing heat time about 90 minutes, molar rate alcohol/oil 8:1, temperature of 60 °C and 0.8% of catalyst. Was reached more than 99% of conversion. However, we can see other conditions that could be applied considering the little difference at the final results. In other words, when employed 70 minutes; 9:1 molar rate; 60 °C and 0.8 % of catalyst we achieved nearby 100% of yield. These conditions were used to synthesize both Indian-nut and Tucum biodiesel.

3.1.1. Preparation of the tucum and Indian-nut biodiesel

It is necessary remember that the oils are from different sources and they were obtained by different process too. The optimization process has been done employing Indian-nut oil only. Exactly 100 g of oil was put into a flask and heated until 60 °C. After then, was added the ethylic alcohol containing the total mass of catalyst. There were not troubles during the reactional time. The purification process was done using distillate water at room temperature. It was around 30 °C. No special process was necessary to segregate the glycerin phase.

3.2. Physico-chemical characterization of the tucum and Indian-nut biodiesel

Physico-chemical properties showed that both biodiesel were very similar at rheological viewpoint, because their viscosity and density are practically equals. Table 2 shows analysis results. The water content proves the efficiency of drying process using argon gas. It was below the maximum limit of 500 ppm. Some ions level like sodium, potassium, calcium, magnesium and phosphorus are below quantification limit of ICP equipment. That way, the biodiesel are in accordance to ANP Resolution. The tucum biodiesel's low iodine index (14.6 g/100g) denotes his saturated character and hence his cloud point (5.0 °C) will be bigger than *Aleurites* biodiesel (-5.0 °C). The iodine index of *Aleurites* biodiesel (150.36 g/100g) reflects a high level of unsaturated chains on his composition. These unsaturated chains can resist lower temperatures than the saturated compounds without freezing.

Table 2. *Aleurites* and *Tucum* biodiesel physicochemical parameters.

PARAMETERS	UNIT	LIMIT	METHOD	RESULTS	
				Tucum	Aleurites
Aspect	-	LII*	Visual	LII	LII
Density at 20° C	kg/m ³	850-900	ASTM D4052	0,8770	0,8789
Kinematic viscosity at 40°C	mm ² /s	3,0-6,0	ASTM D445	4,54	4,12
Water mass, max.	mg/kg	500	ASTM D6304	261,6	160,1
Sodium + Potassium, max.	mg/kg	5	NBR 15553	<LQ**	<LQ
Calcium + Magnesium, max.	mg/kg	5	NBR 15553	<LQ	<LQ
Phosphorus, max.	mg/kg	10	NBR 15553	<LQ	<LQ
Copper corrosivity, 3h a 50 °C, max.	-	1	ASTM D130	1 a	1 a
Cloud filter point pour, max.	°C	19	ASTM D6371	5,0	-5,0
Iodine index	g/100g	Anotate	EN 14111	14,67	150,36
Free glycerin	% mass	0,02	EN 14105	0,00	0,00

* Impurities free and limpid.; ** LQ: Quantification limit.

Total glycerin and glycerides content are not displayed because they are a parameter directly linked to ester content. Thus, in the tucum biodiesel we can not expect them are according to maximum limit due tucum ester content is only 79.8%. In other hand, total glycerin of *Aleurites* biodiesel (0.075%) was completely in agreement with that limit which can not be more than 0.25% of total glycerin. Free glycerin is an important parameter, especially in order to provide information about purification process. In this case, two biodiesel presented non quantitative mass of glycerin due to efficient washes.

3.3. ¹H NMR biodiesel analysis

When comparing indian nut and “tucum” biodiesels ¹H NMR spectra (e.g. Fig. 1 and 2) is possible to see differences, such as unsaturation level and compositional profile. Absence of representative peaks around 2.1 ppm in “tucum” spectrum, assigned to the methylene protons attached to the unsaturated carbon, shows its high degree of saturation.

Beyond this, near to 5.3 ppm the peak assigned to the H from CH unsaturated is in agreement with the previous observation about pi bonds. In the Glycerides chains presents in tucum biodiesel there is almost none pi bond beyond those of carbonyl groups. Observing chromatograms overlap (e.g. Fig.3), we can note the real composition's difference between both oils and biodiesel from tucum and *Aleurites*.

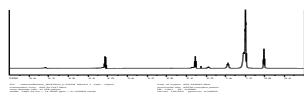


Figure 1. ^1H NMR Aleurites biodiesel spectrum.

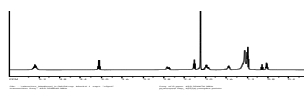


Figure 2. ^1H NMR “tucum” biodiesel spectrum.

3.4. Ester content

One of the most important reactional results is the ester content. This parameter represents how efficient was the reactional process. The principal target of this paper is to show how useful can be the optimization from an experimental design in order to apply it to others oils with different properties. If the ester contents yield are similar, so these same conditions could be applied. The *Aleurites* biodiesel synthesise presented yield about 99%. This result is almost the same as the one previously obtained during the optimization process. When those reactional conditions were applied to synthesise ethylic tucum biodiesel, the result achieved was only 79.8% for ester content. The minimum level described on Brazilian national legislation is 96.5%.

The chromatograms superimposed, e.g. Fig. 3, shows the composition differences between biodiesels from “tucum” and indian nut in terms of carbon chain length. In order to prove this, some ethylic ester standards were run on GC and their retention time (RT) were registered: C8:0, RT= 2.5 min; C12:0, RT=7.0 min; C14:0, RT= 8.0 min; C17:0, RT=14.2 and C24:1, RT=25.4 min. With this data, we can prove the saturated character of tucum oil. In the chromatogram could be seen that the majority of compounds from tucum biodiesel are between 2.5 and 15.0 minutes. In this interval there are C8:0, C10:0, C12:0, C14:0 and C16. Even a little after that, there are some peaks attributed to C18:0, or a small peak assigned to C18:1, but nothing after 17.5 minutes. Regarding *Aleurites*, most peaks are above 12.0 min and below 18 min. That interval covers saturated and unsaturated chains like C16:0, C18:0, C18:1, C18:2 and C18:3. Among those peaks, majority lies above 15.0 minutes, region of occurrence of peaks corresponding to esters with more than 17 carbons.

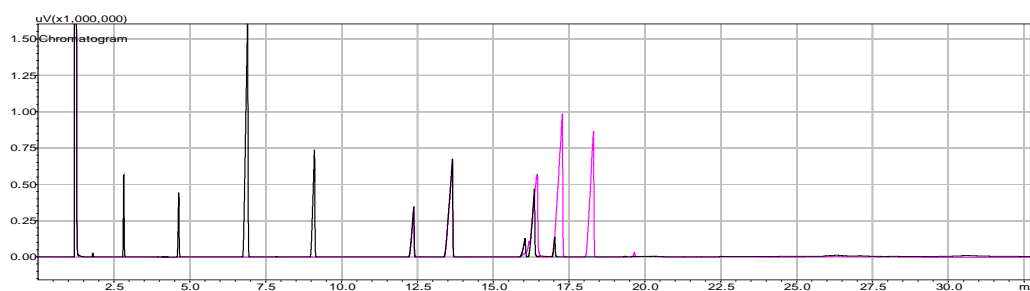


Figure 3. Superimposed “tucum” and indian nut biodiesels chromatograms (pink: Indian-nut biodiesel; black: tucum biodiesel).

3.5. “Tucum” biodiesel preparation yield under the best conditions found to indian nut biodiesel preparation.

The yield achieved to “tucum” biodiesel prepared, applying the best conditions developed by experimental design on indian nut oil, was very low. The preparation procedures were the same to both oils. Only during work up procedures there were some differences between them. Because of the acidity presented by “tucum” oil (soap generation) and its shorter carbon chains, the washing process generated more emulsions than during indian nut biodiesel work up; “tucum” biodiesel was washed much more times to remove soap excess and to break any emulsions. This can be one of the causes for the low yield of esters obtained from “tucum” oil. Other causes for the unsuitable behavior of “tucum” oil under the best experimental conditions developed for indian nut oil conversion to biodiesel may be its impurities, not removed during manual oil extraction process, and the manual oil extraction itself.

4. Conclusions

The oil content of “tucum” and indian nut seeds is greater than soybean grain. Ethanol showed technically suitable as a reagent to biodiesel production from indian nut and “tucum” oils. Indian nut oil has considerably more unsaturated esters than “tucum” oil, what explains its lower resistance to oxidation. Experimental central compound design and surface response methodology were efficient for optimization of the reactional conditions (time, temperature, molar ratio ethanol/oil and mass of catalyst) to obtain biodiesel from ethanol and indian nut oil. The optimized conditions led to an almost stoichiometric yield of biodiesel confirming the forecast of the technological viability of indian nut oil to obtain high yields of ethylic biodiesel. The same optimized conditions did not apply for “tucum” oil. Further experiments with “tucum” oil obtained by the same extraction procedure used to indian nut oil are necessary. Experimental design is an important tool to optimize chemical preparations. However, its relationship with raw materials characteristics must be carefully observed.

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