

# ESTERIFICATION AND TRANSESTERIFICATION ASSISTED BY MICROWAVES OF CRUDE PALM OIL. HOMOGENEOUS CATALYSIS

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**Abstract**— Main propose in this study was to obtain alkyl ester from crude palm oil (CPO), using microwaves like heating source, in a process of two stages by means of homogeneous catalysis; the first stage (esterification), was made using sulfuric acid catalyst, to diminish the acid value of the oil, avoiding the soap formation and facilitating the separation of the phases. The second stage (transesterification) was made using sodium methoxide catalyst. The behavior in the crystallization of the product using differential scanning calorimetry, cloud point ASTM D2500 and pour point ASTM D97 was evaluated. The obtained biofuels fulfill the requirements of the American standards for biodiesel and the propose methodology for the synthesis presents environmental advantages and of increase in the reactivity, as opposed to the traditional methods of heating.

**Keywords**— Esterification, Transesterification, palm oil, microwave, homogeneous catalysis.

## I. INTRODUCTION

Biodiesel is a mixture of mono-alkyl esters of long chain fatty acids, is an alternative fuel made from renewable sources as vegetable oils and animal fats. It is biodegradable, non-toxic, show low emission profiles and also is beneficial environmentally (Fangrui and Milford, 1999).

In Colombia, the prospects for the production of energy sources are focused on the oil palm, where our country is the fifth world producer and sixth exporter this oil (Divya and Tyagi, 2006).

However, presents operating problems at low temperatures for its high content of saturated fractions that crystallize and can block the filters of the engines. One of the alternatives to reduce the flow properties at low temperatures (FPLT) of methyl esters from oil palm is use alkyl esters, obtained through of transesterification with branched alcohols, that prevent the agglomeration and formation of crystals of these methyl esters.

Alkyl esters can be produced through transesterification of triglycerides, which are separated by immiscibility and higher density (Marchetti *et al.*, 2007; Ma and Hanna, 1999; Vicente *et al.*, 2004).

Transesterification or alcoholysis is the displacement of one alcohol from ester by other alcohol in a similar process to hydrolysis, except that is used alcohol instead of water. This process has been used intensively to reduce the viscosity of triglycerides. The general reaction

of transesterification using methanol is showed in Fig. 1. Transesterification is a process of reversible steps and proceed essentially with the mixture of reagents. However, the presence of a homogeneous or heterogeneous catalyst, acid or basic, accelerates the reaction (Marchetti *et al.*, 2007).

The conventional techniques of synthesis for the transesterification reactions commonly use basic homogeneous catalysts (sodium and potassium hydroxides and alkoxides). The use of these catalysts present environmental and technical disadvantages, because of the neutralization processes of its salts, which in turn, generate cost overrun on the separation and purification of final product (Burt and Meuly, 1944). The use of acid catalysts to the transesterification reduces this problem, but more reaction times are required.

Very few studies have been made with the aim to obtain alkyl esters and all are obtained by homogeneous catalysis (Lee *et al.*, 1995). Yields of these reactions are very low by the high steric hindering that presenting the branched alcohols. To increase the conversion, in this work, we propose use assisted reactions by microwaves.

Application of the microwaves (MW) to chemical systems represents a new method to accelerate the chemical reactions through a faster and more efficient heating, which gives a low processing-time, increasing in the productivity, best recovery of volatile elements and compounds, low contamination levels, significant procedures, small volume of reagents, and low environmental impact. However, microwaves do not interact in a similar way with all materials, and there is the risk of explosions by overheating.

Microwaves are electromagnetic radiation with a frequency between 300 MHz to 300 GHz, where the most commonly used domestically and industrial, is that of 2450 MHz. (Bougrin and Loupy, 2005).

It was discovered in 1946 by Percy and only until 1980 was employed in different areas of chemistry. Microwaves technology has many applications and is a promising source of development of products at indus-

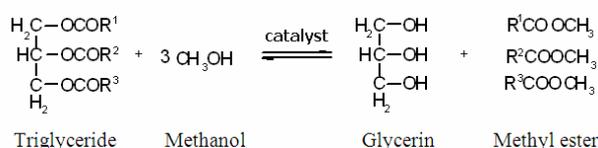


Figure 1. General reaction for the transesterification of triglycerides with methanol.

try level, such as biodiesel. The development of innovative strategies for organic synthesis is a central theme of research in developing new products with pharmaceutical potential (Bhattacharyya, 2005).

Dielectric heating can come from dipolar polarization as consequence of the interaction of dipole-dipole of polar molecules with electromagnetic field. They produce dissipation of energy in form of heat by agitation and friction generated when the dipoles change their orientations by alternation of the electrical field to high frequency (Perreux and Loupy, 2001).

## II. METHODS

### A. Experimental Section

The alkyl esters production was performed using the esterification-transesterification method, and this methodology consists of two phases:

#### *Free fatty acid (FFA) esterification*

The crude palm oil no refined, was employed to makes an esterification of FFA using alcohols as: methanol (MeOH), isopropyl (IsoprOH), isobutyl (IsobuOH), 2-butyl (2-BuOH) and isopentyl (IsopentOH) alcohols analytic grade, Merck trademark. In this process a molar ratio 1:8 oil:alcohol, 2.5%  $H_2SO_4$ , and stirring magnetic system with reflux were used. After that the reaction is conducted, we make a phase separation, washing and drying were carried out. The final value of acidity obtained for this oil was 1%. On the other hand, the reaction monitoring was carried out with the aim to determine the decreasing of acidity index employing ASTM D664 (2005) norm.

#### *Transesterification*

The oil obtained in the first stage esterificated with methanol, reacts with isopropyl, isobutyl, 2-butyl and isopentyl alcohols, analytic grade, and with catalysts: 3%  $H_2SO_4$  and 0.9% sodium methoxide, using 1:30 and 1:27 molar ratio oil: alcohol respectively. The experiments were conducted at laboratory scale employing glass reactors of 100 mL, with reflux system, temperature control and magnetic stirring, the heating system is through microwave radiation, using a Panasonic multi-mode domestic oven. The furnace has a nominal power of 1000 W, and the power percent employed was 100%. Sodium methoxide was obtained by reaction between methanol, analytic grade, with metallic sodium.

The reaction begins with the mixing of reagents (oil, alcohol and catalyst), near to boiling point of the alcohol concerned. After the reaction time elapsed, the system is washed with water to neutral pH with the aim to remove the glycerin and catalyst and then is conducted an evaporation process to extract the excess of water and glycerin.

Monitoring the conversion percent (%convGL) in the transesterification reactions, was conducted by means of determination of free glycerol, based on standard AOCS Ca 14-56 (1995), for oils and fats. This method quantifies the mount of free glycerol obtained by means of the reaction with periodic acid, which excess is titrated with a thiosulphate solution employing as in-

dicator a starch solution. The conversion percent was calculated respect to the theoretical glycerin obtained after saponify the oil.

The behavior in the crystallization of the product using differential scanning calorimetry, cloud point, ASTM D2500 (2005) and point of fluency or discharged, pour point, ASTM D97 (2005), was evaluated.

## B. Results

### *FFA esterification*

The decreasing in the acidity index with the time can see in Figures 2 and 3, for conventional and microwaves heating respectively. The order in final acidity obtained for the alcohols is: methanol < isopropyl alcohol < isobutyl alcohol < 2-Butyl alcohol < isopentyl alcohol.

The initial value in the first 30 seconds, counted from the instant reach the reaction temperature, is more significant in the microwave case because exist an accelerated increase of the localized temperature, and hence in the molecular effective collisions.

In the methanol case, the two heating systems decreasing the acidity value to 1 in 60 minutes. In the branched alcohols, this value is reached in higher times to one hour, but is lower when it is use microwaves. This is because the solvents interacting with the radiation increasing the rotation of dipoles, generating friction, and dissipating energy in form of heat.

Can be seen three regimes that categorized the progress of the reaction. Initially, mass transfer is limited by the low miscibility of reagents (two or three phases), when is beginning the formation of the ester, these act

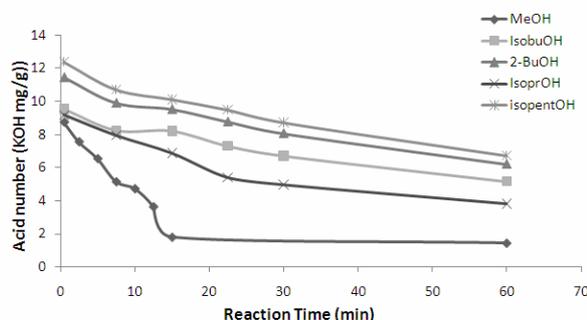


Figure 2. Esterification of palm oil-alcohols- $H_2SO_4$ , through conventional heating.

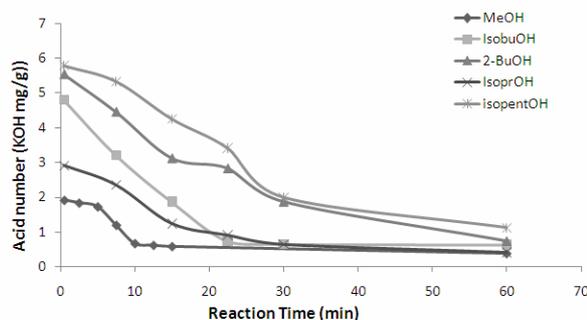


Figure 3. Esterification palm oil-alcohols- $H_2SO_4$ , microwave heating.

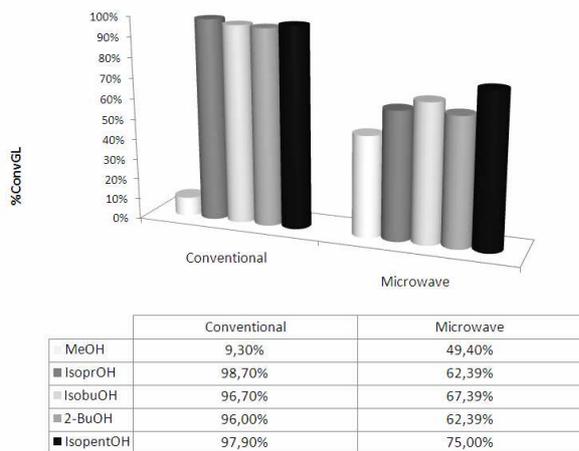


Figure 4. Transesterification comparison in acid medium by conventional and microwaves heating

as emulsifiers increasing the rate of reaction, this is the limiting step of the reaction, and finally the rate decreases.

The reasons for these facts are:

- By increasing the temperature, the viscosity of the oil is reduced, contributing to the diffusional restrictions by effects of viscosity of the FFA in the oil that would be smaller, and the homogenization process would be favored.
- Esterification reactions that are carried out under microwaves are activated efficiently with short reaction times and phase separations, decreasing by-products and a reduced energy consumption.

It is possible esterify free fatty acids with alcohols of high molecular weight at reasonable times, using microwave, but they remain more expensive than methanol, and for this reason is decided esterify with methanol and then transesterify with other alcohols proposed.

### Transesterification

#### Acid homogeneous catalysis

The alcoholysis also can be catalyzed by hard acids as sulphuric, hydrochloric, phosphoric, and sulphonic acids. However, the reaction times are higher than the basic homogeneous catalysis (Lotero *et al.*, 2005; Narváez *et al.*, 2007). The main advantage in the use of the acid homogeneous catalysts is in the esterification of free fatty acids, where no problems with of formation of soaps.

To achieve good yields and favor this reaction, high molar ratios of oil:alcohol are used, being 30:1 ratio the most common (Zhang *et al.*, 2003).

Comparing the reaction, between the two types of heating, with  $H_2SO_4$ , we see that with five hours of reaction, the conversion increase for the methanol when microwaves is used, but in the other alcohols, the yield decrease, which is possible conclude that the transesterification in acid medium is not favored, because the interaction is not effective by the low polarity of medium, and the formation of intermediates (See Fig. 4).

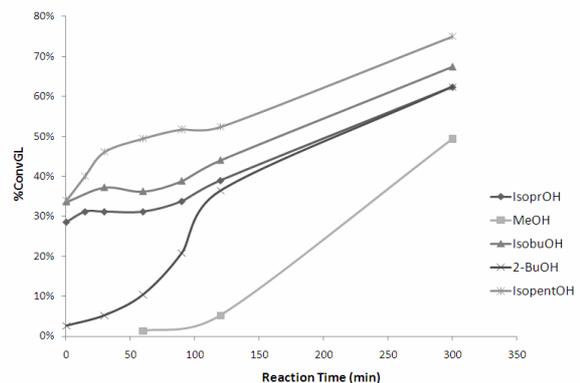


Figure 5. Transesterification comparison in acid medium by microwaves heating using different alcohols.

Ascending order for the conversion reaction using microwaves is: methanol<2-Butyl alcohol< isopropyl alcohol< isobutyl alcohol < isopentyl alcohol (See Figure 5), where the generated effect is mainly thermal due to the increase in reaction temperature, and the use of alcohols with high boiling points minimize the mass transfer to controlled regime and promote molecular collisions more energized making the reaction more favored (Nye *et al.*, 1983).

The disadvantage of employ acid catalysts is that it presents corrosion and environmental problems that have decreased their use to industrial level. However, due to its versatility in treating of FFA has been proposed as an economically viable strategy for the production of biodiesel from fats with a high content of FFA (Zhang *et al.*, 2003).

One advantage of this catalysis is the low susceptibility to the presence of FFA in the raw material, but is very sensitive to the concentration of water. Canakci and Van Gerpen (1999), show that with 0.1% water, the yield of reaction is reduced to 5%, and the reaction is inhibited. An increase in the concentration of water affects the transesterification more than esterification, due to the carboxylic acid functional groups of FFA interact more easily with polar compounds facilitating the alcoholysis and is more critical in the acid catalysis than basic catalysis. Water can form aggregates around protons diminishing its acid strength and deactivating the catalyst.

Making the dried of the esterification products of the FFA, the yield of acid transesterification increase as is showed by the results obtained.

Using conventional heating, the transesterification in acid medium is three times slower than reaction in basic medium, as is showed in Fig. 6 for methanol. In the case of molecular weight higher, and branched alcohols, the transesterification is favored for the acid medium because there is an increase in the electrophilia, while in the basic catalysis, the nucleophilia increase, and due to the high steric hindering of the alkoxides formed, the reaction is not favored. Moreover, the increase in reaction temperature favors of the alkyl esters.

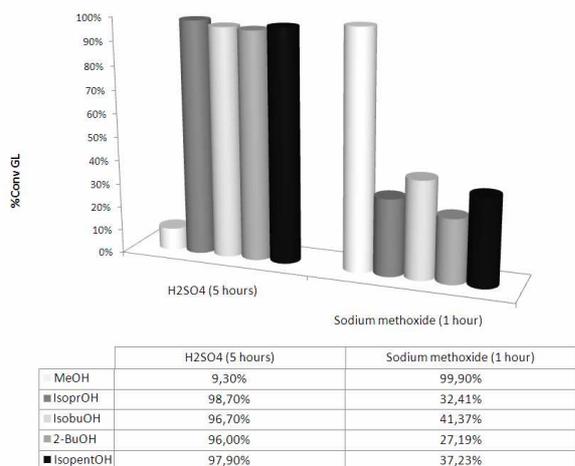


Figure 6. Transesterification comparison in acid and basic media and conventional heating.

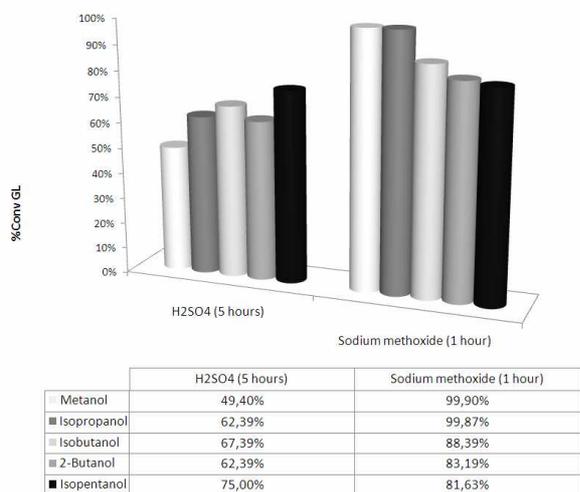


Figure 7. Transesterification comparison in acid and basic media and microwaves heating.

In the microwave heating, the transesterification reaction is faster through basic catalysis (see Fig. 7), this because the dipole moment of compounds is higher and there is more interaction with microwaves by rotation of dipoles and ionic movement that generate friction and a more effective heating, increasing the molecular collisions and favoring the reaction rate.

**Basic homogeneous catalysis.**

The use of alkoxides with high molecular weight in the transesterification reaction leads to low conversions compared with the methoxide, due to the increase of the steric hindering which difficult the nucleophilic attack. For this reason, sodium methoxide as catalyst for the transesterification reaction is selected.

There is an increase in the reaction yield when microwaves are employed, as is showed in Fig. 8. In this figure, we can observe that with one hour of reaction for all alcohols, the conversion percent is higher than 80%, and only methanol present similar yields in either meth-

ods, and hence the ascending order for conversion to glycerin is:

Isopentyl alcohol < 2-Butyl alcohol < Isobutyl alcohol < Isopropyl alcohol < Methanol

The main effect that influences in the conversion is the overheating of the solvent. Now, as the value to the loss factor or  $\tan \delta$  increases in the same order, then there is a greater efficiency in the absorption of microwave energy and its transformation into heat, and although the system is kept at a range of constant temperature varies point to point within the reaction system. Other effect generated is the basicity of the alkoxide ion, so that when the system is more basic, this is more nucleophilic, and the reaction is more favored. Moreover, the dipole moment presents a higher value and interacts with the microwaves through rotation of dipoles in an alternating electric field of high frequency generating collisions that dissipate its energy as heat. The methoxide ion is a small group, a high concentration can cause Claisen condensation reactions undesirable which generate an increase in the viscosity of the product.

As shown in Fig. 9, at the beginning of all the reactions there is an increase in the conversion, but after 30 minutes of reaction this remains almost constant, this is

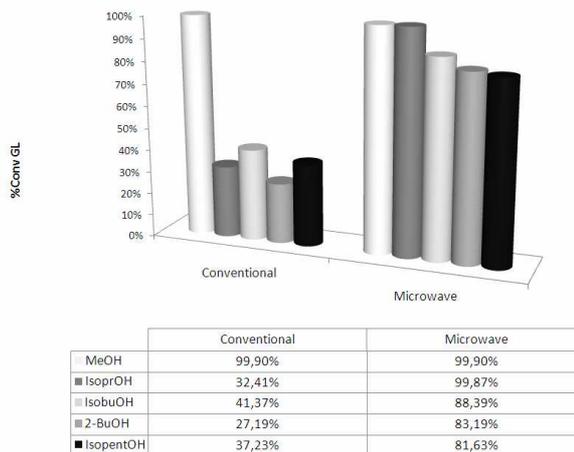


Figure 8. Transesterification comparison employing different alcohols and sodium methoxide as catalyst. Conventional and assisted by microwaves systems. Reaction time, 60 minutes.

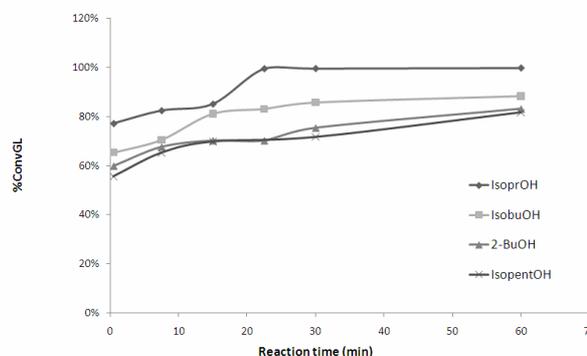


Figure 9. Monitoring of the transesterification reaction using different alcohols and sodium methoxide as catalyst. Assisted by microwaves system.

because initially, the catalytic specie, the methoxide, interacts more with the MW, while in the end the alkoxide ion corresponding presents a higher steric hindering and the reaction is difficult. To ensure a higher yield, the concentration of the methoxide, amount of alcohol and a reaction time higher, about 2 hours, are required.

### Characterization of alkyl esters

The product obtained in this work consist in a 15:85 methyl:alkyl ester mixture. From thermograms in Figures 10 to 13, can be established that the descending order in the crystallization temperature,  $T_c$ , is:

Methyl>Isoamyl>Isobutyl>Isopropyl>2-Butylester

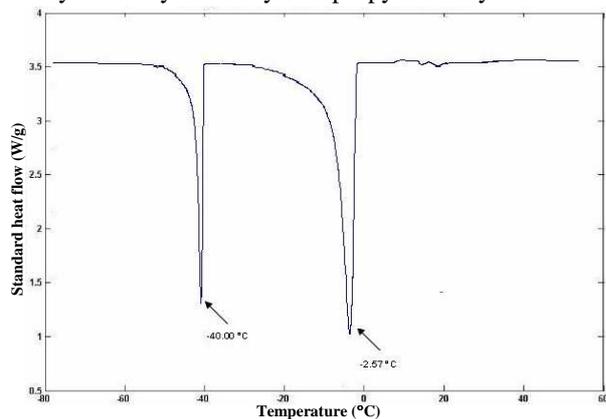


Figure 10. Cooling thermogram for isopentyl ester.

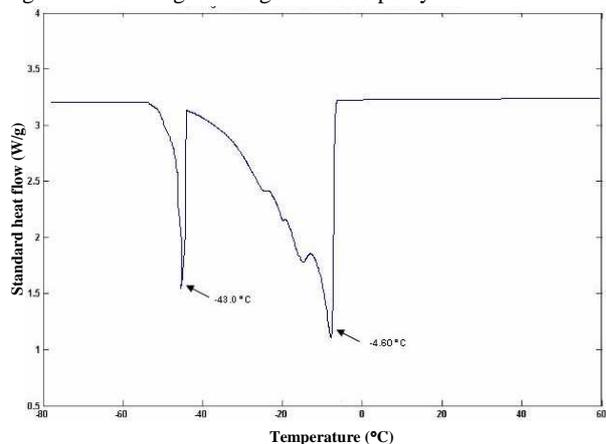


Figure 11. Cooling thermogram for isobutyl ester.

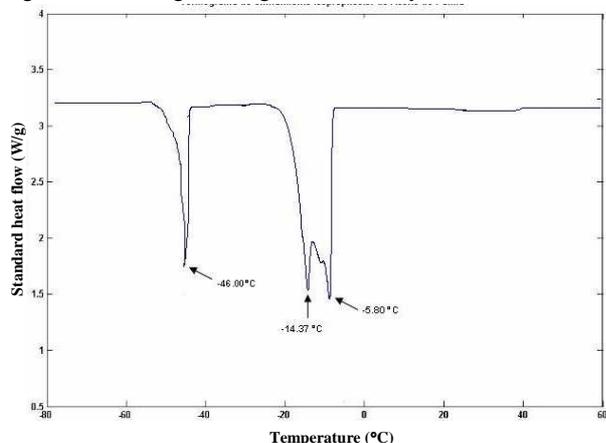


Figure 12. Cooling thermogram for isopropyl ester.

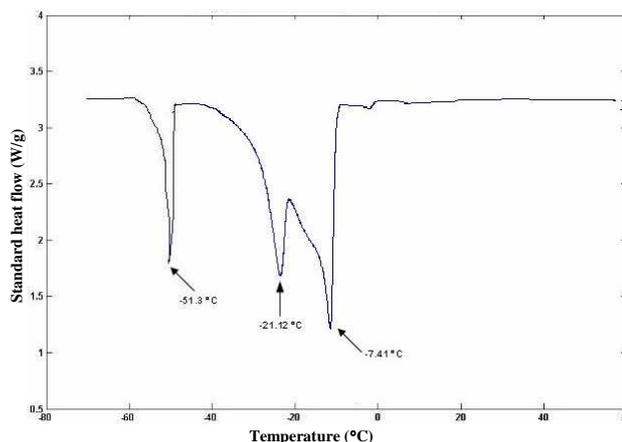


Figure 13. Cooling thermogram for 2-butyl ester.

Table 1. Flow properties at low temperature (PFBT) of alkyl esters.

BRANCHED ALCOHOLS		
PROPERTY	Cloud point (°C)	Fluidity point (°C)
METHYL ESTER	18	12
ISOAMYL ESTER	9,0	-9,0
ISOBUTYL ESTER	8,5	-3,0
ISOPROPYL ESTER	7,0	-3,0
2-BUTYL ESTER	7,5	-6,0

Crystallization curves for alkyl esters show two zones corresponding to saturated and unsaturated fractions. However, there are several peaks which can overlap. This is due to the different composition of the methyl:alkyl ester mixture.

In Table 1, shows the properties of flux at low temperature of alkyl esters (PFBT).

Cloud and fluidity points of each alkyl ester are lower than those for the respective methyl ester, and this is explained because the branching and largest chain that present the alcohol affect the crystalline forms more stable of saturated compounds present. One hypothesis to explain physically the effect of the alkyl group of the alkyl esters mixtures is that these tend to form thin films during the agglomeration or nucleation of crystals and the presence of alkyl branched groups affects the spacing between individual molecules in the layers causing rotational disorder in the hydrocarbon chains that translates into a crystal formation and initial packing less stable than in the case of methyl esters.

Respect to the flow properties at low temperature of the different alkyl esters from branched alcohols can be observed that have similar points cloud. The lowest point cloud corresponds to isopropyl esters, which is possible obtain a reduction of 10 Celsius degree respect to the value of that property for methyl esters. The alkyl esters from branched alcohol with a higher molecular weight (isopentyl esters) have the lowest point of fluency. With the substitution of the methyl group by isopentyl group a reduction in the point of fluency of 21 Celsius degree is obtained.

### III. CONCLUSIONS

The methodology for obtain alkyl esters from crude palm oil in two stages (esterification-transesterification), is a good alternative to increase the yield in the production.

The esterification stage of the FFA is favored with the use of MW due to the increase of the localized temperature, produced by the rotation of dipoles.

In the basic catalysis case, the transesterification stage is favored with microwaves because there are specific and thermal effects in the reaction producing an increasing in the nucleophilia and polarity of the intermediates that interact with microwaves, while in the second case the electrophilia is increased, and only we have thermal effects by overheating of the solvent.

The alkyl esters have lower values in the flow properties in cool, compared with the methyl esters, in costs and good operability the isopropyl ester is recommended.

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Received: January 13, 2009.

Accepted: November 26, 2009.

Recommended by Subject Editor: Ana Lea Cukierman.