

## Simultaneous optimization on biolubricants obtained through a quaternary mixture of vegetable oils: application of the desirability function

### Otimização simultânea de biolubrificantes obtidos através de mistura quaternária de óleos vegetais: aplicação da função desejabilidade

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#### Resumo

Para reduzir os impactos ambientais e os custos da produção de biolubrificante, este trabalho propõe o uso de misturas de óleos vegetais que não foram quimicamente modificados. Formulações de biolubrificantes foram propostas com o uso de óleos de pinhão-manso, mamona, amêndoa de macaúba e polpa de macaúba, pois estes possuem propriedades físico-químicas potenciais para gerar um biolubrificante de alto desempenho. Foi utilizado um planejamento de misturas quaternárias do tipo centroide simplex com a função desejabilidade para a melhoria simultânea do índice de viscosidade e lubricidade das blendas. Bons resultados para essas propriedades foram obtidos para algumas blendas, principalmente com óleo de polpa de macaúba, que apresentou desempenho comparável ou superior aos óleos vegetais quimicamente modificados. Macaúba tem sido apontada como uma nova matéria-prima para biodiesel, diesel verde e combustíveis sustentáveis de aviação (SAF), e seu uso como biolubrificante pode agregar valor a esse novo óleo de palma, promovendo benefícios sociais, econômicos e ambientais.

**Palavras-chave:** Biolubrificante. Óleo vegetal. Planejamento de mistura quaternária. Otimização de múltipla resposta. Função desejabilidade.

#### Abstract

To reduce the environmental impacts and the costs of the production of biolubricant, this work proposes the use of vegetable oil mixtures that have not been chemically modified. Formulations of biolubricants were proposed with the use of jatropha curcas, castor, macauba kernel, and macauba pulp oils since these have potential physical-chemical properties to generate a high-performance biolubricant. A simplex centroid quaternary mixture design was used with the desirability function for the simultaneous improvement of the viscosity index and lubricity in the blends. Good results for these properties were obtained for some blends, especially that with macauba pulp oil, which presented comparable or superior performance to those for vegetable oils chemically modified.

Macauba has been pointed out as a new feedstock for biodiesel, green diesel, and sustainable aviation fuels (SAF), and its use as eco-lubricant can aggregate the value of this new palm oil, promoting social, economic, and ambient benefits.

**Keywords:** Biolubricant. Vegetable oil. Quaternary mixture design. Multiple response optimization. Desirability function.

### **Nomenclature**

ASTM - American Society for Testing and Materials

CO - castor oil

FID - Flame ionization detector

GC - Gas chromatography

HFRR - High Frequency Reciprocating Rig

JC - *Jatropha curcas*

KMac - macauba kernel oil

PMac - macauba pulp oil

WSD - wear scar diameter

## **1. Introduction**

Lubricating oils are widely used in the industrial and automotive sectors. Among the different types of lubricants, mineral oil derivatives are the most commonly used, although they are not biodegradable and can potentially damage the environment. Around 50% of the lubricants sold worldwide are released to the environment because of volatility, spillage, total loss, or serious accidents (Salimon et al., 2012). They can directly contaminate the water, soil, and atmosphere, affecting not only the survival of plants and animals but also the health of human beings (Nagendramma & Kaul, 2012).

Environmental regulations have been getting more stringent. Besides that, it is extremely important to consider resource conservation and disposal issues. As a result of this, the forecast for the worldwide demand for shared eco-friendly/biodegradable lubricants can get between 15% and 30% until 2025 (Nagendramma & Kaul, 2012).

Vegetable-based oils are one of the biodegradable base stocks. These oils are mainly composed of triacylglycerides and smaller amounts of mono- and diglycerides, in addition to free fatty acids, phospholipids, steroids, water, and some impurities (McNutt & He, 2016). The use of vegetable oils as lubricants presents some environmental advantages such as high biodegradability and low toxicity, in addition to presenting a closed carbon cycle.

In terms of performance benefits, high lubricity, high viscosity index, high flash point and low loss by evaporation can be cited (Nagendramma & Kaul, 2012). Lubricity is the ability of a fluid to prevent friction and wear between moving metal surfaces under a load (Syahir et al., 2017). The viscosity index (VI) is related to the variation of the oil viscosity with the temperature variation. The higher the VI, the more stable will be the viscosity concerning variations in temperature, which is the desired behavior. The long linear chains present in the triacylglycerides, and the polar functional groups of fatty acids, give vegetable oils good flow and lubricating performance, even at low temperatures (McNutt & He, 2016; Syahir et al., 2017).

High-performance biolubricants from vegetable oils have been proposed in the last years. The research is especially about structural changes in the carbon chains of the oils, but the blending of pure oils is another possibility (Ting & Chen, 2011). The objective is to improve properties such as viscosity, viscosity index, lubricity, and oxidative stability (Nagendramma & Kaul, 2012; Salimon et al., 2012). The use of transesterification and epoxidation reactions to generate esters with better lubricating properties was discussed by Panchal et al. (2017). They used different reaction conditions and performance-enhancing additives (Panchal et al., 2017). As shown in another study, an interesting alternative to obtain biodegradable greases was the hydrogenation of oleic, linoleic,

or linolenic acids. The products, saturated compounds, produced a lubricant of lower bioaccumulation and high biodegradability (Kania et al., 2015). The chemical modification of oleic acid was also used to obtain triester derivatives. The strategy of blending pure oils was used by Sajeeb et al. (2010) to improve lubricant properties. They reported that the addition of 50% of mustard oil to the coconut oil, showed superior performance in comparison to the use of coconut oil alone. In this work, the blends were prepared by varying volume (%) of mustard oil from 10 to 50% (Sajeeb & Rajendrakumar, 2019). Whatever the processes were chosen for the development of the biolubricant, the experimental design can be a useful tool to the planning stage.

Experimental design methods are of fundamental importance for improving the product realization process. The application of these tools can improve process yields, reduce the development time and the overall costs. The factorial experiment is a strategy in which different factors of a process can be varied together, and the complexity of its interactions can be studied. It has been widely used for the optimization of reaction parameters as well as for improving the properties of blends. When the product is a mixture of materials, each component is a factor, and the method is called a mixture experiment. In this situation, Simplex designs can be used to study the effects of mixture components on the response variable. In the field of renewable fuels, for example, mixture design has been used for the optimization of biodiesel properties (Orives et al., 2014). It is interesting to notice that the conditions that optimize one parameter can negatively interfere with another. Thus, it is desirable to have a way of performing a simultaneous optimization of the multiple responses, which can be obtained with the desirability function. This tool was proposed by Derringer and Suich (Derringer & Suich, 1980) and can be used to find, maximize, or minimize a given response by simultaneous optimization. Then, the levels of the factors that will produce more satisfactory answers are determined for a studied model.

As previously discussed, chemical changes in the triglyceride chains have been proposed to improve lubricant properties. Although the interesting results, these reactions demand consumption of reagents, water, and energy, as well the separation of the products of interest. They can also form by-products and waste. Therefore, to reduce the environmental impacts and the costs associated with the production of biolubricant bases, this work proposes the use of mixtures of vegetable oils that have not been chemically modified. A mixture design was used to plan biolubricant formulations made from jatropha, castor, macauba kernel, and macauba pulp oils.

Macauba is a palm tree (*Acrocomia aculeata*) with an extensive natural occurrence in Brazil. The trees have been identified as a viable alternative for the recovery of degraded areas and for planting in permanently protected areas. They can also be planted in lands that are unsuitable for growing foods or intercropped with other plants. Macauba represents an important source of income for family farming because the fruits present high productivity of oil, about 6500 L/ (ha. year) (Pires et al., 2013). The oil can be extracted from the pulp or the kernel, and both oils have interesting properties for biofuel production (Knothe & Steidley, 2005). However, the macauba pulp oil acquires a high acidity in a short period, which limits its applications and reduces its commercial value. Then, macauba oil has been used for the production of soap. Given the high sustainability of the macauba and the other positive points, the development of more noble products from the oil of this fruit is fully justifiable. The use of macauba oil as a lubricant base can add value to macauba farming and generate income in the fields.

Considering the relevance of sustainable products with cleaner production, the objective of this work was the development of biolubricants by the optimized mixtures of vegetable oils, without chemical conversions. This innovative work aims to create products of industrial interest using the simple blending process, that can yield relevant financial, social, and environmental gains. The mixtures were optimized for use as a potential lubricant base, for applications in machinery and equipment in the food industry. Biolubricants are environmentally compatible when there are losses to the environment during industrial operations, making them an attractive alternative. It should be noted that these must be used in applications where there is no possibility of contact between the food and the lubricated part (Syahir et al., 2017).

The properties of jatropha, castor, macauba kernel and macauba pulp oils were evaluated. Then, a simplex centroid quaternary mixture design was applied together with the total desirability statistical function. Viscosity index and lubricity were the quality parameters improved in the blends.

## 2. Methodology

### 2.1 Raw Materials

Four samples of vegetable oils were used. Three of them, *Jatropha curcas* (JC), macauba kernel oil (KMac), and macauba pulp oil (PMac), were obtained from local producers, whereas castor oil (CO) was purchased from Sulfal Química Ltda.

### 2.2 Physicochemical properties

The samples were characterized by the following tests: acidity index, saponification index, moisture content, oxidative stability, viscosity at 40°C and 100°C, viscosity index, fatty acid profile, and lubricity.

The acidity index was determined according to ASTM D664 using a Metrohm automatic titrator titre 804 Titrando. The Karl Fischer method was used to determine the moisture content of the samples in a Metrohm Coulometer 831 KF apparatus, as determined by ASTM D6304. For determination of oxidative stability, the samples were submitted to the Rancimat method using a Metrohm model 843 apparatus according to EN 14112. The kinematic viscosities of the samples were determined at 40 °C and 100 °C in a THERMO HAAKE-PHOENIX thermostatic bath using a Cannon Fenske viscometer, by ASTM D445. The viscosity index was calculated as determined by ASTM D2270.

The lubricity was determined by the ASTM D6079 method using PCS Instruments Lubricant, High-Frequency Reciprocating Rig (HFRR) model, and Meiji ML7000 Techno microscope with a magnification capability of 100X. The result of this essay is known as WSD (wear scar diameter), the arithmetic average of the diameters of wear provoked on a steel pipe, and it is reported in micrometers ( $\mu\text{m}$ ).

### 2.3 Fatty acid composition

For the identification of the fatty acids present in the samples, they were initially subjected to acid-catalyzed derivatization involving hydrolysis and methylation steps. They were then analyzed by gas chromatography on a Shimadzu GC Gas Chromatograph with an FID detector. The chromatographic conditions used were the following: 0.20  $\mu\text{m}$  film of poly(bis-cyanopropylsiloxane) (SP-2340-Supelco) as the stationary phase, 60 m x 0.25 mm chromatographic column; oven programmed from 70 °C with a heating rate of 40 °C/min to 230 °C, where the temperature was maintained for 10 minutes; injector temperature of 250°C and the detector temperature was 260 °C; injection volume of 1  $\mu\text{L}$ ; helium carrier gas with a linear velocity of 28.1 cm/s; split ratio equal to 50 and analysis time of 55 min.

### 2.4 Experimental design

Viscosity index and lubricity were used as response variables for the simplex centroid mixtures design. For a mixture of four oils, the design was composed of 15 experiments, one of

which was the central point. The desirability function was calculated by normalizing the response variables. In the normalization, the desirable values were defined to be zero (0) for the wear scar diameter (WSD) and one (1) for the viscosity index. These values were chosen considering that the smaller the WSD, the better the lubricity, while for the viscosity index, the higher values are most interesting. The Program Statistica 10.0 was used for data processing.

### 3. Results and Discussion

#### 3.1 Characterization of vegetable oil samples

Parameters such as acidity index, moisture content, and oxidative stability are parameters that are related to the state of degradation of the oil. Kinematic viscosity, viscosity index, and lubricity are parameters associated with the performance of a lubricant.

Regarding the tests associated with the state of degradation of the oils, a high acidity was observed for the macauba pulp oil (PMac), in addition to high moisture content and low oxidative stability (Table 1). This high acidity of PMac, compared to macauba kernel oil (KMac), is justified by the fact that this sample comes from fruit pulp, whose moisture content is higher than that of the kernel. The presence of water favors the hydrolysis of triglycerides and the release of free fatty acids (ASTM 5185-13, 2014). Also, the macauba fruit is exposed to lipase-type enzymes present in soil microorganisms when the fruit falls to the ground. This exposure contributes to the increase in the acidity of macauba pulp oils. These enzymes are also present in higher concentrations in the pulp oil than in the kernel oil, which explains the difference in acidity between them.

**Table 1 - Results of the physicochemical characterization of *Jatropha curcas* oil (JC), castor oil (CO), macauba kernel oil (KMac), and macauba pulp oil (PMac).**

Properties	Method	JC	CO	KMac	PMac
Acidity (mgKOH.g <sup>-1</sup> )	ASTM D 664	5.93±0.05	0.90±0.40	1.75±0.05	92.80±1.40
Moisture (mg.kg <sup>-1</sup> )	ASTM D 6304	1207.1	514.4	622.0	2661.6
Oxidative stability (h)	EN14112	7.3±0.1	82.7 ± 0.1	19.9 ± 0.2	1.9 ± 0.1
Kinetic viscosity at 40°C (mm <sup>2</sup> .s <sup>-1</sup> )	ASTM D 445	34.14±0.1	250.92±1.77	28.81±0.0	32.77±0.02
Kinetic viscosity at 100°C (mm <sup>2</sup> .s <sup>-1</sup> )	ASTM D 445	8.32±0.05	21.11±1.54	5.94±0.01	6.64±0.01
Viscosity index	ASTM D 2270	165.9±0.3	98.7±0.6	144.4±0.1	146.0±0.1
Saturated fatty acids (%)	GC <sup>a</sup>	19.75	1.36	66.53	23.31
Unsaturated fatty acids (%)	GC <sup>a</sup>	74.22	97.41	32.83	68.51
WSD (µm)	ASTM D 6079	146	112	164	86

<sup>a</sup> GC = gas chromatography

A correlation between the moisture content and the acidity of these oils was observed. As expected, the higher the oil acidity the higher the moisture. In general, the maximum value for the water content in industrial lubricating oils is 1000 mg.kg<sup>-1</sup>. Satisfactory results for this quality parameter were observed for CO and KMac oil. Instead, the moisture content of the PMac was the highest (2662.6 mg.kg<sup>-1</sup>), which was already expected for oils with high acid content. The presence

of water promotes the hydrolysis of the triacylglycerides to release more free fatty acids, and the oil can become corrosive to certain components of the machines, such as seals and bearings (Stepina & Vesely, 1992). Water also accelerates the oxidation of the oil, and when the moisture content is high, the formation of an oil-water emulsion can occur. In these cases, the oil must be subjected to a drying process to remove the water. Anti-corrosive additives can be used to prevent or reduce damage (Aarnisalo et al., 2007).

Castor oil (CO) was the oil with the highest oxidative stability among the samples, and the oil from macauba pulp was the most unstable. The low oxidative stability of the PMac sample was already expected, not only because of the higher moisture content but also of the higher acidity. Considering the influence of the chemical composition on the oxidative stability of vegetable oils, it is expected that the more unsaturated oils will be less stable because oxidation occurs preferentially at the double bonds. The results obtained agree with the expected. The less stable oils were those from the macauba pulp oil and the oil from *Jatropha curcas* (JC), whose unsaturated fatty acid contents were 68.51% and 74.22%, respectively.

One of the key parameters to be evaluated in a lubricant is the kinematic viscosity, which is fundamental in hydrodynamic lubrication. The viscosity of a fluid depends on the interaction between its molecules. High kinematic viscosities at 40°C and 100°C were observed for castor oil. The results were very different from those of the other vegetable oils, but they corroborate that showed by Salih et al. (Salih et al., 2011). This result is explained by the presence of ricinoleic acid, the main constituent of castor oil. The hydroxyl groups on ricinoleic acid form intermolecular hydrogen bonds (Ogunniyi, 2006). As a result, there is greater interaction between the molecules, making them more closely grouped and more resistant to flow. This difference in viscosity of castor oil relative to the other oils was higher at 40°C but decreased when the test was performed at 100°C. In this condition, the higher kinetic energy of the molecules at 100°C difficult the form the hydrogen bonds, and the difference between the viscosities becomes smaller.

The viscosity indexes of the samples were calculated using the viscosities measured at 40°C and 100°C. This parameter is related to the behavior of the viscosity of the oil when its temperature is varied. The index is directly proportional to the stability of the viscosity with the temperature variation, and a higher index is preferred. Except for castor oil (98.7), all the other oils had viscosity indexes between 144.4 and 165.9. This result indicates that the viscosity of the castor oil is more susceptible to the variation in temperature than the other oils studied. In the work of Salimon et al. (2012)(Salih et al., 2012), the viscosity index ranged from 45 to 145, but the best results were obtained for triesters resulting from a sequence of reactions.

Lubricity can be determined by measuring the wear produced by the friction between metallic surfaces in the presence of the oil under analysis. The smaller the wear produced in the test piece, the greater the lubricity of the oil, that is, the greater the protective capacity. Thus, higher values of wear scar diameter (WSD) are related to the lower lubricating capacity of the oil. The best result for the lubricity test was observed for the macauba pulp oil, with a WSD equal to 86 µm. The high lubricity of this oil might be related to the presence of polar organic compounds, such as carboxyl (-COOH) and hydroxyl (-OH) groups, from free fatty acids, in addition to the ester functions of triglycerides. The polar chains interact strongly with the positive charges on the metal surfaces, the molecules align themselves, and resistant films are formed. The strong film requires additional energy to be penetrated. This results in greater lubrication capacity, and lower energy consumption in lubricating applications (Syahir et al., 2017). The high acidity of PMac, attributed to the polar chains of free fatty acids, justifies the greater lubricity presented by this oil in comparison with the others. By the way, the free fatty acids cannot explain the good lubricity obtained for castor oil (WSD = 112 µm), which acidity was the lowest among all the samples. In this situation, good lubricity can be justified by hydroxyl groups from ricinoleic acid. As a comparison, in the work of Salimon et al. (2012), WSD values ranged from 122 to 243 µm for synthetic ester oils (Salimon et al., 2012). Sajeeb et al. (2019) reported that the mixture of coconut and mustard oil, in the proportion of 1:1, showed superior performance (WSD = 486 µm) in comparison to the use of coconut oil alone (WSD = 600 µm) (Sajeeb & Rajendrakumar, 2019).

The composition of the oils in terms of fatty acids was determined by gas chromatography and the results are presented in Table 2. In this table, the composition of the castor oil is presented using data from the literature. It was not possible to perform the assay on this sample because the method to be used differs from that of the other samples as a result of the presence of the hydroxyl group in ricinoleic acid. The C18:2 (linolenic acid) and C18:1 (oleic acid) acids predominate in the *Jatropha curcas* oil; C12:0 (lauric acid) and C18:1 acid predominates in KMac, and finally, the C18:1 and C16:0 (palmitic acid) acids predominate in PMac. The use of raw materials containing a predominance of medium or unsaturated fatty acids, such as oleic acid or linoleic acid is suitable for improving the cold properties of the oil (Hoekman et al., 2012) and reducing the crystallization temperature (Salih et al., 2012). However, lubricants with a high content of saturated fatty acids, such as lauric acid and palmitic acid in KMac and Pmac, can solidify at low temperatures because they are saturated. Thus, they do not present advantages as lubricants for applications with wide thermal variations (Syahir et al., 2017). Oils containing the highest content of oleic acid are potential substitutes for mineral lubricating oils and synthetic esters (Erhan et al., 2006). These oils also have higher thermo-oxidative stability than oils rich in linoleic acid because they have one less double bond in each chain. Among the four oils studied, the highest percentage of oleic acid, high lubricity, and a high viscosity index were observed for the oil from macauba pulp. Therefore, considering these results, PMac can be considered to possess the best characteristics for use as a biolubricant base.

**Table 2 - Fatty acid composition of *Jatropha curcas* oil (JC), castor oil (CO), macauba kernel oil (KMac), and macauba pulp oil (PMac) obtained experimentally and reported in the literature.**

Number of carbons	Fatty acid	Experimental (%)			Reported in the literature (%)			
		JC	KMac	PMac	JC <sup>a</sup>	CO <sup>b*</sup>	KMac <sup>c</sup>	PMac <sup>c</sup>
C8:0	caprylic	-	03.81	00.17	-	-	05.30	-
C10:0	capric	-	03.34	00.14	-	-	03.70	-
C12:0	lauric	00.20	38.27	01.34	-	-	41.90	00.60
C14:0	miristic	00.14	09.66	00.53	-	-	10.20	00.30
C16:0	palmitic	14.24	08.14	18.33	25.25	0.72	09.40	18.80
C18:0	stearic	04.86	03.31	02.77	04.40	0.64	03.30	02.60
C21:0	henicosanoic	00.31	-	0.03	-	-	-	-
C16:1	palmitoleic	00.73	0.06	02.75	-	-	-	-
C18:1n9c	oleic	32.63	29.43	50.31	19.78	2.82	21.30	53.30
C18:2n6c	linoleic	39.02	03.20	-	37.72	3.74	03.40	16.00
C18:2n6t	linolelaídic	01.62	-	-	-	-	-	-
C18:3n3	linolenic	00.19	-	00.89	12.68	-	-	-
C20:1	gondoic	00.03	00.14	14.56	-	-	-	-
C22:0	behenic	-	-	-	-	-	-	-
C24:1	nervonic	-	-	-	-	-	-	-
C18:1nOH	ricinoleic	-	-	-	-	90.85	-	-

<sup>a</sup> (Sinha et al., 2015), <sup>b</sup> (Guo et al., 2018), <sup>c</sup> (Silva Freitas et al., 2021);\* Only literature data are listed.

### 3.2 Mixture Design

In this part of the work, a quaternary mixture design was used to improve the viscosity index and the lubricity (WSD) of vegetable oil mixtures. The objective was to formulate mixtures of vegetable oils that yielded the lowest value for the WSD (better lubricity) and the highest value for the viscosity index (lower susceptibility of viscosity to temperature variations).

A simplex centroid design and the total desirability function were used to find the best proportion of the mixtures to be used as a biolubricant base. The overall desirability was obtained by combining the normalized individual desirabilities found with a geometric mean, given by Equation (1):

$$D = (d_1(Y_1) \times d_2(Y_2) \times d_3(Y_3))^{\frac{1}{k}} \quad (1)$$

where  $D$  is the overall desirability;  $d_k (1, 2, \dots, k)$  is the individual desirability within the interval  $0 \leq d_k \leq 1$  from the combination of the transformed responses in the geometric mean;  $Y_k (1, 2, \dots, k)$  is each of the responses of the original set (Vera Candiotti et al., 2014).

**Table 3 - Matrix of the simplex centroid mixture design of *Jatropha curcas* oil (JC), castor oil (CO), macauba kernel oil (KMac), and macauba pulp oil (PMac).**

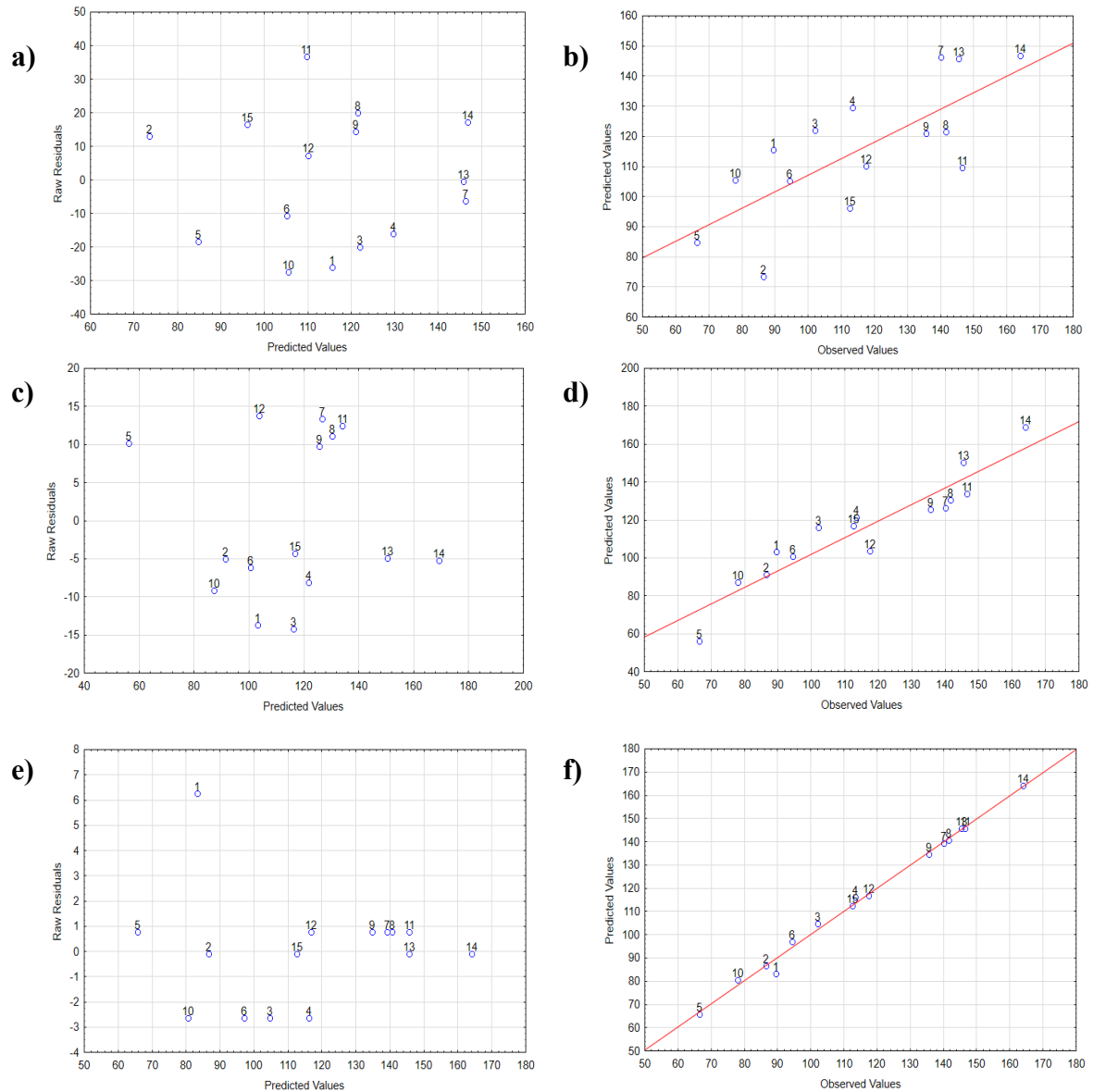
Mixture	Oil content of the blends (%)				WSD ( $\mu\text{m}$ )	Viscosity Index	Desirability
	JC	CO	KMac	PMac			
1	100	0	0	0	146	165.9	0.44
2	0	100	0	0	112	98.7	0.00
3	0	0	100	0	164	144.4	0.00
4	0	0	0	100	86	146.0	0.75
5	50	50	0	0	136	137.4	0.41
6	50	0	50	0	140	148.3	0.43
7	50	0	0	50	146	147.9	0.36
8	0	50	50	0	142	136.9	0.36
9	0	50	0	50	66	100.8	0.18
10	0	0	50	50	118	142.1	0.55
11	1/3	1/3	1/3	0	114	133.0	0.51
12	1/3	1/3	0	1/3	94	128.6	0.56
13	1/3	0	1/3	1/3	102	153.8	0.72
14	0	1/3	1/3	1/3	78	109.1	0.37
15	25	25	25	25	90	141.5	0.70

The matrix of the simplex centroid mixture design for the four oils is shown in Table 3. In the first stage, the results of WSD and VI were fitted for linear, quadratic, and special cubic models. The analysis of variance (ANOVA) indicates, at a 95% confidence level, that the cubic terms were not significant (Table 4). However, comparing the raw residuals plots, the observed versus predicted values plots (Figure 1), and the values of coefficients of determination ( $R^2$ ) and of determination adjusted ( $R^2_{\text{adjusted}}$ ) it is possible to notice that the special cubic model had the best fit. The comparison was shown only for the variable WSD, but the other models had similar aspects.

**Table 4 - ANOVA for the regression models.**

<i>Variab les</i>	<i>Model</i>	<i>SS model</i>	<i>df mod el</i>	<i>MS mode l</i>	<i>SS residu al</i>	<i>df residu al</i>	<i>MS residu al</i>	<i>F.</i>	<i>p</i>	<i>R<sup>2</sup></i>	<i>R<sup>2</sup> adjust ed</i>
<i>WSD</i>	<i>Linear</i>	6514. 27	3	2171. 42	5339. 67	11	485.4 2	4.4 7	0.02 76	0.54 95	0.426 7
	<i>Quadrati c</i>	10334 .02	9	1148. 22	1519. 91	5	303.9 8	3.7 8	0.07 87	0.87 18	0.641 0
	<i>Special Cubic</i>	11783 .20	13	906.4 0	70.74	1	70.74	12. 81	0.21 56	0.99 40	0.916 5
<i>VI</i>	<i>Linear</i>	4096. 43	3	1365. 48	1064. 78	11	96.80	14. 11	0.00 04	0.79 37	0.737 4
	<i>Quadrati c</i>	4765. 82	9	529.5 4	395.3 8	5	79.08	6.7 0	0.02 48	0.92 34	0.785 5
	<i>Special Cubic</i>	5063. 95	13	389.5 3	97.25	1	97.25	4.0 0	0.37 43	0.98 12	0.736 2
<i>Desirab ility</i>	<i>Special</i>	0.742	13	0.057	0.001	1	0.001	39.	0.12	0.99	0.972
	<i>Cubic</i>	9		1	4		4	52	39	81	8

SS: Sum of Squares; df: degrees of freedom; MS: Mean Square



**Figure 1 - Comparison of the proposed models: raw residuals and predicted versus observed plots for linear (a,b), quadratic (c,d), and special cubic (e,f) models for the variable WSD**

The general function adjusted, correspondent to a special cubic model, is presented in Equation (2) and the coefficients and interaction effects are in Table 5.

$$\hat{Y}_X = \sum_{i=1}^4 \beta_i x_i + \sum_{i \leq j}^4 \sum_j \beta_{ij} x_i x_j + \sum_{i \leq j}^4 \sum_{j \leq k}^4 \sum_k \beta_{ijk} x_i x_j x_k \tag{2}$$

where  $Y$  is the predicted response;  $x_i$ ,  $x_j$ , and  $x_k$  are independent variables that correspond to the proportion of oil in the mixture;  $\beta_i$  is the regression coefficient for each linear effect term and  $\beta_{ij}$  and  $\beta_{ijk}$  are the binary and ternary interaction effect terms.

**Table 5 - Coefficients from the special cubic model for determination of viscosity index and wear (WSD) in mixtures of *Jatropha curcas* oil (JC), castor oil (CO), macauba kernel oil (KMac), and macauba pulp oil (PMac).**

Samples	WSD		Viscosity Index		Desirability	
	Coefficients and Interaction Effects	<i>p</i>	Coefficients and Interaction Effects	<i>p</i>	Coefficients and Interaction Effects	<i>p</i>
(A)JC	145.60	0.036731	166.05	0.037762	0.436038	0.055370
(B)CO	112.60	0.047461	98.80	0.063327	0.000442	0.992599
(C)KMac	164.10	0.032598	144.48	0.043381	0.000442	0.992599
(D)PMac	86.60	0.061632	146.12	0.042896	0.748345	0.032316
(AB)	22.48	0.681054	16.18	0.793557	0.753486	0.153746
(AC)	-62.52	0.369890	-31.66	0.629619	0.816963	0.142210
(AD)	118.48	0.212342	-36.59	0.586183	-0.933874	0.124891
(BC)	9.48	0.855517	57.58	0.443551	1.433404	0.081971
(BD)	-135.52	0.187254	-90.30	0.311783	-0.801826	0.144803
(CD)	-34.52	0.554894	-16.66	0.787862	0.706676	0.163501
(ABC)	-573.19	0.282050	-134.44	0.746005	1.267406	0.490358
(ABD)	-496.69	0.318939	188.70	0.659845	7.804979	0.099475
(ACD)	-805.69	0.207259	380.57	0.444017	7.378405	0.105124
(BCD)	-610.69	0.266739	-327.98	0.491066	-0.472369	0.766497

For the determination of the wear (WSD), the coefficients of the JC, CO, and KMac oils showed significant values at the 95% confidence level. The interaction effects with positive results indicate a synergistic effect, that is, they increase the value of the WSD variable. On the other hand, negative values represent antagonistic effects. The higher the numerical value of this effect, the lower the WSD. Considering that a good lubricating oil protects the surface against wear, the antagonistic effects, with negative signs, are the most favorable.

Regarding the viscosity index, the most significant coefficients for the model were related to JC, KMac, and PMac oils. For this variable, the synergistic effects are the most favorable, as they contribute to higher VI values. The higher the VI value, the lower the susceptibility of the mixture to temperature variations.

The use of response surfaces or contour plots obtained from ternary mixtures provides flexibility for the formulation. The choice of the oil may be linked to availability or value in the market, for example. If a specific oil is not available, the proportions of the others can be adjusted, improving the variables of interest. Considering the lubricity, the green regions in the contour plots (Figure 2) should be prioritized, as it is the region of the mixtures that provide lower WSD values. The best results were obtained with mixtures of PMac with CO. However, as expected, the presence of CO affects the viscosity index (Figure 3). For this parameter, the best blends will be those from the red regions of the diagrams.

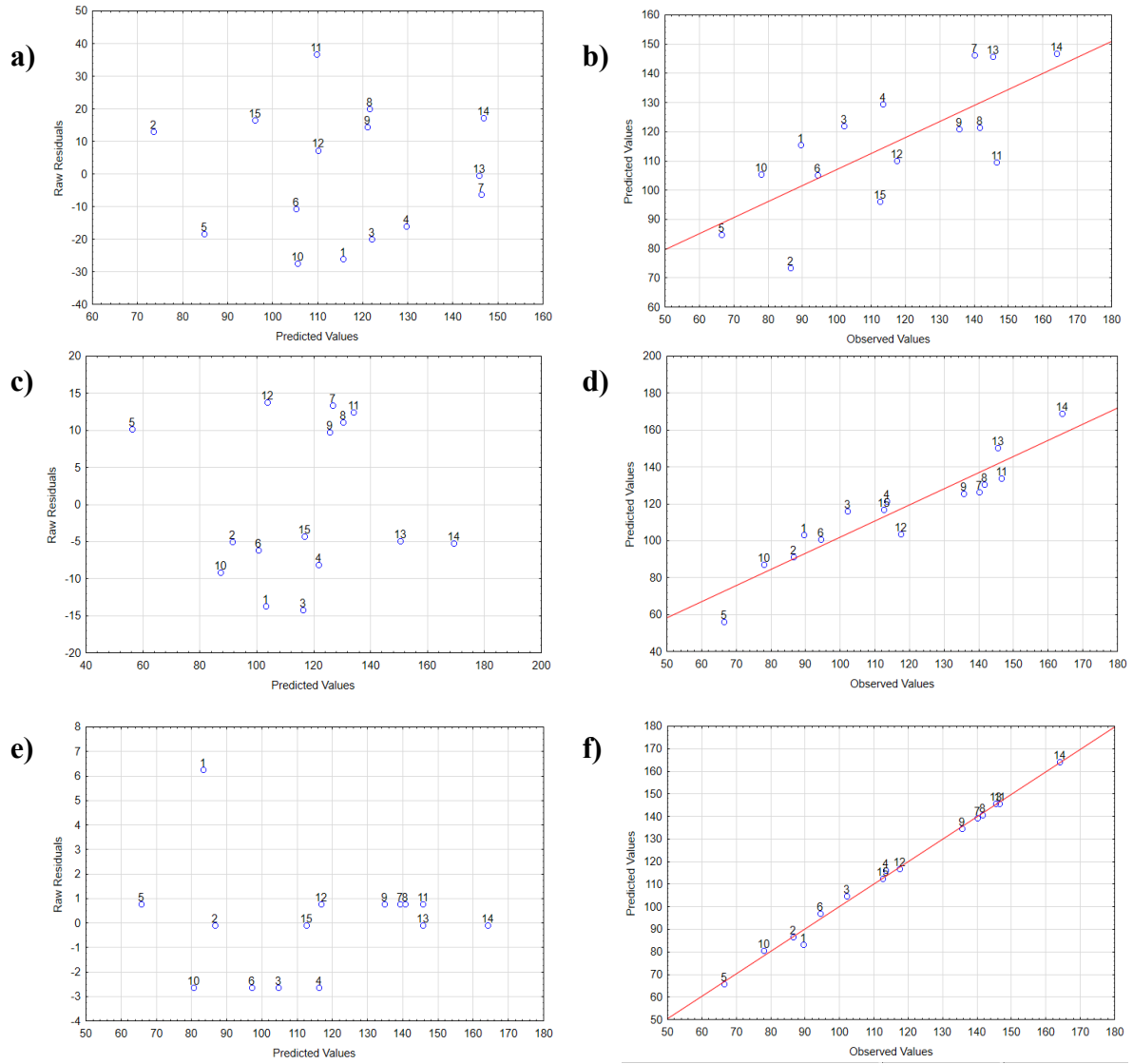
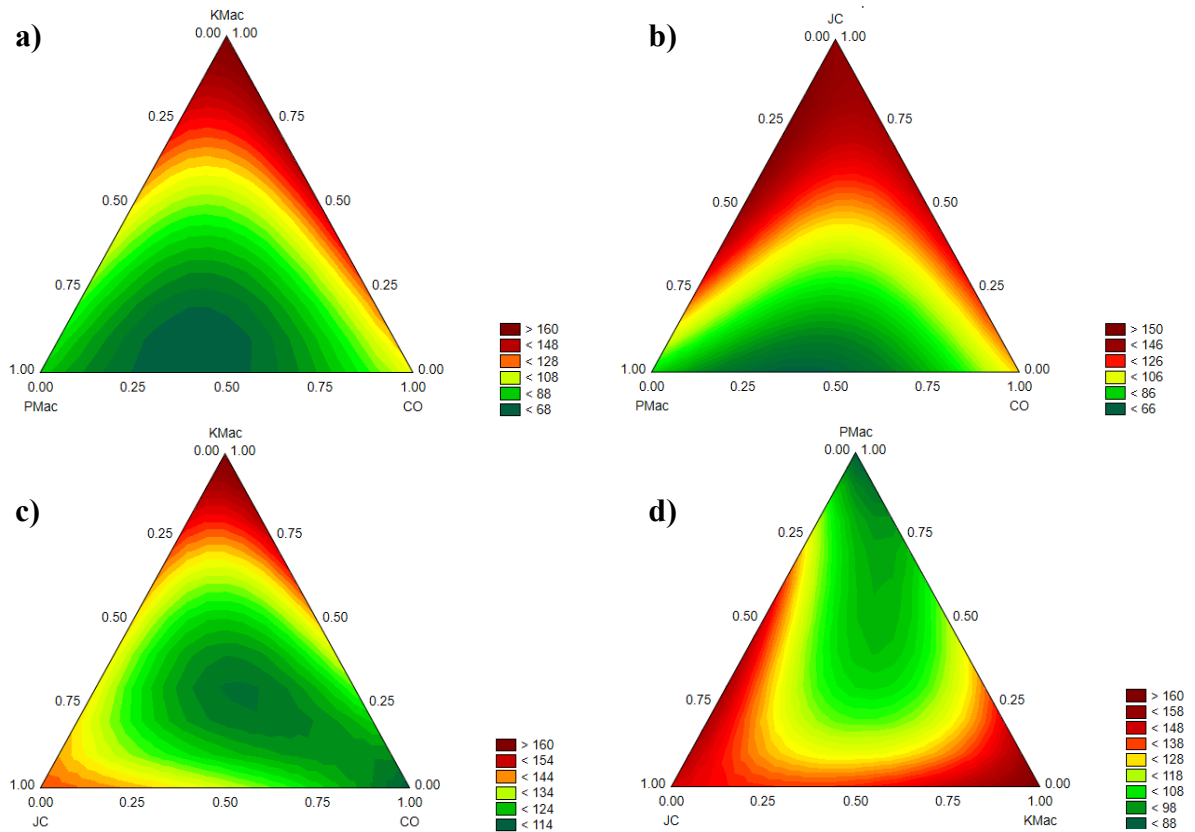


Figure 2 - Contour plots for WSD of ternary mixtures of vegetable oils.

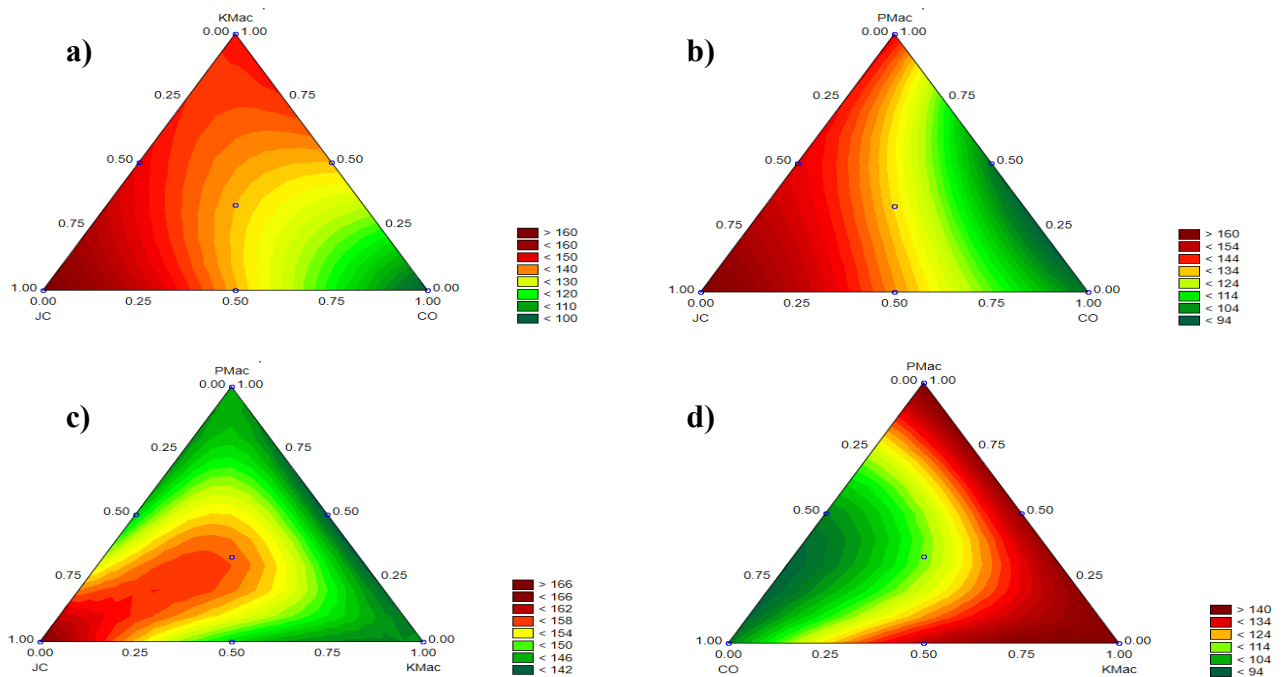


**Figure 3 - Contour plots for viscosity index of ternary mixtures of vegetable oils.**

As can be seen, the individual analysis of the variables can difficult decision-making. Thus, a new model was developed using the desirability function, aiming at the simultaneous optimization of the variables. The results found for WSD were normalized to a minimum value (zero) because the smaller the wear, the greater the lubricating power of the sample. For the viscosity index, the results were normalized to a maximum value (one) because this index is inversely proportional to the sample's ability to lose viscosity with a given increase in temperature.

Simultaneous optimization of the two response variables generated a result that maximized a single ratio for the best biolubricant. Based on the global desirability for simultaneous optimization of WSD values and viscosity index, the best results for application as a biolubricant were obtained for the use of macauba pulp oil alone. The application of this oil is interesting to generate smaller wear and higher viscosity index, simultaneously, being able to present a good use as a biolubricant.

Considering the response surfaces obtained for desirability of ternary mixtures (Figure 4), it can be concluded that the definition of the best proportions of oils necessary to obtain a higher viscosity index and a smaller wear will depend on the type of the oil that one wants to use and the costs of obtaining the oil. The use of a high proportion of one oil and low proportions of the others is possible.



**Figure 4 - Response surfaces for the desirability of ternary mixtures of vegetable oils.**

The ternary mixture of Figure 4a showed that in the absence of macauba pulp oil, a mixture of 50% *Jatropha curcas* oil, 25% castor oil, and 25% macauba kernel oil also provided a decrease in wear (increased lubricity) and an increase in viscosity index. However, by observing the response surfaces of (Figure 4b - 4d), when macauba pulp oil is combined with other vegetable oils, the optimum region of the model is obtained for the formulation containing 100% of this oil (PMac). Both the macauba pulp oil alone and some mixtures of the oils have produced good preliminary results for use as a biolubricant.

#### 4. Conclusion

Macauba oil has interesting properties and a great potential for use in different applications. In this work, macauba pulp and macauba kernel oils were analyzed for use as a biolubricant base, alone or in blends with *Jatropha curcas* and castor oils. The vegetable oils were characterized by physical-chemical parameters and by composition. The results indicated that the lubricity and the viscosity index for macauba pulp oil were interesting for application as a biolubricant, despite its high acidity and low oxidative stability. Considering these results, macauba oils were used with castor and *Jatropha curcas* oils in a simplex centroid quaternary mixture design, aiming to improve the parameters viscosity index and lubricity. The optimization was done both in isolation, for each parameter, and simultaneously, with the desirability function. The special cubic regression model was used to fit the data in the three conditions, with high coefficients of determination. The best formulation was that containing 100% macauba pulp oil. Alternatively, adequate blends of this oil with *Jatropha curcas*, castor, and macauba kernel oils might provide similar lubricities and viscosity indices. This work showed that pure macauba pulp oil and some blends with the other oils, without any chemical modification, provided comparable or superior lubricities that those obtained for vegetable oils subjected to different types of transformations. This result might represent more practicality and economy for the process of production of biodegradable and non-toxic lubricant bases. Social, economic, and ambient benefits can result from the application of the findings of this

study. Especially in the case of macauba oil, an oil obtained from a native palm tree of widespread occurrence in South America.

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