

Study of the oxidative stability of oils vegetables for production of Biodiesel

Estudo da estabilidade oxidativa de óleos Vegetais para a produção de Biodiesel

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ABSTRACT: Biodiesel is technological and estrategical Brazilian oportunity once this country has abundant vegetable species which oils are extracted to produce this biofuel. Oleaginous viability depends on its technical, economical and social-environmental competitiviness. Fatty acid variety determines its thermal and oxidative stability, mainly polyunsaturated ones. In this point of view, this papers aims evaluate oxidative stability and resistance to thermal decomposition of pequi, buriti and macauba oils. These fatty acids profiles are in agreement with literature data. Comparing thermal and oxidative stability of these oils, it can be seen pequi oil is more easily to oxidate than buriti and macauba oils when PetroOXY and Rancimat methods are employed.

Keywords: Oils, composition chemical; biofuel; stability oxidative

RESUMO - O biodiesel é uma oportunidade tecnológica e estratégica para o Brasil, tendo em vista que o País possui em abundância espécies vegetais de onde se extraem óleos para a produção deste biocombustível. A viabilidade de cada oleaginosa para produção do biocombustível depende da sua competitividade técnica, econômica e sócio-ambiental. A variedade de ácidos graxos presentes nos óleos, principalmente os polinsaturados, determinam a disposição destes aos processos de degradação térmica e oxidativa. Tendo em vista a problemática, o objetivo do trabalho foi avaliar a susceptibilidade oxidativa e resistência à decomposição térmica dos óleos vegetais de pequi, buriti e macaúba. Os óleos vegetais com proporções variáveis dos ácidos graxos mostraram concordância com dados encontrados na literatura. Os resultados de estabilidade térmica e oxidativa, pelos equipamentos PetroOxy e Rancimat mostraram maior tendência à oxidação para o óleo de pequi quando comparado aos óleos de buriti e macaúba.

Palavras-chave: óleos; composição química; biodiesel; estabilidade oxidativa

INTRODUCTION

The potential use of biofuels has proved promising in the world, as a growing market due to several factors such as the contribution to the environment and for being a source of renewable energy to replace diesel and other petroleum.

The production of biodiesel is a technological and strategic opportunity to Brazil, given that the country has abundant plant species from which to draw oil, raw materials necessary for the production of this fuel, which is already in the production of alcohol of cane

sugar an excellent example in this direction (HASS, 2001).

Biomass sources available and considered appropriate to the consolidation of renewable energy programs, vegetable oils and animal fats appear as an excellent alternative for biodiesel production. Fats and oils undergo a transesterification process that results in biodiesel (FERRARI, 2005).

Biofuel obtained from vegetable oils brings some characteristics of the raw material, such as susceptibility to thermal and oxidative degradation, directly relating to the availability of air, temperature

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and the presence of unsaturated fat acids (RODRIGUES, 2009). The speed of the oxidation reactions depend on the number and position of double bonds (RAMOS, 2003). Thus, the bis-allyl positions of hydrogen are effectively more susceptible to auto-oxidation reactions by reducing the thermal stability of vegetable oils due to the decrease in temperature and oxidation induction time - OIT, altering sensory factors, color and increased viscosity (DANTAS, 2007).

According to the American Oil Chemists' Society - AOCS (1999) the oxidative stability of oils and fats analyses follow the Cd 12b-92 methodology. According to this methodology Rancimat equipment can be used to determine the oxidative stability of oils and fats (ANTONIASSI, 2001) measuring the induction period (IP). The use of Rancimat equipment is regulated by the ANP agency (2008) for quality control of biodiesel, based on European norms EN 14112 (British Standard, 2003) which establish as minimum 6 hours of testing for the stability of the sample.

Another methodology point to the use of PetroOXY equipment, which registers the IP when the sample is exposed to oxidation by intense flow of oxygen under pressure at a given temperature. Based on the measurement of oxygen uptake by the sample, the analysis time (IP) is recorded as the time required for the sample absorbs 10% of the oxygen pressure (RODRIGUES, 2010).

OBJECTIVE

The aim of this study is to evaluate the oxidative susceptibility and resistance to thermal decomposition of selected vegetable oils by the Rancimat and PetroOxy methodology.

MATERIALS AND METHODS

Samples of vegetable oil in natura were obtained directly by mechanical pressing. Vegetable oils used in this study were pequi (*Caryocar brasiliense*), buriti (*Mauritia flexuosa*) and macaúba (*Acrocomia aculeata*).

The oils were esterified according to Maia and Rodriguez-Amaya (1993) to obtain the chromatographic data of the samples. The ester content was obtained by Gas Chromatography coupled with mass spectrometry (GC-MS), equipped with a split injector (1:50) from Shimadzu, Model GCMS-QP2010 with auto sampler. The capillary column used was DB-23 (30 mx 0.25 mm x 0.25 mM) and 50%-cyanopropyl-metilpolisiloxano as a stationary phase and helium as carrier gas, at a flow rate of 96 mL.min⁻¹.

Acid index, peroxide index and iodine index analyses of the oils were performed according to methods described in literature for oils and fats (IAL, 2008).

Oxidation stability of the samples were measured in a Rancimat equipment mark Metrohm model 743 regulated by EN 14 112, where 3 g of sample was aged in a stream of air (10 L / ha 110 ° C) in the measuring cell supplied by distilled and deionized water. The induction period (IP) was determined by measuring the conductivity. The sample is considered stable if PI equals or exceeds the 6 hours of analysis.

PetroOXY equipment was also used to measure the oxidative stability. 5 ml of the sample under pressure of 700 kPa of pure oxygen at room temperature. Temperature was raised up to 110 ° C. The oxidative induction time is given as the time required for the sample absorbs 10% of the pressurized oxygen available for the test.

RESULTS AND DISCUSSION

Table 1 shows the composition of fatty acid methyl esters obtained by chromatography.

Table 1 – Fatty acid profile of the oils by GC-MS.

FATTY ACID	PEQUI	BURITI	MACAUBA
C12:0 lauric	-	-	34,19
C14:0 miristic	-	-	6,96
C16:0 Palmitic	38,09	18,49	7,03
C18:0 Stearic	2,67	-	3,08
C18:1 Oleic	54,19	74,49	39,32
C18:2 Linoleic	-	-	5,42

The values found in this study show similar composition the data reported in literature (LIMA et al., 2007, ALBUQUERQUE et al., 2005; HIANE et al., 2005), being considered satisfactory the production of biodiesel.

The oils studied showed different profiles in the composition of fatty acids having predominance of unsaturated acids as Oleic with 54,19%, 74,49% e

39,32% in the oils of pequi, buriti and macaúba respectively and excellent level of saturated oils as palmitic and lauric. Second Souza et al (2013) the biodiesel obtained of oils with elevated levels of fatty acids monounsaturated and saturated must submit good stability oxidative and properties of flux, characteristics relation to good performance as fuel, demonstrating the quality of oils exposed in this study.

Table 2 shows the physical-chemistry properties of the oils in especially the acidity index, iodine index, peroxide index and kinematics viscosity.

Second Gonçalves et al (2009) the oily residues should contain a maximum the acidity of 1 mg KOH/g for that meets the levels desired of acidity in the norms of the ANP of 0,5 mg KOH/g in biodiesel and Hartman (1973) says that above this level can cause reactions of saponification. So only the sample of macaúba (0,82 mg KOH/g) presented within of the specifications and the others need of pretreatment for that can be used in the production of biodiesel.

The iodine index estimates the degree of unsaturation of a triglyceride, being a parameter of great importance as regards the your oxidative stability (LÓBO et al 2009). The high values shown in Table 2 indicate levels considerable of fatty acids unsaturated, as seen in Table 1.

The peroxide index (PI) is an estimate of the degree of degradation of the raw material which according to ANVISA (2009) the maximum value allowed is 10 meq / kg. Thus the results of the study show that the selected samples are within the standards and can be used for the production of biodiesel and an exception may be macaúba oil by not showing detection levels

The kinematic viscosity found in this work could be within the standards when compared to results obtained by Brock et al (2008) in soybean oil, corn, sunflower and cotton, the ambient temperature, have values of 41.2 mm² s⁻¹ ; 41.3 mm² s⁻¹; 47.3 mm² s⁻¹ respectively.

Tabela 2 – Physical and chemical analyzes of oils

VEGETABLES OILS	IA (mg KOH/g)	I.I (mg I ₂ /100g)	I.P (meq/kg)	Kinematics viscosity (mm ² s ⁻¹)
Pequi	2,45	45,13	1,38	42,94
Buriti	5,40	75,00	1,29	41,78
Macauba	0,82	33,51	ND	31,92

Oxidative stability is an important property for edible oils, lubricants and fuels. This information is useful to help the conditions and storage time and also confirm the need to define the use of antioxidants to improve these parameters (CORSINI & JORGE, 2006)

The oxidation of vegetable oils and biodiesel occur at different speeds, taking into account the amount and

position of unsaturations in the chain. This tendency to oxidation increases as increase the degree of unsaturation. One way to assess this parameter is given by the oxidation index (OI), which can be calculated through of Equation 1, described in Waynick (2005).

Equation 1: Calculation of index oxidation

$$IO = \frac{0,02(\% \text{ oleic}) + (\% \text{ linoleic}) + 2(\% \text{ linolenic})}{100}$$

The Table 3 below shows the results obtained using the data of composition of the fatty acids in the

Table 1 and applying in Equation 1

Table 3.Oxidation index of vegetable oils

VEGETABLE OILS	IO CALCULATED
Pequi	0,011
Buriti	0,062
Macaúba	0,062

The IO may be used to predict the oxidation resistance presented by the oils, based on the percentage of unsaturated fatty acids (Table 1), applying Equation 1.

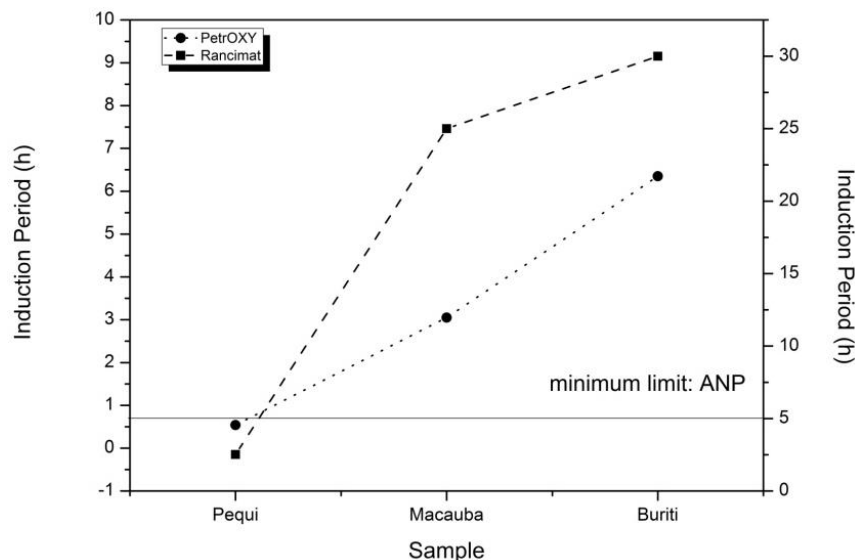
The oxidative stability results obtained from Rancimat and petroOXY (Figure 1) showed higher tendency to oxidize to the pequi oil. Comparing buriti and macaúba oils, the latter was more stable in

PetroOxy equipment, which may be related to a higher percentage of saturated fatty acids (51.26), and buriti oil higher percentage of unsaturated fatty acids (74.49%), demonstrating that a PI less than the macaúba sample, which has in its composition a higher percentage of saturated fatty acids.

The lower values of IP obtained in PetroOXY equipment, when compared to the values obtained by

the Rancimat, is due to a pressure of 700 kPa used atmosphere. allowing greater contact with the oxidizing

Figure 1: Induction period by Rancimat and PetroOxy.



CONCLUSION

The chromatographic analysis showed that the oil content of methyl esters is in agreement with literature data. The calculated IO imply lower resistance to oxidation to pequi oil, confirmed by data obtained in Rancimat and PetroOxy equipments.

The oxidative stability obtained from the Rancimat equipment was: buriti > macauba > pequi. Although there have been registered for more than 6 h IP for samples buriti macaúba and the presence of carotenoids and tocopherols in buriti oil may have contributed to a greater PI, since they are substances that slow the oxidative processes.

Samples of buriti and macauba showed IP greater than six hours, but it is known that buriti oil has a high content of carotenoids and tocopherols which are natural antioxidants.

The PetroOxy showed the following order of stability: macauba > buriti > pequi. The greater stability of macaúba compared to buriti can be attributed to the content of saturated (51.26%) and low content of monounsaturated (39.32%) while the content of oleic acid in buriti oil is 74.49%. The oxygen pressure used in the equipment significantly reduced analysis time, finding lower PI for samples with higher content of unsaturated.

Among the analyzed oil evaluated in this work, buriti and macauba showed better potencial for biodiesel production.

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