

ESTERIFICATION AND TRANSESTERIFICATION ASSISTED BY MICROWAVE OF CRUDE PALM OIL. HETEROGENEOUS CATALYSIS

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Abstract— The principal objective of 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 heterogeneous catalysis; the first stage (esterification), was made using Dowex 50X2, Amberlyst 15 and Amberlite IR-120 resins catalysts, 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 potassium carbonate catalyst. The behavior in the crystallization of the product using differential scanning calorimetry, cloud point ASTM D2500 (2005) and pour point ASTM D97 (2005) 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, heterogeneous catalysis.

I. INTRODUCTION

The conventional techniques of synthesis for the transesterification reaction with high yields commonly use homogeneous catalysts from inorganic acids and bases, preferentially, sodium and potassium hydroxides and alkoxides. The use of these catalysts have technical and environmental disadvantages, because of the neutralization processes of its salts, which in turn, generate cost overruns on the separation and purification of final product. In the last years, the works reported on development of heterogeneous catalysts for the transesterification reactions in acid and basic medium, have been quite extensive. (Kaita *et al.*, 2002; Furuta *et al.*, 2004; Lin and Radu, 2006; Bossaery, 1999; Park *et al.*, 2008; Mbaraka, 2003; Bournay *et al.*, 2005; Basu and Norris, 1996; Stern *et al.*, 1999; Sanjib and Anju., 2005; Suppes *et al.*, 2001; Barakos *et al.*, 2007; Arzamendi *et al.*, 2008; Kim *et al.*, 2004; Xie *et al.*, 2007; Gryglewicz, 1999; Bournay *et al.*, 2005; Haitao and Xie, 2006; Kiss *et al.*, 2006; Corma *et al.*, 1998; Leclercq *et al.*, 2001; Ma *et al.*, 2008; Chen *et al.*, 2007; D'Cruz *et al.*, 2007), standing out clearly the trend of replacing these homogeneous catalysts, and this contributes to the elimination of additional stages of the process and improve the economy of the same. Because of its advantages, het-

erogeneous catalysts: they can be removed from of the reaction medium, can be recycled, the chemical structure and in some cases allows its holder guide reactions to certain products or reduce those that are undesirable, they offer the possibility of developing friendly processes with the environment, allow to be used for long periods of time without losing business and do not present dangers in handling or storage (Marchetti *et al.*, 2007).

Very few studies were performed to obtain alkylesters 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.

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 Dr. Percy and only until 1980 was employed in different areas of chemistry.

Almost any type of organic reaction requiring heating or thermal conditions can be performed using microwave radiation. Microwave dielectric heating is dependent on the ability of a solvent or matrix to absorb microwave energy and to convert it into heat (Lidström *et al.*, 2001). The matrix absorbs the radiation by two mechanisms: dipole polarisation and conduction.

When irradiated at microwave frequencies, the ions or dipole of the sample align in the applied electric field. As the applied field oscillates, the dipole or ion field attempts to realign itself with the alternating electric field and, in the process, energy is lost in the form of heat through molecular friction and dielectric loss. The amount of heat generated by this process is directly related to the ability of the matrix to align itself with the frequency of the applied field. If the dipole does not have time to realign, or reorients too quickly with the applied field, no heating occurs (Perreux and Loupy, 2001)

Microwave irradiation produces efficient internal heating (in situ heating), resulting in even heating throughout the sample, as compared with the wall heat transfer that occurs when an oil bath is applied as an energy source. Consequently, the tendency for the initiation of boiling is reduced, and superheating above the boiling point of the solvent (Kappe, 2004)

II. METHODS

A. Experimental Section

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

Esterification

It employs a oil:alcohol molar ratio 1:20, 10% of resins Dowex 50X2, Amberlyst15, Amberlite IR-120, a magnetic stirring system with reflux, finished the reaction, there is a separation of phases and rota-evaporation to recover alcohol, the value of the final acidity to this oil is 1%.

Transesterification

The oil esterificated with methanol (MeOH), obtained in the first stage reacts with isopropyl (IsoprOH), isobutyl (IsobuOH) alcohols, analytic grade 2-butyl (2-BuOH) and isopentyl (IsopentOH) alcohols, and the catalyst: potassium carbonate, commercial grade. The experiments were conducted at the laboratory in glass reactors of 100 mL, with reflux system, temperatures near the boiling point of the alcohol and respective magnetic agitation. Using a molar ratio oil:alcohol 1:20 and 3% of catalyst

Not required washing in the two stages, only filtration and rota-evaporation to recover the excess alcohol employed.

The heating system is through microwave radiation, in a Panasonic domestic oven multimode. The furnace has a nominal power of 1000W and the percentage of power used was 100 percent.

Monitoring the conversion rate (conv % G) 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. And an analysis of fatty acid composition by gas chromatography: using a gas chromatograph Agilent 6890N, employing a column AT-WAX of 60 meters long, and 0.32 μm internal diameter, and a thick film of 0.25 μm and hydrogen as a carrier gas was used. Due to the absence of standards of alkyl esters, analysis was done by direct comparison with the standard chromatogram of methyl ester and results are reported as an area percentage of each alkyl ester.

The properties of alkyl esters obtained after optimization, to verify that meet international standards as fuels, such as: API gravity at 60 °F ASTM D287 (2005), cloud point ASTM D2500, point of fluency or discharged (pour point) ASTM D97 (2005), calorific ASTM D240 (2005), viscosity at 40 °C ASTM D445 (2005), flash point (C) ASTM D93 (2005) and cetane number ASTM D613 (2005) were evaluated.

B. Results

Esterification

The acidity values obtained for a reaction time of 60 minutes using microwave heating are lower than using conventional heating and, the acidity order obtained for the catalysts is: Dowex<Amberlite<Amberlist, and the order for the alcohols: Methanol<isopropyl alcohol

<isobutyl alcohol<2-butyl alcohol<isopentyl alcohol as can be seen in Figures 1 to 5.

Performing monitor the reaction between 30 seconds and 60 minutes with MW can be seen that all curves obtained have an exponential behavior.

For alcohols branched esterificated with resins, must increasing the reaction time over 60 minutes to reduce the acidity to a value below 1, see Figures 6 to 8.

The reasons that explain these facts are:

By increasing the temperature, is reduce the viscosity of the oil, which contributes to the diffusional restrictions by effects of viscosity of the FFA in the oil are minors and the homogenization process be favored.

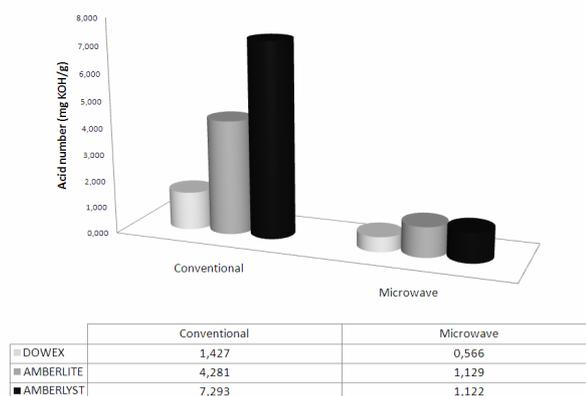


Figure 1. Esterification of palm oil with methanol at 60 minutes of reaction.

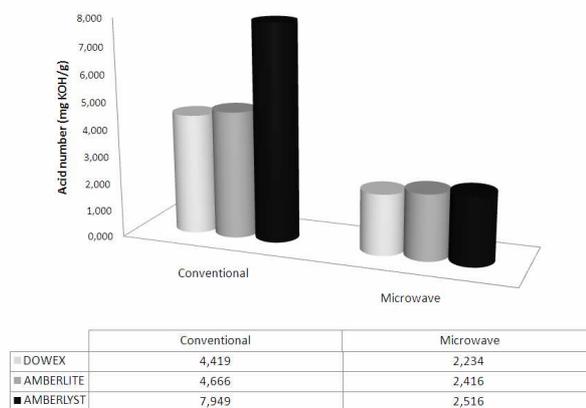


Figure 2. Esterification of palm oil with isobutyl alcohol at 60 minutes of reaction.

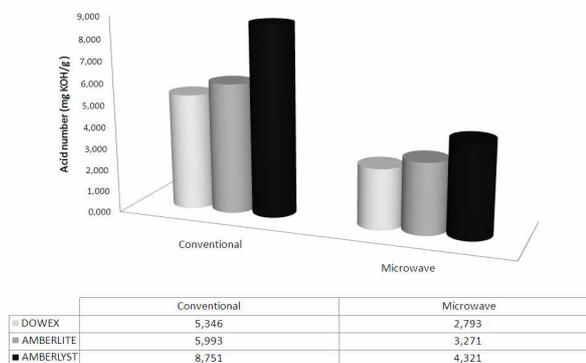


Figure 3. Esterification of palm oil with 2-Butyl alcohol at 60 minutes of reaction.

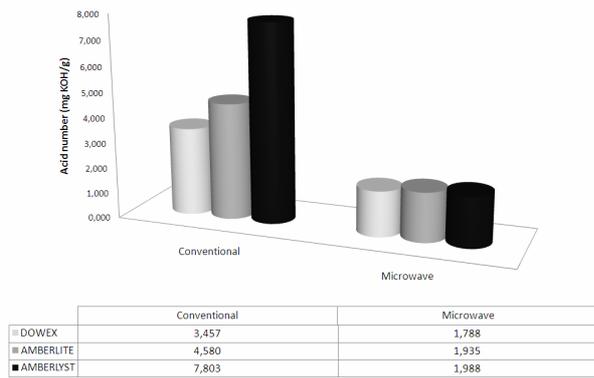


Figure 4. Esterification of palm oil with isopropyl alcohol at 60 minutes of reaction.

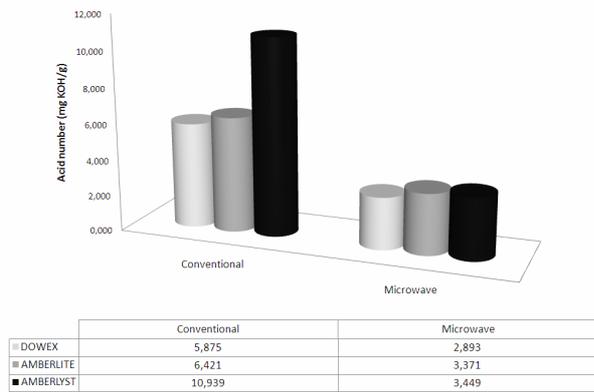


Figure 5. Esterification of palm oil with isopentyl alcohol at 60 minutes of reaction.

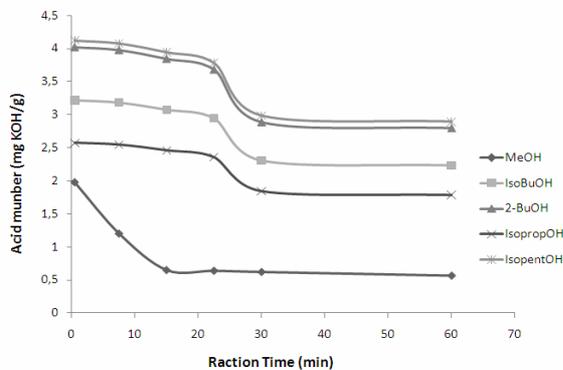


Figure 6. Esterification of crude palm oil-alcohols-DOWEX resin, 60 minutes of reaction.

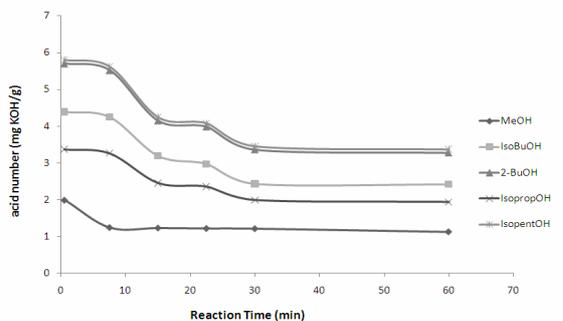


Figure 7. Esterification of crude palm oil-alcohols-AMBERLITE resin, 60 minutes of reaction.

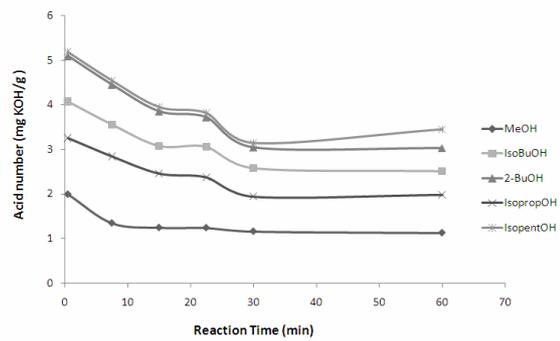


Figure 8. Esterification of crude palm oil-alcohols-AMBERLYST resin, 60 minutes of reaction.

Dowex microreticular resin presents the lowest divinylbenzene (2%), which has a lower cross-linking that produces a high expansion of the resin in a polar medium, and the resin can expand their pores up to 400%, enabling the income of the voluminous substrate (FFA) and its protonation. Moreover, this resin is swelled by solvent effects.

Amberlyst 15 macroreticular resin is activated due to its surface area, and the protons located on the outer surface seem that catalyse the esterification because the interiors are inaccessible due to high cross-linking.

The content of divinylbenzene in resins based on polystyrene limit the contact between the fatty acid and the internal acid sites of the resin, especially for a higher percentage of 8% in cross-linking agent.

Kinetics reaction is not affected by the heating method, there are no differences in the rate reactions when is used conventional heating or MW, as described (Toukoniitty *et al.*, 2005; Konrad, 2000), but the reaction is favored by polar solvents that interacting with the radiation increasing the rotation of dipoles, generating friction and dissipating the energy as heat, which makes an increase in the localized temperature, and the order for the $\tan \delta$ value for the alcohols is: methanol > isopropyl alcohol > isobutyl alcohol > 2-butyl alcohol > isopentyl alcohol, which is consistent with the order found from highest to lowest yield in the reaction. Moreover, the resin suffer an overheating.

- The use of sulphuric acid as catalyst increase the pollution in the final product, because it can generate SO_x.
- Gradual decreasing of the reaction rate is due to water generated, independent of the heating method, because of this is introduced into the pores of the resin and blocking the access of the FFA acid and the alcohol to the sulphonic groups. For this reason, the water must be eliminated finally by rota-evaporation.
- The water must be removed from reaction medium because:

Moves the equilibrium towards products.

It could promote hydrolysis of the sulfate groups supported, causing leaching of the active acid sites

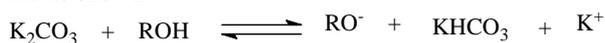
and deactivating the catalyst in the form of SO_4^{2-} , HSO_4^- y H_2SO_4 groups.

- Methanol can induce dehydration of catalyst causing deactivation of the acid sites.
- The catalytic activity increases with the increase in the diameter of the pore, for materials with small pore, the accumulation of water and methanol around hydrophilic acid sites can prevent the access of FFA molecules. The strength of the acid sites favors the reaction, for example, sulphonic groups attached to aromatic rings are more acids than aliphatic groups.
- An increase in the hydrophobicity of the resin increase the catalytic activity.
- It is advisable to use in beds packed for resins microreticular type, because of its minor amount of DVB gives less mechanical stability.

Transesterification

The literature on the subject of basic carbonates as catalysts for the reaction of transesterification is somewhat ambiguous as to classify it as homogeneous or heterogeneous catalyst. In this article potassium carbonate will be classified as a heterogeneous catalyst that presents a true dissolution degree in reagents and products of the reaction. Jeromin *et al.* (1990) use for the transesterification reaction sodium carbonate and bicarbonate in fats or vegetable oils, animal or plant with acidity indices below 1. The U.S. patent 2006/0058540 A1 (Siegfried and Eckbard, 2006) shows the high conversions presented by potassium carbonate, mixtures of sodium and potassium carbonate as well as sodium and potassium silicates.

The alkaline potassium carbonate reacts with the alcohol forming the ion alkoxide and potassium bicarbonate as shown.

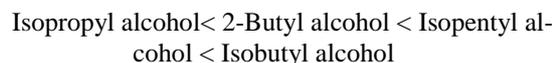


The formation of potassium bicarbonate instead of water, reduces significantly the formation of soap. However, the carbonate anion is a weak basis and reacts very slowly with the alcohol. For this reason, it require large amounts of catalyst (> 3%), to obtain results similar to the homogeneous catalysts.

The salts of carbonate have been used to replace basic catalysts in the transesterification reaction. Suppes *et al.* (2001) transesterificates soybean oil and tallow with ethylene glycol, diethylene glycol, glycerin and triethylenglycol using M_2CO_3 ($\text{M} = \text{K}, \text{Na}$) and MCO_3 ($\text{M} = \text{Mg}, \text{Ca}, \text{Zn}$) at temperatures above 200°C and alcohol / TG relation more than 8. High conversions were obtained in less than three hours. Also, these heterogeneous catalysts catalyse the reactions of hydrolysis, so that the water decreases its performance considerably. These catalysts have been used in reactors packed bed by its low cost, availability and low solubility in fats and oils. This type of reactor provides good performance because it promotes the contact catalyst-reactants (Lotero *et al.*, 2006).

There is no difference in the conversion percent obtained for methanol using conventional heating and microwaves, but for other alcohols show an increase in the use of microwaves. However, obtained values are very low and is recommended increase the concentration of the catalyst, oil:alcohol ratios more high and greater reaction times.

Ascending order of conversion percent, conv. % (see Figure 9), is:

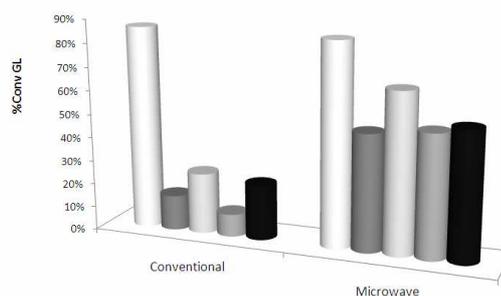


Main factor that influence this order is nucleophilicity of the alkoxides obtained, primary alkoxides as the isobutoxide and isopentoxide are more stable because they have less steric and inductive impediment to introduce electrons in the reactive group facilitating the nucleophilic attack.

The initial conversion obtained is less than when homogeneous catalysts are used, but there is an exponential increase in the conversion, see Fig. 10.

Characterization of alkyl esters

Crystallization peaks, total saturation and insaturation percent, for alkyl esters are registered in Table 1. Descending order of Tc is:



	Conventional	Microwave
MeOH	86,31%	85,63%
IsoprOH	14,85%	49,51%
IsobuOH	25,78%	67,59%
2-BuOH	9,55%	52,00%
IsopentOH	23,47%	54,59%

Figure 9. Monitoring of transesterification reaction using different alcohols and potassium carbonate as catalyst. Three hours of reaction.

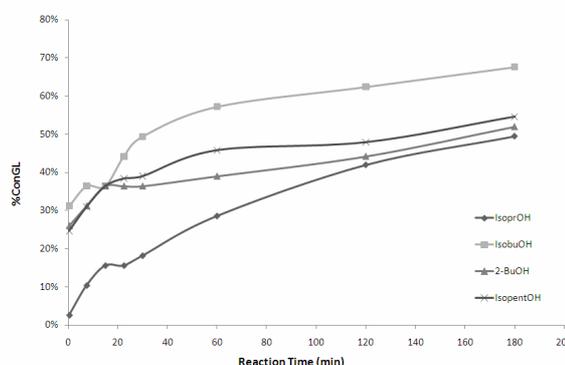


Figure 10. Monitoring of transesterification reaction using different alcohols and potassium carbonate as catalyst. Three hours of reactions. Microwaves assisted system.

Methyl > Isoamyl > Isobutyl > Isopropyl > 2-Butyl ester
Crystallization curves for alkyl esters show two zones corresponding with saturated and unsaturated fractions. However, there are several peaks that can overlap them because of different composition of the methyl-alkyl ester mixture (see Tables 2 and 3).

In Table 3, the properties of alkyl esters, which are meet with international standards is showed.

Table 1. Composition of methyl-alkyl ester mixtures obtained by chromatography.

	Saturated %	Unsaturated %
Methyl ester	8.261	9.922
Isoamyl ester	39.811	42.008
Total	48.072	51.93
Methyl ester	7.752	8.732
Isobutyl ester	40.200	43.315
Total	47.952	52.047
Methyl ester	9.780	1.612
Isopropyl ester	51.612	36.996
Total	61.392	38.608
Methyl ester	10.81	9.834
2-Butyl ester	44.596	34.76
Total	55.406	44.594

Table 2. Crystallization temperatures of methyl-alkyl ester mixtures.

	Exothermal peaks Tco (°C)		
	1	2	3
Methyl ester	-2.57	-40.00	
Isoamyl ester			
Total			
Methyl ester	-4.60	-43.00	
Isobutyl ester			
Total			
Methyl ester	-5.80	-14.37	-46.00
Isopropyl ester			
Total			
Methyl ester	-7.41	-21.12	-51.30
2-Butyl ester			
Total			

Table 3. Pure fuel properties from branched alkyl esters.

PROPERTY	BRANCHED ALCOHOLS				
	Methyl ester	Isoamyl ester mix- ture	Isobutyl ester mix- ture	Isopropyl ester mix- ture	2-butyl ester mix- ture
API gravity at 60 °F	30.21	32,1	32,3	32,5	32,3
Cloud point (°C)	18	9,0	8,5	7,0	7,5
Fluidity point (°C)	12	-9,0	-3,0	-3,0	-6,0
Calorific power (BTU/LB)	17380	17500	17565	17605	17598
Viscosity at 40 °C (cSt)	4.490	5,465	5,896	5,123	6,025
Flash point (°C)	30	110,0	125,0	109,0	100,0
Cetane number	48	51,78	51,66	51,42	51,98

III. CONCLUSIONS

The results show that microwaves as heating source accelerate the chemical reactions, decreasing time reaction and increase the yield of end product, in FFA esterification case, the main effect is the dielectric and localized heating of polar solvents and the heterogeneous catalysts used, rather than reasons that affect the mechanism of the reaction.

Pre-esterificated oil show indicated acidity to react after in a transesterification reaction to obtaining biodiesel.

Use branched alcohols and with molecular weight higher, serves to obtain alkyl esters that can be used as additives to decrease the cold flow properties of the palm oil, but its obtaining is disadvantaged by the steric impediment that decrease the reactivity of these, while microwaves favor these reactions.

Water must be removed from reaction to shift the equilibrium and avoid poisoning of the catalyst.

Lowest content of cross-linking agent favors the reaction, since it allows dilatation of resin and access of bulky groups to reactive sites.

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Received: January 13, 2009.

Accepted: November 26, 2009.

Recommended by Subject Editor: Ana Lea Cukierman.