



## **STRATEGY TO BIODIESEL PRODUCTION THROUGH THE REACTIVE DISTILLATION COLUMN USING PALM OIL AS FEEDSTOCK**

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### **ABSTRACT**

Biodiesel can be used as a substitute for fossil diesel. However, its high price mainly due to the costs associated to feedstock and production process is still a problem. This work presents the study on the feasibility of using palm oil produced in Angola, with an acid index between 10 - 21mg KOH/g, for biodiesel production in batch reactors and in a reactive distillation column. To find the most favorable operating conditions for biodiesel production from crude and heated palm oil, esterification and transesterification experiments were first carried out in a batch stirred reactor. The methanol/oil molar ratio varied from 3:1 to 7:1 and the catalysts/oil weight percentage varied from 0.4 to 1.2%. Finally, the produced biodiesel was analysed for the density, viscosity, acid number and refractive index using the reference methods, whereas the FAME content was measured by near infrared spectroscopy. The results show that using a molar ratio methanol/oil of 6:1, 0.8

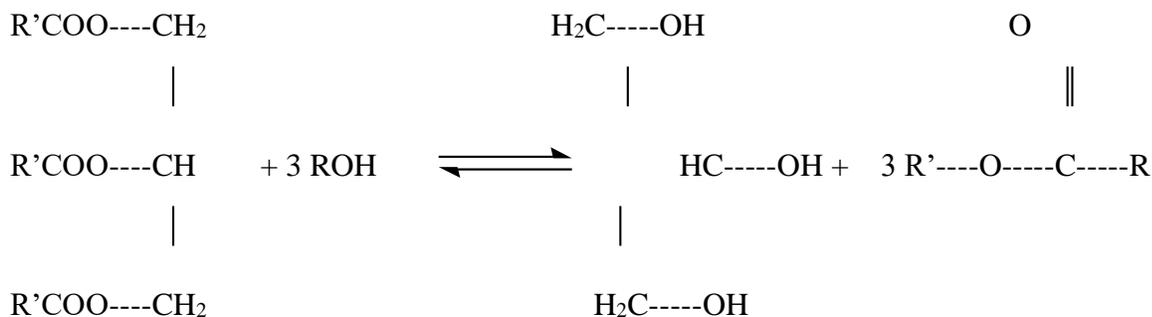
% H<sub>2</sub>SO<sub>4</sub> and KOH, 63 ± 2 °C and 1 hour of reaction led to the production of a biodiesel that comply with international standards in terms of the density, viscosity, acid number and FAME content. A reactive distillation column for biodiesel production was also assembled. This column enables the realization of the esterification and transesterification reactions in series. In the experiments it was possible to obtain a 96% reduction of the initial fatty acids content of palm oil but the yield of the transesterification reaction was give good conversion but, it is necessary to adjust and optimize the operating conditions, such as the reagents and catalysts flow rates and their residence time.

**Key Words:** palm oil, biodiesel, batch reactor and reactive distillation column.

## 1. Introduction

Biodiesel is a good alternative to fossil diesel because it is produced from renewable feedstocks, is biodegradable and non-toxic (KRAWCZYK, T., 1996) and it can be used in diesel engines without serious modifications. The environmental benefits of using biodiesel are also related to the decrease in the emissions of several air pollutants such as particulate matter, carbon monoxide, sulphur and polycyclic aromatic hydrocarbons [Tesser et al., 2010; Bakeas et al., 2011]. One of the major issues of large-scale use of biodiesel is its high cost, which is strongly dependent on feedstock's prices. Therefore, the use of low cost oil, like the Angolan palm oil, may be an interesting alternative.

The commercial production of biodiesel is mainly based on homogeneous basic catalysts like, for example, sodium or potassium methoxides because these basic catalyzed processes are faster and less corrosive than the acid ones [Felizardo et al., 2006; Shahid et al., 2011]. The global reaction that describes the production of biodiesel is presented in Figure 1. 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 the alcohol, glycerides, soaps, catalyst and glycerol, and has to be washed and dried to comply with the quality standards [Baptista et al., 2008].



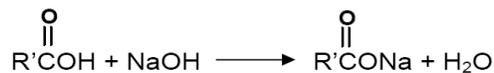
**Figure 1:** Transesterification reaction

According to the reaction presented in Figure 1, to shift the equilibrium towards the products it is necessary to use an excess of alcohol [Felizardo et al., 2006; Dantas, 2011; Colombo et. Al. 2016]. However, although the reaction yield increases with the

molar ratio of methanol to oil, a higher quantity of alcohol also increases the production costs (HE et al., 2006). So, it is important to optimize this variable.

It is worth mentioning that for oil or fats with a high content of free fatty acids (FFA>4%), like this Angolan palm oil, the formation of soaps through the reaction presented in Figure 2, for NaOH is a serious problem. In fact, soaps formation lead to several problems during the separation of the biodiesel and glycerol phases that decrease the mass yield of the process [Gerpen et al., 2004, Felizardo et al., 2008]. Hence, when the FFA content is higher than 4% a

pre-treatment is required [Felizardo et al., 2008]. This pre-treatment may be an acid catalyzed esterification reaction with methanol according to reaction presented in Figure



**Figure 2:** Saponification reaction of FFA.



**Figure 3:** Esterification reaction of the FFA with methanol.

The presence of water in the reaction mixture is also 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 oil at high temperatures, which can also lead to a colour change and to a viscosity increase [Felizardo et al., 2006; Freedman et al., 1984].

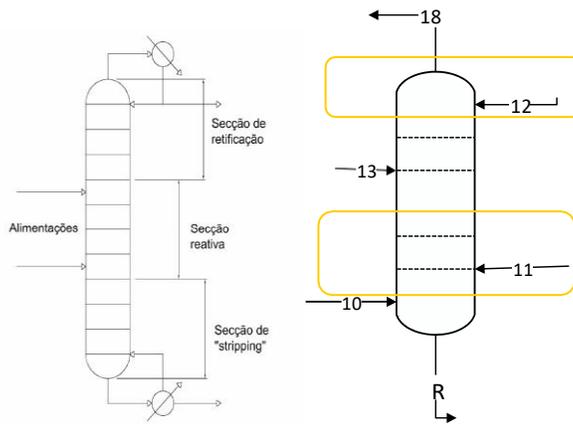
This work presents the study of the use of crude and heated Angolan palm oil, with a high content of free fatty acids (10–21 mg KOH/g), as a feedstock for biodiesel production.

For other hand, the Reactive Distillation (RD) is a combination of reaction and distillation column to which it enjoys a number of specific advantages over conventional sequential approach of reaction followed by distillation or other separation techniques. This process increase the conversion, better heat control, effective utilization of reaction heat, scope for difficult separations and the avoidance of azeotropes are a few of the advantages that are offered by RD.

The introduction of an in situ separation process in the reaction zone or vice versa leads to complex interactions between vapor– liquid equilibrium, mass transfer rates, diffusion and chemical kinetics, which poses a great challenge for design and synthesis of these systems.

The suitability of RD for a particular reaction depends on various factors such as volatilities of reactants and products along with the feasible reaction and distillation temperature. Hence, the use of RD for every reaction may not be feasible. Exploring the reactions for RD, itself is an area that needs considerable attention to expand the domain of RD processes. Although invented in 1921, the industrial application of reactive distillation did not take place before the 1980's.

For this work was explored the study of esterification and transesterification reaction using the same reactive distillation column with design defined with two steps, as show in the Figure 3b.



**Figure 4:** Reactive distillation column used in this study.

Reactive distillation (RD) is an innovating process, which combines both distillation and chemical reaction into a single unit [7], which saves energy (for heating) and materials. Therefore, the RD technology offers many benefits as well as restrictions over the

conventional process of reaction followed by distillation or other separation approaches. Reducing capital cost, higher conversion, improving selectivity, lower energy consumption, the reduction or elimination of solvents in the process and avoidance of azeotropes are a few of the potential advantages offered by RD. This technique is especially useful for equilibrium-limited reactions such as esterification and transesterification reactions.

Conversion can be increased far beyond what is expected by the equilibrium due to the continuous removal of reaction products from the reactive zone. This helps to reduce capital and investment costs and may be important for sustainable development due to a lower consumption of resources (Chokchai Mueanmas, Kulchanat Prasertsit and Chakrit Tongurai, 2010).

## 2. Materials and Methods

All the chemicals were Analytical Grade and the aqueous solutions were prepared with deionized water.

### Palm Oil Production

Palm oil was mechanically extracted by pressing of the cooked palm fruits collected. The oil obtained in this operation was washed with hot water during approximately 3 hours. After phases' separation, the lighter phase containing the oil is dried before characterization. The production of palm oil was held at Esperança Farm located in Kwanza Sul Province of Angola, a process that was followed "in loco".

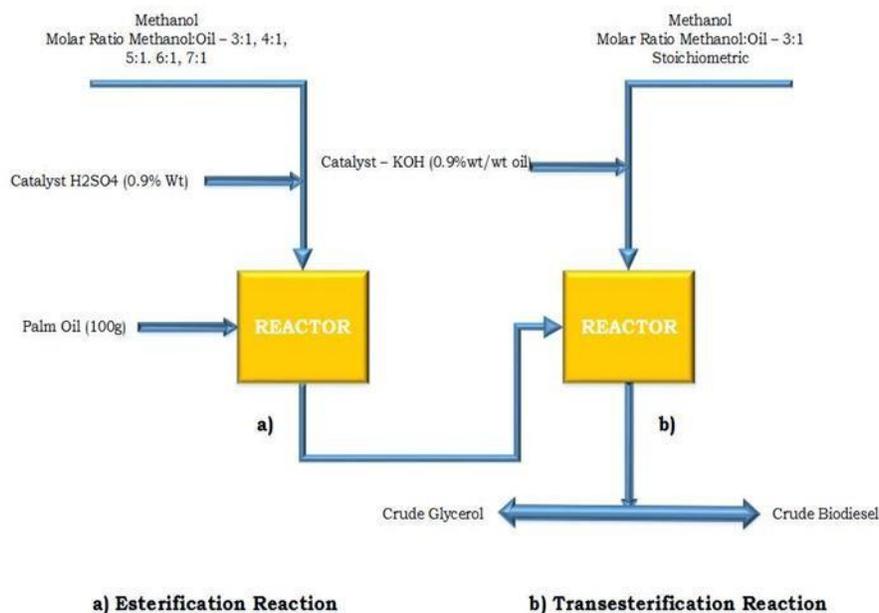
### Biodiesel Production in Batch Reactor

After production, crude and heated palm oil were analyzed for the several physic-chemical characteristics to establish the best conditions for its conversion into biodiesel. These operating conditions were subsequently used in the reactive distillation column but the initial mass converted in feed flow rate in the column.

The procedure included two steps: the first was the acid catalyzed esterification reaction of the free fatty acids, followed by the alkaline catalyzed transesterification of the oil's triglycerides.

Based on the stoichiometric mass balance of the esterification and transesterification reactions, the mass of reagents and catalysts required for each experimental condition were calculated. For the esterification reaction it was assumed that the free fatty acids are in the form of oleic acid in accordance with EN14104 standard.

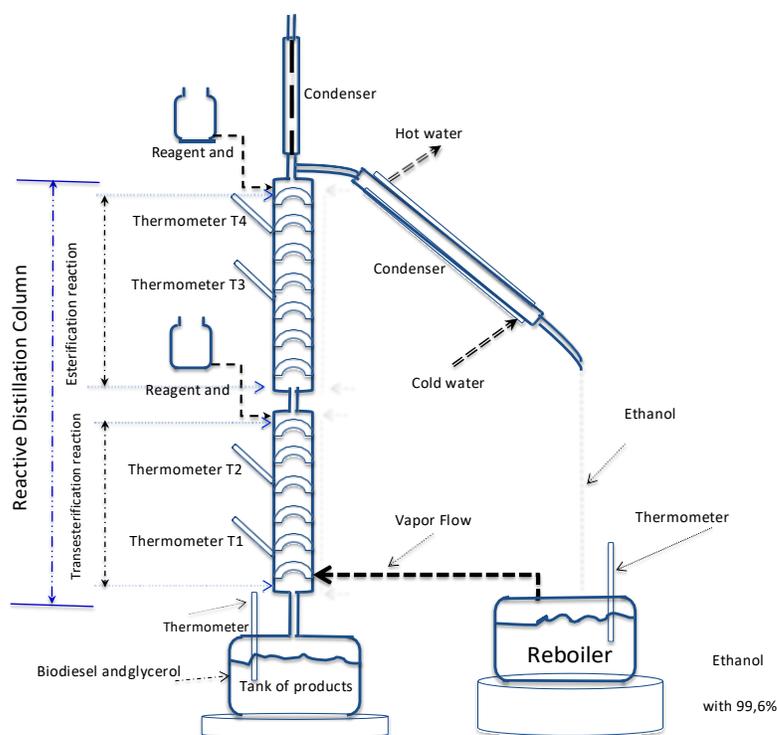
The procedure used in the esterification/transesterification reactions was: the oil sample was transferred into a stirred tank reactor equipped with a reflux condenser and magnetic stirrer. Heating was provided by a heating plate (usually 63°C). Then, a mixture of methanol and catalyst was added to the oil. Sulphur acid was used as the esterification catalyst, whereas KOH was used to catalyze the transesterification reaction. After esterification, KOH dissolved in methanol was added to the reactor and the transesterification reaction was carried out for 1 hour. At the end of the reaction time, the excess of methanol was recovered by simple distillation and the glycerol rich-phase was separated from the methyl ester layer in a decantation funnel. The heavier glycerol phase was removed and crude biodiesel was washed with water, with a 0.1M HCl solution and once again with water, dried and weighted. Figure 4 presents the process diagram.



**Figure 5:** Diagram of the process [Barros et al., 2008]

## Biodiesel production in Reactive Distillation Column

The installed reactive distillation column (Figure 5) allows to carry out the esterification and transesterification reactions in series in two steps: one is used to esterification and other for transesterification reactions. The column operates at atmospheric pressure and thermocouples are inserted along the spine to monitor the thermal stability of the equipment. Thus, palm oil and the acid catalyst dissolved in methanol are fed in the top of the column. Methanol is heated in a reservoir in the bottom of column and there is the continuous production of methanol vapors that go from the bottom to the top of the column in counter-currently with the descending oil and catalysts streams. The feeding point of the alkaline catalyst diluted in methanol is at the entrance of the second step. The non-reacted methanol that reaches the top of the equipment is condensed and returned to the methanol reservoir. Samples of the reaction mixture are collected for analysis using the procedure describes in the international literature.



**Figure 6:** Distillation Reactive (DR) Column Diagram used in this study

It is worth emphasizing that the use of this type of reactive distillation column allows the implementation of the esterification and transesterification reactions in a single device capable of ensuring an excellent conversion rate. These conditions are possible due to the characteristics of the equipment that allows a very efficient mixture between the liquid and vapor phases. On the other hand, the packing inside in the column promotes an intense turbulence and favours the efficient mass transfer. As mentioned above, this equipment also allows the recovery of the excess of methanol on the top with a high purity and its reflux to the bottom of the column.

## Determination of Physical-chemical properties of Palm Oil and Biodiesel

The acid value of the oil and biodiesel were obtained by titration with KOH solution, the viscosity was determined by Ubbelohd viscosimeter, the density was determined by using the automatic densimeter and the refractive index was determined with an Abbe refractometer. The FTIR spectra were acquired by using a spectrophotometer ThermoScientific: nicolet is10. The FAME content of the purified biodiesel samples was evaluated using near infrared spectroscopy (NIR) against a previously developed calibration (Baptista et al., 2008). In this case, the near-infrared diffuse transmittance spectra of the biodiesel samples were acquired by using an ABB BOMEM MB160 (Zurich, Switzerland) spectrometer equipped with an InGaAs detector and a transmittance probe from SOLVIAS (Basel, Switzerland). The spectra were recorded in duplicate for each sample at room temperature (24-26°C), with the aid of the Galactic Grams software package (Galactic Industries, Salem, NH, USA), in the wave number range of 12,000-4,000 cm<sup>-1</sup>, with a spectral resolution of 16 cm<sup>-1</sup>.

### 3. Results and Discussion

#### Characterization of Palm Oil

The properties of the crude and heated palm oil are presented in Table 1. The two oil samples have similar properties, but heating

the oil at 150°C for 20 min lead to a slight increase in the viscosity and a significant reduction in the oxidative stability because of the loss of the natural antioxidants of palm oil. It is known that during heating and frying vegetable oils undergo degradation by hydrolytic and oxidative reactions that may lead to the increase of viscosity [Felizardo et al., 2006].

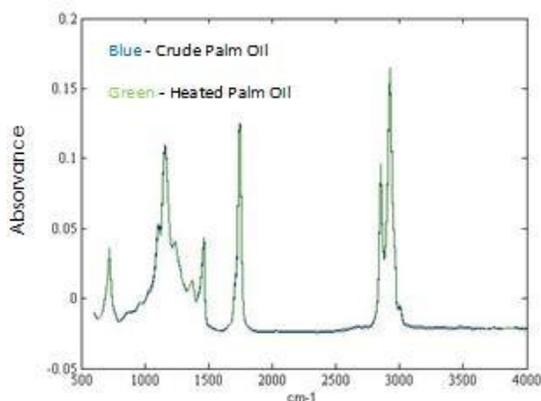
**Table 1:** Characterization of Crude and heated palm oil

Oil	Density [kg/m <sup>3</sup> ]	Kinematic viscosity [mm <sup>2</sup> /s] at 40°C	Acidity [mg KOH/g]	Refraction Index	Oxidative stability [h]
Crude palm oil (reddish colour)	906.9	30.1	15 – 21*	1.461	15.4 ± 1.6
Heated palm oil (light orange)	908.1	35.8	13 – 9*	1.461	2.4 ± 1.0

\* Sample from different reservoirs.

The FTIR spectra of the two oil samples (Fig. 6) confirm that they are similar. The spectra allow to identify the typical bands of vegetable oil such as the one located at 720 cm<sup>-1</sup> attributed to the  $-(CH_2)_n-$  e  $-HC=CH-$  cis bending, 1100 - 1170 cm<sup>-1</sup> corresponds to the vibrations of the C-CH<sub>2</sub>-O group, the asymmetric stretching of C-O-C and C-C bond stretching. The intense peak located at 1745 cm<sup>-1</sup> corresponds to the carbonyl radical and is characteristic of the esters. The band at 2852 cm<sup>-1</sup> is due to the symmetric stretching of CH(-CH<sub>2</sub>-) and at 2921 cm<sup>-1</sup> that

corresponds to the asymmetrical stretch of CH(-CH<sub>2</sub>-) saturated bonds that are abundant in palm oil [Baptista, P., 2007; Guerrero et al.,2013].



**Figure 7:** FTIR spectra of crude (blue) and heated (green) palm oil.

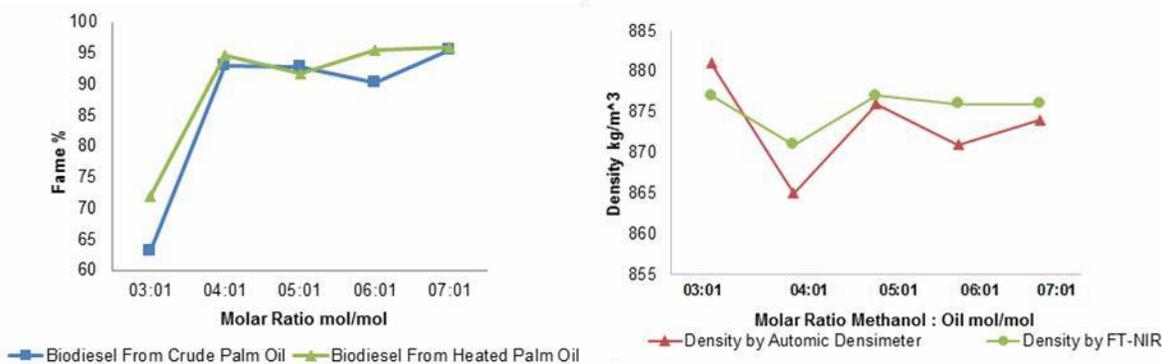
### **Effect of Methanol: Oil Molar Ratio on Biodiesel Production and Density**

The methanol to oil molar ratio is an important factor because, as mentioned above, it affects the yield of esterification and transesterification reactions, phases' separation and also the overall cost of the process.

Figure 6 shows the effect of increasing the molar ratio of methanol to oil used in the esterification reaction, whereas the stoichiometric amount of fresh methanol was always used in the transesterification stage. The results presented in Figure 6 make it possible to conclude that the use of the lowest amount of methanol led to the production of a biodiesel containing less than 80% of FAME. The highest FAME content was reached for a methanol/oil molar ratio of 4 or higher. Furthermore, the behaviours of crude and heated oil were similar. The analysis of the FTIR spectra of biodiesel produced from these oil samples also shows this similarity, which could be anticipated from the oils spectra presented in Figure 5.

For the other hand, biodiesel's density is a property that influences the atomization of fuel in the engine and is affected by the type of raw materials, degree of transesterification and presence of contaminants (Baptista et al., 2008). This property is directly related to the molecular structure of FAME molecules and the larger the length of the carbon chains of the alkyl ester and the lower the number of double bonds, the higher the density of biodiesel (Baptista et al., 2008). However, the presence of impurities like triglycerides, glycerin, alcohol, etc., is also an issue (Felizardo et al., 2006; Wolf et al., 2009).

Density was determined by using an automatic densimeter and was also predicted based on near infrared spectra using previously establish calibrations [Figures 8 (b)]. For other hand, the effect of the methanol to oil ratio used was evaluated in terms of fame %, as shown in Figures 8 ().



**Figure 8:** Effect of the methanol to oil ratio used in the esterification reaction on biodiesel properties in relation of FAME % (a) and Density (b). Conditions: Esterification: H<sub>2</sub>SO<sub>4</sub> 0,9% w/w of oil, 63°C, 1h; Transesterification: KOH 0,9% w/w of oil, 63°C, 1h, molar ratio methanol: oil 3:1, 500rpm. Density of biodiesel from crude palm oil measured using different methods (ANP 07/2008 - BRASIL: 860 -900 kg/m<sup>3</sup>; EN14214 - EU: 860 - 900 kg/m<sup>3</sup>; ASTM D6751 EUA:

The above results show that to produce biodiesel complying with the EN 14214 from palm oil it is necessary to use a methanol to oil molar ratio in the esterification and transesterification reactions of 4:1 and 3:1, respectively. It is known that, within certain 05:01, the increase of the methanol excess also favours biodiesel and glycerine phases' separation and increases the mass yield of the process [Felizardo et al., 2006]. Therefore, the methanol: oil ratio used in the subsequent studies was 6:1.

As seen, the density values measured with the densimeter and based on the nir spectra are in accordance and shows that even the sample produced with the lower amount of methanol has the density within the interval imposed by the different quality norms. It was also found that heating the oil did not significantly affect the density of biodiesel samples.

### Effect of Molar Ratio Methanol: Oil on the Kinematic Viscosity of Biodiesel

The viscosity reduction is one of the advantages of doing the oil's transesterification before its use as a fuel. Moreover, the viscosity is considered one of the most important parameters for evaluating the biodiesel because a high viscosity reduces the atomization efficiency in the combustion chamber and favors the formation of engine deposits (Wolf et al., 2009). The viscosity of purified biodiesel is related to its esters' content and a higher viscosity corresponds to a lower conversion (Felizardo et al., 2006; Baptista et al., 2008). This variable is also used to monitor the oxidative degradation of biodiesel during storage. In fact, biodiesel's degradation during storage lead to an increase of its viscosity.

As expected, the results from this study show that the higher the value of biodiesel density, the greater the viscosity value and the lower the FAME content because the transesterification

reaction allows a significant reduction of the viscosity. Indeed, biodiesel's viscosity is related to the content of esters and so the biodiesel produced with molar ratio 3:1 has higher viscosity (mm<sup>2</sup>/s) and the lower FAME content (%).

With the exception of the viscosity of the sample produced with the lower amount of methanol for both crude palm oil and the heated oil, the viscosity's values are within the range allowed by the standard APN 07/2008, EN 14214 and ASTM 6751.

### **Acid Index of Biodiesel**

The acid number is a measure of the free fatty acids' amount in oils or biodiesel. The measurement of this property is very important because it influences the aging mode of biodiesel (Felizardo et al. 2006) and a high value of acid index can favor the deposition of sediments on the motor and pump wear and fuel filter (Colombo, 2011). In this work, the biodiesel samples had an acid number in the range of 0.53 - 0.56 mg KOH/g, which is slightly higher than 0.5 mg KOH/g imposed by EN14214.

### **Effect of the Amount of Catalysts**

It is known that the use of a higher amount of catalyst should increase the reaction rate [Felizardo et al., 2006]. The effect of increasing the amount of the acid catalyst used in the esterification reaction and basic catalysts used in the transesterification on the FAME content of biodiesel, for a molar ratio of methanol/oil of 6:1.

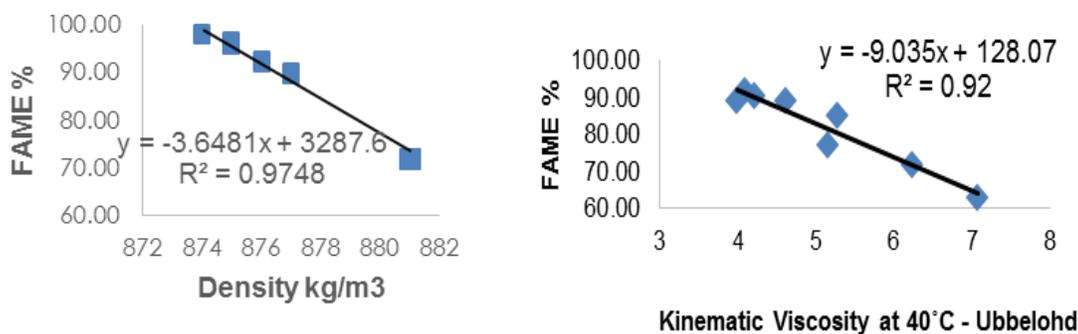
The FAME content of biodiesel is significantly affected by the catalysts amounts. In fact, increasing the amount of acid and alkaline catalysts from 0.6 % to 0.8 % led to a 10% increase in the FAME content. It is worth noting that the lower FAME content of the biodiesel produced in the experiments carried out with 1.2% of H<sub>2</sub>SO<sub>4</sub> and KOH can be explained by the partial consumption of KOH in the neutralization reaction of the acid catalyst used in larger amounts in the esterification stage, since this process does not involve any intermediate washing step between the two stages. According to the results, the use of 0.8 or 1% of H<sub>2</sub>SO<sub>4</sub> and KOH in the esterification and transesterification reactions, respectively, allows the production of biodiesel with more than 94% of FAME from the acidic Angolan palm oil in only one stage.

### **The Effect of the Reaction Temperature**

Temperature affects the rate of the esterification and transesterification reactions and the esters yield and it is known that the conversion increases with temperature (Felizardo et al., 2006; Ding et al., 2012). In this work, the effect of the temperature was studied between 40°C and 63°C but no significant differences in terms of the FAME content of biodiesel were observed. In fact, the FAME content of the samples varied from around 97% to 87% when the temperature increased from 45 °C to 60 °C. These results may be related to the problems associated with the temperature control and also to the error of about 2% associated with the determination of the FAME content in these samples [Baptista et al., 2008].

## Relationship between the FAME content and the other properties of biodiesel

The mathematical relation between the FAME content and the density and the viscosity of biodiesel was evaluated. The establishment of these relations allows the determination of the FAME content from the density or viscosity values that are rapidly determined in the laboratory. From these figures and despite the small number of samples, it is possible to conclude that the FAME content of Angolan palm biodiesel can be estimated from its density or kinematic viscosity values with correlation coefficients higher than 0.97 and 0.92, respectively.



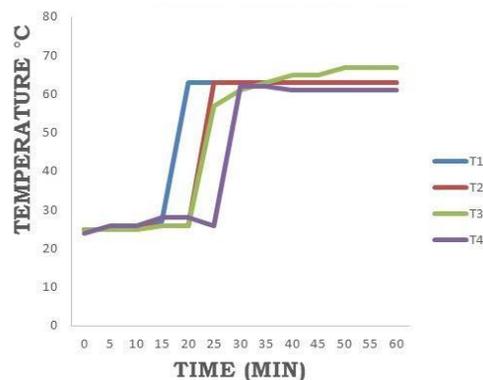
**Figure 9:** Relation between the FAME content and density (a) and viscosity of biodiesel (b).

On the other hand, according to the studies of Santos et al. (2012), the refractive index at 40°C also decreases linearly with the increase of the FAME content of soybean biodiesel with a correlation coefficient of 0.9997. For palm biodiesel, it was possible to analyze only seven samples but anticipates that the linear relation between these two variables can exist. Thus, the results presented herein show that density, kinematic viscosity and the refractive index can be very useful for the rapid and low cost control of the FAME content of palm biodiesel.

### Reactive Distillation Column

There was a reactive distillation column performance evaluated based on this dynamic equipment, as seen in the Figure 10, below, where it was observed that the process stability from the temperature measurement condition favors the insertion of the reactant on the column and the ascended vapour. Moreover, the described thermal stability enables the temperature profile describing this equipment to show that the temperature is stabilized along of this equipment, which flows only in the liquid phase throughout this equipment.

The evaluation did here showed the typical temperature profile obtained along the column and confirms that it is possible to reach the boiling temperature of methanol used in this study as reactive temperature to know the conversion of triglyceride to biodiesel and glyceride.



**Figure 10:** Dynamic of the distillation column obtained during the heating of methanol (T-thermopar 1 to 4).

The use of reactive distillation column allows the implementation of esterification and transesterification reactions in same device to take the conversion rate of oil palm. These are possible because of the characteristics of this equipment are based on a strong interaction between the liquid and vapour phases. On the other hand, the internal packing inside in the distillation column increases the turbulence of the phases and improves the chemical reaction between the reactant. The phenomena characteristics explored in this study involve the heating and evaporating of methanol that ascends vertically, interacting with the reagents mixture. With these phenomena, increase the area of mass transference and, consequently, the alcohol purification initially fed into the equipment as excess. Thus, the alcohol withdrawn from top with high purity was condensed and refluxed to the bottom of the column. On the other hand, the mixture of triglycerides and fatty acids fed to the top of the column were descends vertically along of this equipment and involves, in the first step the esterification using an acid catalyst and in the second step, using basic catalyst. For second step, the basic catalyst was used in excess to neutralize of the acid catalyst, from first step, and to ensure the basic catalytic action in the second step (Wolf Maciel et al, 2001). The products obtained in the bottom of the column are recovered using one decanter funnel where the two phases of these reactions are separated to give the light phase with biodiesel and the heavy phase with glycerol (Figure 6).

The results obtained in one of the experiments are shown, in Table 2, that the yield of the esterification reaction described by the decrease of the acid value was high. However, the results from transesterification reaction give low conversion due to the low residence time of liquid that flow from the top to bottom of the column. Although, it is necessary to perform an optimization of the several operating variables, the installation and start-up of the column was achieved. The last experiment we see that the step of esterification the reaction occurs with high conversion. But, new study will be implemented to know the better performance need to total conversion of triglycerides to biodiesel.

**Table 2:** Biodiesel production in the reactive distillation column.

Sample N°	Acid Value [mg KOH/g]	Conversion of FFAs [%]	Density [kg/m <sup>3</sup> ]	FAME [%]
Heated palm oil	14.41	0.0	905	0.0
1	6.01	58.29	910	<12
2	4.91	65.93	912	<12
3	1.09	92.43	912	<12
4	0.54	96.25	910	<12

#### 4. Conclusions

Palm oil heating led to a slight increase of the kinematic viscosity at 40°C, from 30 to 36 mm<sup>2</sup>/s, and to a significant decrease of the oxidative stability from 15h to 2h. Thus, as expected, the heating process led to the elimination of the oil antioxidants. However, the FTIR spectra of the two oil samples were similar and, except from the oxidative stability, the heating process did not affect the final properties of biodiesel.

The methodology used in this study involved the production of biodiesel from palm oil containing 7-11% of FFA by carrying out the esterification and transesterification reactions in only one stage and without the usual intermediate washing and drying steps. Thus, using a molar ratio methanol / oil of 6:1, 0.8 % H<sub>2</sub>SO<sub>4</sub> and KOH, 63 ± 2 °C and 1 hour of reaction led to the production of a biodiesel that complies with the EN 14214 specifications concerning the density, kinematic viscosity, FFA and FAME contents. The assembling of a reactive distillation column for the production of biodiesel and the preliminary start-up experiments were also carried out.

The reactive distillation column used in this study give us new alternative to develop of esterification and transesterification reaction using only one device enable to purification of recycle reactant used in excess to improve the quality of biodiesel production.

When the reactive distillation column was used, we combine the more important operation (reactor and distillation) in same process as integration process to develop the new strategy to reduce of equipment number and the utility in the chemical industry.

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