STUDY OF MOLAR RATIO IN BIODIESEL PRODUCTION FROM PALM OIL

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ABSTRACT

Biodiesel is a renewable biofuel that is nowadays a real alternative to fossil diesel. Its use has several environmental benefits related to the decrease of CO_2 emissions as well as several other air pollutants. Biodiesel is mainly produced by a transesterification reaction where the oils or fats react with a short chain alcohol, usually methanol, in the presence of a catalyst. At an industrial scale homogeneous alkaline catalysts, such as sodium or potassium hydroxide or methoxyde, are usually used. The aim of this work is to study the use of crude and heated palm oil with a high content of free fatty acids (13 – 18 mgKOH/g) as feedstock for biodiesel production. The high content of free fatty acids (FFA) makes this type of oil inadequate for the use in an alkaline catalyzed transesterification reaction without a pre-treatment. Therefore, an acid catalyzed esterification reaction was carried out to reduce the acidity before the transesterification reaction. In this study, the methanol:oil molar ratio was optimized. The results show that using palm oil as feedstock it is possible to produce a biodiesel with a fatty acids methyl esters content higher than 96.5%, which is the minimum values imposed by the international standards. Furthermore, the heating of the oil at 150ºC for 20 min did not significantly affect the yield of the transesterification reaction and the density, viscosity and refractive index of biodiesel.

Key words: palm oil, molar ratio, biodiesel.

INTRODUCTION

Biodiesel is produced from renewable feedstocks and is biodegradable and non toxic (KRAWCZYK, T., 1996) and is therefore a good alternative to fossil diesel. The environment benefits of using biodiesel are also related to the decrease of the emissions of CO_2 and several other air pollutants such as particulate matter, carbon monoxide, sulphur and polycyclic aromatic hydrocarbons [Tesser et al., 2010; Bakeas et al., 2011]. However, one of the main problems for biodiesel commercialization is its high cost and the type of oil, usually semi-refined vegetable oils, represents a wide part of the total costs of biodiesel production. Therefore, the use of low cost oils like palm oil, which is widely available in Africa and Asia, is interesting.

The commercial production of biodiesel is mainly based on homogeneous basic catalysts using, for example, sodium or potassium methoxide as catalyst because basic catalysis is faster and less corrosive than the acid one [Felizardo et al., 2006; Shahid et al., 2011]. The global reaction that describes the production of biodiesel using methanol as the alcohol is presented in Figure 1. As shown, one mole of triglyceride reacts with 3 mol of methanol to produce 3 mol of biodiesel, which is a mixture of fatty acid methyl esters, and 1 mol of glycerol. After reaction, the glycerol rich-phase is separated from the ester layer or crude biodiesel either by decantation or centrifugation. Crude biodiesel contains contaminants such as methanol, glycerides, soaps, catalyst and glycerol, and has to be washed and dried to comply with the quality standards [Baptista et al., 2008].

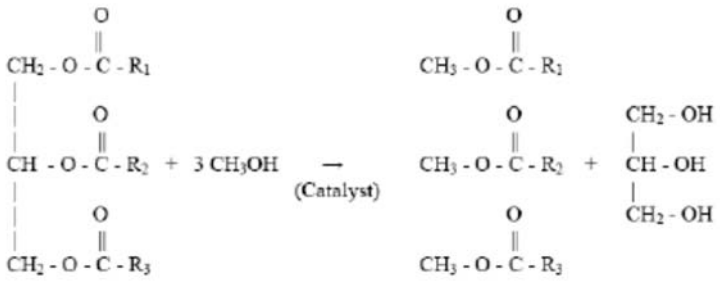


Figure 1-Transesterification reaction. R_1, R_2 and R_3 represent the fatty acid chains.

According to Figure 1, the methanol to oil molar ratio is one of the most important variables and to shift equilibrium towards the products it is always used and excess of methanol [Felizardo et al., 2006; Dantas, 2011], which should be optimized.

An excess of alcohol is used to ensure that the reaction occurs only in the sense of conversion of triglyceride to methyl esters therefore, a molar ratio alcohol: oil greater than the stoichiometric results in higher conversion esters in a shorter period of time (Dantas, 2011). This behavior based on the principles of thermodynamic equilibrium is described by the principle of Le Chatelier which states that if a dynamic equilibrium is disturbed, can be reached new equilibrium stage to reverse the disorder. In this case, with the increase of the excess reagent, the system should shift the equilibrium to reverse the change resulting from the displacement of higher equilibrium conversion of reactants to products.

The yield of the reaction increases with the molar ratio alcohol: oil and the use of excess alcohol turn possible to shift the chemical equilibrium. However, the excessive increase of the reagent provides greater cost recovery (HE *et al.,* 2006). For oils with high free fatty acids, for example, waste frying oils, reactions are performed with the use of acid catalysts and often with excessive molar ratio to above 15: 1 (Leung; GUO, 2006).

The presence of water in the reaction mixture is a problem. In fact, water promotes hydrolysis reactions that convert the methyl esters into FFA thus leading to the decrease of the reaction yield. FAME hydrolysis is also promoted by the heating of the vegetable oils at high temperatures. Furthermore, during the heating the viscosity and acidity of the oil increases and it becomes darker [Felizardo et al., 2006].

It is worth mentioning that for oils or fats with a high content of free fatty acids (FFA>4%), like crude palm oil, the formation of soaps due to the reaction of the alkaline catalyst with the FFA is a serious problem. In fact, soaps formation through the reaction presented in Figure 2 lead to several

problems during the separation of the biodiesel and glycerol phases that decrease the global yield of the process [Gerpen et al., 2004, Felizardo et al., 2008]. Therefore, when the FFA content is higher than 4% a pre-treatment is required [Felizardo et al., 2008]. This pre-treatment may be carried out through an acid catalyzed esterification reaction with methanol presented in Figure 3 that led to the production of biodiesel molecules.

Figure 2 - Saponification reaction of FFA.

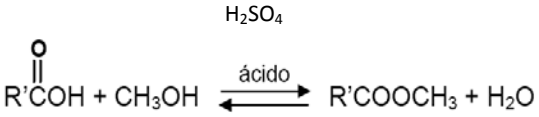


Figure 3- Esterification reaction of the FFA with methanol.

This work presents the preliminary study of the use of crude and heated palm oil produce from local (Angola) palm fruits with a high content of free fatty acids (13 – 18 mgKOH/g) as feedstock for biodiesel production.

MATERIALS AND METHODS

All the chemicals were Analytical Grade and the aqueous solutions were prepared with deionised water. The acid value of the oils was obtained by titration with a KOH solution (prEN 14104), the viscosity was determined using an Ostwald viscosimeter, the density of the oils was determined using the pycnometer and the refractive index was determined with an Abbe refractometer. Some of the FTIR spectra of the samples were acquired using an ThermoScientific, modelo: nicolet is10. The FAME content of the purified biodiesel samples was evaluated using mid infrared spectroscopy (MIR) against previously developed calibration (Baptista, 2007). In this case, the MIR spectra were collected with a resolution of 16 cm^{-1}, using a FT-MIR equipment from BOMEN (FTLA2000-100, ABB) with a DTGS detector. A horizontal total attenuated reflection accessory (HATR), from PIKE Technologies, with a ZnSe crystal was used.

EXPERIMENTAL PROCEDURE

Palm oil was mechanically extracted by pressing of the boiled or cooked palm fruits collected in Kwanza Sul – Angola. Afterwards, the oil is washed with hot water during approximately 3 hours. Then, after phases separation, palm oil phase is separated by decantation and dried before characterization.

The procedure used in the esterification/transesterification reactions was: the oil sample was transferred into a stirred tank reactor equipped with a reflux condenser and immersed in a temperature-controlled water bath and heated until the desired temperature (usually 63°C). Then a mixture of methanol and catalyst was added to the oil. Sulphuric acid was used as the esterification catalyst, whereas KOH was used to catalyze the transesterification reaction. In the end of the esterification reaction period (1h), the acid value was measured and the transesterification reaction

was carried out for 1 h with addition of KOH dissolved in methanol. After separation of the glycerol phase and methanol recovery by distillation, the biodiesel phase was washed with water, with a 0.1M HCl solution and once again with water and dried. Figure 4 presents the diagram of the process.

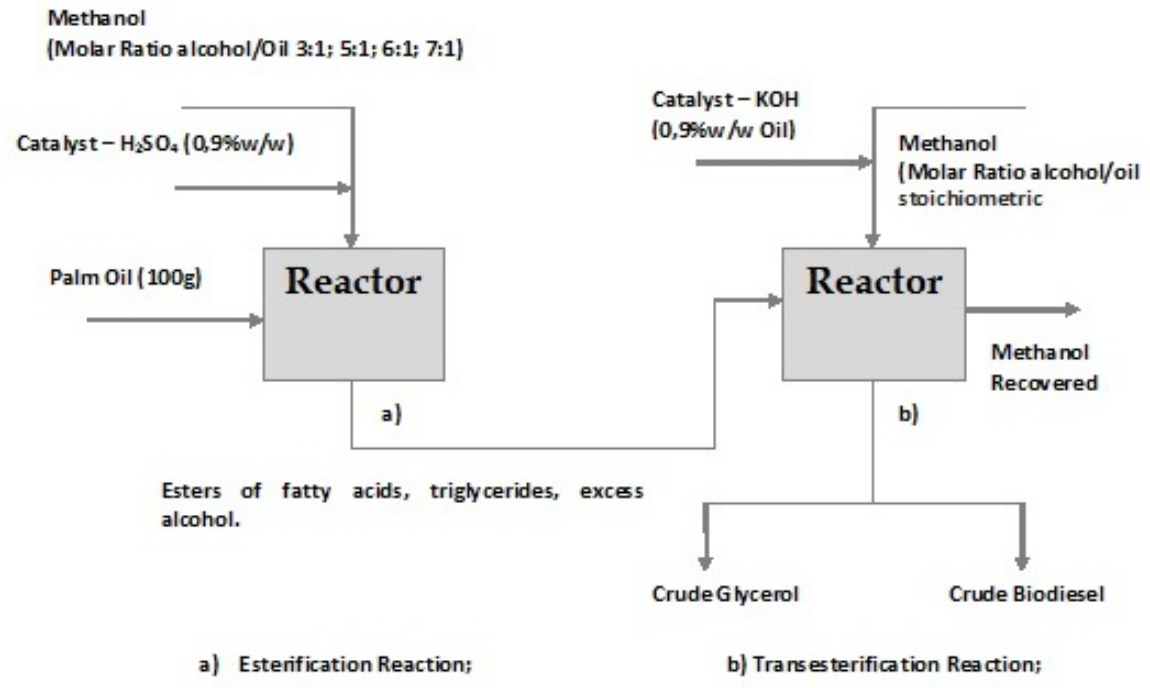


Figure 4: Diagram of the process [Barros et al., 2008]

RESULTS AND DISCUSSION

Characterization Of Palm Oil

The properties of the as received and heated palm oil are presented in Table 1. As seen, the two oil samples have similar properties. However, as mentioned above, there was a slight increase of the oil viscosity after the heating at 150 ºC for 20min.

Table 1: Characterization of crude and heated palm oil

Feedstock	Acid Index (mgKOH/g)	Density (kg/m^3)	Viscosity (mm^2/s)	Refractive Index	Oxidative Stability
Crude Palm Oil	16.6	906.9	30.1	1.461	15.4±1.6
Heated Palm Oil	14.8	908.1	35.8	1.461	2.4±0.8

Palm oil has reddish color, due to its high content of natural carotenoids. These components found in its composition are the main functional feature, as they bring important benefits to health. It is also rich in tocopherols and tocotrienols, most of which consists of γ-tocotrienol, α-tocotrienol and δ-tocotrienol (Sampaio, 2011). As a result of these characteristics and high content of saturated chains such as C16:0, palm oil is highly stable to oxidation.

During heating, there is a color change from red to yellow. On the other hand, according to Table 1, the heating also causes an increase in the density and viscosity oil (light) because is reported in the literature that the heating of vegetable oils promotes the polymerization of triglyceride oil (Naima et al. 2013).

As for the acid index there is a significant reduction that results from the evaporation of the more volatile fatty acids (Sampaio, 2011). The refractive index of the oils, which is related to its chemical composition did not change.

As described in the literature (Jaarin et al., 2012), although the fatty acids composition not significantly altered, the heating causes oxidation of the oil, with a consequent increase in the peroxide content, and the degradation of natural antioxidants mentioned above. For this reason, as shown in the above Table, the oxidative stability of oil decrease from 15h to 2h after heating.

Oxidative stability is a measure of the susceptibility to oxidation when exposed to air and oxygen, in addition to the amount of natural antioxidants oil depends on the number of unsaturated carbon chains that is the smaller oxidative stability is the greater number of unsaturations (Felizardo, 2010).

The FTIR spectra of the two oil samples (Fig. 5) confirm that the samples present similar spectra. Furthermore, it is possible to The spectra presents the typical bands vegetable oils such as the one located at 720 cm^{-1} attributed to the –(CH_2)n- e -HC=CH- cis bending, 1100 - 1170 cm^{-1} correspond to the vibrations of the C-CH2-O group, the asymmetric stretching of C-O-C and C-C bond stretching. The intense peak located at 1745 cm^{-1} corresponds to the carbonyl radical and is characteristic of esters. The band at 2852 cm^{-1} is due to the symetric *stretching of* CH(-CH_2-) and at 2921 cm^{-1} that is correspondent to the assimetric stretch of CH(-CH_2-) saturated bonds that are abundant in palm oil [Baptista, P., 2007; Guerrero et al., 2013].

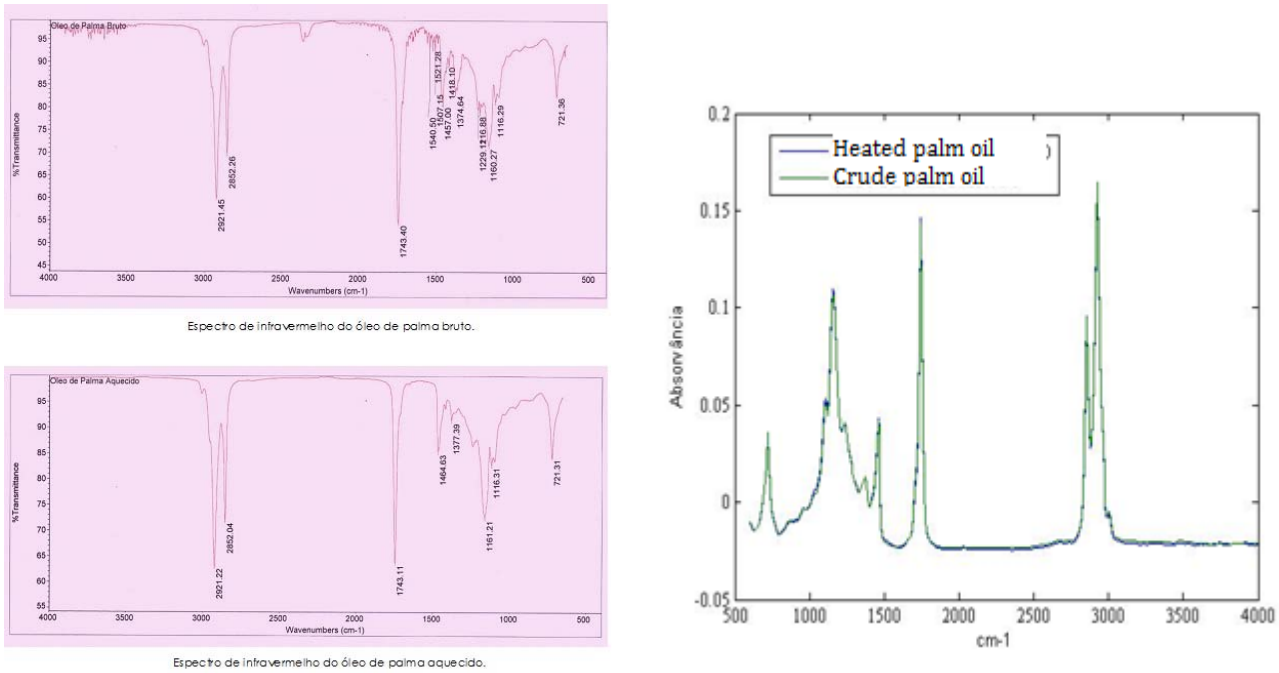


Figure 5: FTIR spectra of crude (green) and heated (blue) palm oil

BIODIESEL PRODUCTION

Table 2 and Figure 6 present the study of the effect of the amount of methanol on biodiesel properties. In what concerns the esterification stage, Table 2 shows that this pre-treatment allowed to reduce the FFA content from values above 14 mg KOH/g down to values below 1 mg KOH/g.

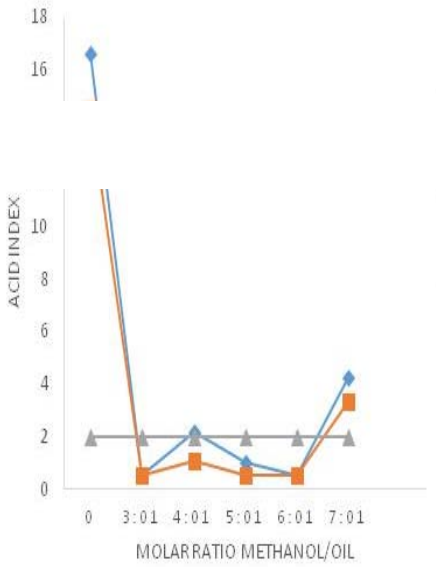
Table 2 and Figure 6 and 7 clearly show that the optimization of the methanol/oil molar ratio is a crucial variable. Thus, for example, in the experiments carried out with the stoichiometric amount of methanol the viscosity of the biodiesel phase obtained is of the same order of magnitude of the oil viscosity and 10 times higher than the limit value imposed in the EN 14214 for biodiesel. Therefore it is possible to conclude that in these conditions the conversion of the oil triglycerides into FAME was very low.

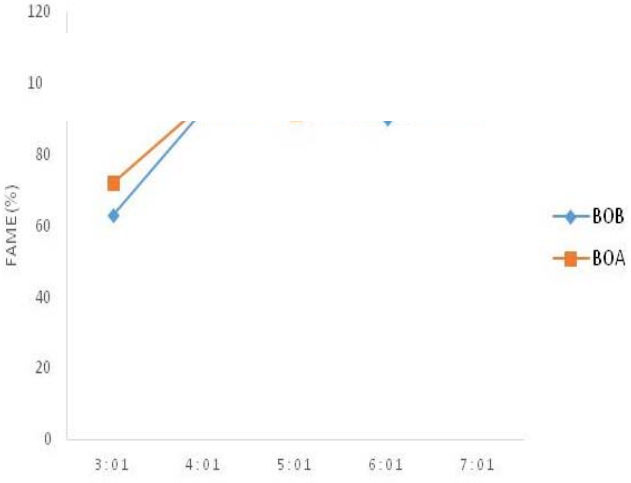
***Table 2**: Influence of the methanol molar ratio on biodiesel production*

Molar Ratio (Alcohol/Oil)	Acid Index (mgKOH/g) after Esterification Reaction	Acid Index of Biodiesel (mgKOH/g)	Density (kg/m^3)	Viscosity (mm^2/s)	Refractive Index	FAME (%w/w)
EN 14214	-	0.5	860-900	3.5-5.0	-	>96.5
3:1	0.5^1	0.5^1	874^1	7.07^1	1.464^1	63^1
	0.5^2	0.5^2	871^2	6.24^2	1.459^2	72^2
4:1	2.2^1	0.5^1	864^1	4.58^1	1.443^1	93^1
	1.1^2	0.5^2	864^2	4.48^2	1.442^2	95^2
5:1	1.0^1	0.5^1	868^1	4.92^1	1.445^1	93^1
	0.5^2	0.5^2	871^2	4.97^2	1.445^2	92^2
6:1	0.5^1	0.5^1	869^1	5.23^1	1.449^1	90^1
	0.5^2	0.5^2	869^2	4.74^2	1.446^2	96^2
7:1	4.2^1	0.5^1	868^1	4.69^1	1.448^1	95^1
	3.3^2	0.5^2	869^2	4.64^2	1.448^2	96^2

[1] *Biodiesel from crude palm oil;*

[2] *Biodiesel from heated palm oil;*





***BOB** – biodiesel from crude palm oil; **BOA** – biodiesel from heated palm oil*

Figure 6: Effect of the methanol to oil ratio on esterification reaction (Conditions: Esterification: H2SO4 0,9% w/w of oil, 63°C, 1h;)

Figure 7: Effect of the methanol to oil ratio on FAME conversion (Conditions: Transesterification:KOH 0,9% w/w of oil, 63°C, 1h)

According to the Figure 6, it is possible to conclude that the molar ratios between 3:1 to 6:1 resulting acid value is less than the value of 2 mgKOH / g considered suitable for the reaction of alkaline transesterification.

There is a relationship between the content of FAME biodiesel and other properties such as viscosity, density or refractive index. Thus, there has been the results obtained in tests carried out allowed to establish this relationship may allow for future trials to have a quick method to estimate, for example, the FAME content based on viscosity analysis. The results are shown in the figure below.

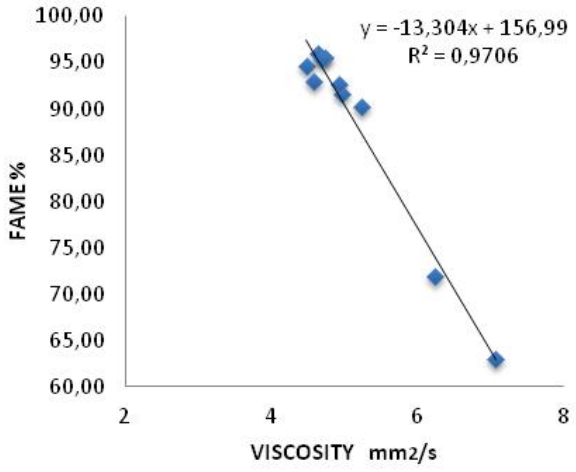


Figure 8: FAME content of the biodiesel as a function of viscosity (Conditions: Transesterification: KOH 0,9% w/w of oil, 63°C, 1h)

It is observed in Figure 8 that the greater FAME conversion corresponds to a lower viscosity. The viscosity is a parameter easy to measure and does not require complicated and expensive

equipment as well, with the results presented here, it suggest that this approach can be very useful for the rapid control and low cost of palm oil conversion to FAME in the biodiesel production process.

The above results show that to produce from palm oil a biodiesel complying with the EN 14214 it is necessary to use a methanol to oil molar ratio of, at least, 5:1. It was also observed that the increase of the methanol excess facilitates the separation of the glycerol from the methyl esters (ME) phase. Figure 7 also shows that the previous heating of palm oil did not affect the properties of the biodiesel. The analysis of the FTIR spectra of biodiesel produced from the two oil samples also shows this similarity, which can be anticipated from the oils spectra presented in Figure 5.

CONCLUSION

The results obtained using crude and palm heated oil as feedstocks for the production of biodiesel are similar at all the molar ratios. It was also found that despite the palm oil heating is not observed physical and chemical changes that compromise the quality of the products obtained. The methodology adopted in this study for the production of biodiesel from palm oil allowed to obtain biodiesel that meets the specifications described in the European standards. In these experimental conditions, it was found that it is necessary to use a molar ratio methanol: oil more than 5 so that the biodiesel produced meets the specifications contained in European Standard, especially for the evaluated properties.

Thus it can be said that the results presented in this study contribute to the scientific and technological development in the methodology for the production of biofuels able to minimize the environmental impacts resulting from the use of fossil fuels.

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