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Thermal behavior of diesel/biodiesel blends of biodiesel obtained from buriti oil

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ABSTRACT. Biodiesel has been obtained from methanolysis of buriti oil. This biodiesel was added in fossil diesel in order to obtain diesel/biodiesel blends. Thermal analysis of blends were carried on 30-600°C range at rate of 10°C min.^{-1}. Kinetic parameters such as activation energy (Ea), pre-exponential factor (A), Gibbs energy ($\Delta^{\neq}G$), enthalpy ($\Delta^{\neq}H$) and entropy ($\Delta^{\neq}S$) of activation were determined by using Coats–Redfern equation. The Ea, $\Delta^{\neq}H$ and $\Delta^{\neq}G$ values presented a linear increase with biodiesel amount added in blends. The heat of combustion of diesel/biodiesel blends was determined, and it was observed that the heat of combustion decreased with the addition of biodiesel in diesel/biodiesel blends.

Keywords: transesterification, vegetable oils, thermogravimetric evaluation.

Comportamento térmico de blendas de diesel/biodiesel de biodiesel obtido a partir do óleo de buriti

RESUMO. O biodiesel foi obtido a partir de metanólise de óleo de buriti. O biodiesel foi adicionado ao diesel fóssil a fim de obter misturas de biodiesel/diesel. Análises térmica das misturas foram realizadas entre 30-600°C com uma taxa de aquecimento de 10°C min.^{-1}. Parâmetros cinéticos como a energia de ativação (Ea), fator pré-exponencial (A), energia livre de Gibbs ($\Delta{\neq}G$), entalpia ($\Delta{\neq}H$) e entropia de ativação ($\Delta{\neq}S$) foram determinadas usando equação de Coats-Redfern. Os valores de Ea, $\Delta^{\neq}H$ and $\Delta^{\neq}G$ apresentaram aumento linear com a quantidade de biodiesel adicionado na mistura. O calor de combustão de misturas de biodiesel/diesel foi determinada, e foi observado que o calor de combustão diminuiu com a adição de biodiesel no diesel e nas misturas de biodiesel.

Palavras-chave: transesterificação, óleos vegetais, avaliação termogravimétrica.

Introduction

Most of the energy consumed in the world comes from petroleum, coal and natural gas, mainly petroleum derived fuels. Exhaust emissions from diesel burning in motor vehicles contain hundreds of compounds, either in the gas or particulate phases, which contribute to global warming (FERNANDO et al., 2006). Several of these compounds have been proved or suspected to be carcinogenics such as: formaldehyde, acrolein, PAHs, nitro-PAHs, benzene, sulphate etc. (MEHER et al., 2006). Among the several alternatives that substitute fossil diesel for environmentally friendly fuels, the vegetable oils are one of the most promising renewable source of liquid fuels (GOMES et al., 2008; KROUMOV et al., 2007). Besides, the vegetable oils present some qualities which distinguish them as sustainable fuels, such as: high caloric power, absence of sulfur in chemical composition, its industrial production does not generate harmful substances, and mainly, the decrease of carbon dioxide gases by their consumption during photosynthesis of vegetable cultivation (PRASAD; SRIVASTAVA., 2000). Thus, these alternative fuels can be mixed with diesel, and in this way, it reduces the demand on diesel oil and minimize the gas emissions that contribute to global warming (CONCEIÇÃO et al., 2007).

The environmental benefits of renewable biodiesel can also provide economical advantages (BORSATO et al., 2010). Brazilian Federal Government can include the biodiesel program in the frame of 'Kyoto Agreement' in the guidelines of the clean development mechanisms. This program demands the addition of 5% (B5) in 2012 (HRIBERNIK; KEGL, 2007). Moreover, this program stimulates the production of biofuels by small Brazilian family farms giving profits to agricultural working men (CRUZ et al., 2007).

Biodiesel production is based on manufacturing of vegetable oils. In this way, Brazil has a great variety of plants that are rich in vegetable oils, which can be used to produce renewable fuels (LECLERCQ et al., 2001). Among them, buriti (*Mauritia exuosa)*, an abundant palm in the Amazon region of Brazil, which supplies raw material for a variety of applications such as: roots for medicines, fruit and trunks to produce foods and drinks. The composition of the oil extracted from the Buriti fruit is 20% of shell and pulp, 30% of white cellulose layer and 50% of seed (wt/wt) (NETO et al., 2007).

The present investigation reports thermal stability, thermal kinetic studies and heat of combustion of buriti oil, biodiesel obtained from buriti oil and diesel/biodiesel blends.

Material and methods

Samples

The composition of the dry buriti fruit is basically formed by peel (exocarp) 31.38 ± 8.87%, pulp (mesocarp) 15.26 ± 7.22%, fiber (endocarp) 14.75 ± 6.02% , seed (endosperm) 38,62 ± 14.54%. The vegetable oil is presented in all fruit, and the dry mass of buriti fruit has 42.50 ± 12.50%.

Buriti oil was obtained from commercial sources and used without further purification. Pure diesel was named B0 and pure biofuel was named B100.

Accordingly, arrays of biofuel/diesel blends were obtained by mixing 2.0, 5.0, 10.0, 20.0 and 50.0% (w/w) of biofuel in diesel, using a roller mixer spinning at constant speed for 30 min., in order to produce B2, B5, B10, B20 and B50 blends, respectively. All experiments were done in triplicate.

Transesterification Reaction

Transesterification reactions were followed by using: 10.0 g of buriti oil, 1.5 g of methanol and 0.1 g of KOH. Potassium hydroxide was completely dissolved in MeOH under stirring in a glass batch reactor equipped with mechanical stirrer. Then, the vegetable oil was added into the mixture and maintained under stirring for 2h at 50°C. The resulting product was washed with a saturated aqueous NaCl solution. The organic phase was separated by decantation and dried with anhydrous magnesium sulfate. Recovered esters were analyzed by HPLC, using a method published elsewhere (FARIA et al., 2009), with a Shimadzu CTO-20A chromatograph with UV-VIS detector at $\lambda = 205$ nm, equipped with Shim-Pack VP-ODS column (C-18, 250 mm, 4.6 mm i.d.).

Thermogravimetric studies

Thermogravimetric curves were obtained from approximately 10 mg of biofuel/diesel and blends samples on a thermogravimetric analyzer model TA-2960 in a dynamic atmosphere using air flux, with heating from room temperature up to 600°C at a heating rate of 10°C min.$^{-1}$ Kinetic thermal parameters were calculated from Coats–Redfern equation (MOURA; PRADO, 2009).

Heat of combustion

An oxygen bomb calorimeter (Parr 1241) was used in order to obtain the heat of combustion of buriti oil, diesel, biodiesel and biofuel/diesel blends. The Parr 1241 is a static and manual calorimeter with a temperature resolution of 0.002°C, capable of oxygen charging pressures up to 40 atm, and can liberate up to a maximum 33,400 J per charge. The fuel samples were placed directly in a stainless steel capsule (2.5 cm in diameter and 1 cm deep) and burned with oxygen at a pressure of 3.0 MPa according to ASTM method D240 (DEOLIVEIRA et al., 2006; GARCIA et al., 2007). Calibration of the calorimeter was done by burning 1.0 g benzoic acid pellets (Parr). Heats combustion for diesel and blends were determined in triplicate.

Results and discussion

Biodiesel produced by methanolysis of Buriti oil was quantified by HPLC analysis (Figure 1) and Table 1 presented the amounts of free fatty acid, mono-, di-, and triglycerides, as well as their conversion to biodiesel.

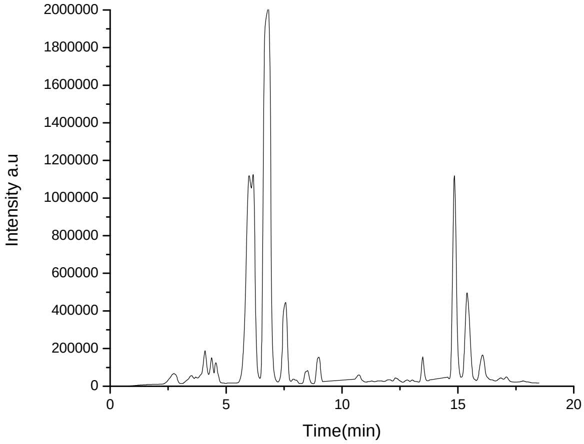

Figure 1. Chromatogram of biodiesel produced by metanolysis of buriti oil.

These results show that the transesterification reaction of buriti oil with methanol catalyzed by KOH occurred as expected with yield production of 94.08% of formed biodiesel.

Table 1. Products and yields of transesterification of buriti oil.

Product	Yeild (%)
Biodiesel	94.08 ± 0.78
Triglycerides	1.67 ± 0.59
Diglycerides	0.98 ± 0.78
Fatty acids and monoglycerides	3.27 ± 0.79

TG curves of the diesel, biodiesel obtained from methanolysis of buriti oil and blends are presented in Figure 2, which showed only one step of mass loss, which was attributed to the volatilization and/or combustion of methyl esters from biodiesel and alkyl compounds from diesel. The obtained mass loss values, decomposition temperature range, and temperature related to DTG peak maximum values are listed in Table 2.

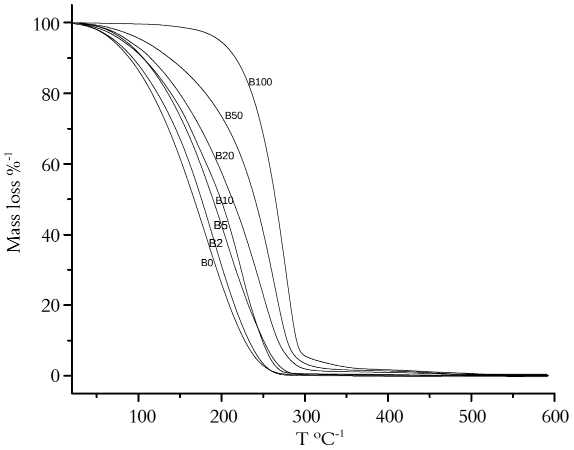

Figure 2. TG of biofuel/diesel blends.

Table 2. Thermal analysis data of diesel, biodiesel and biofuel/diesel blends.

biofuel/diesel blends	Temperature range / °C	DTG peak Temperature / °C	Total mass loss (%)
Diesel	339-534	456.01	100
B2	341-542	463.80	100
B5	343-554	479.61	100
B10	347-562	498.35	100
B20	353-565	522.06	100
B50	360-562	537.57	100
B100	440-573	551.63	100

Kinetic studies were followed in order to understand the effect caused on the thermal behavior by biodiesel addition in the fuel blends.

Once the kinetic information can be extracted from dynamic experiments, which can be determined using a large number of differential and integral methods, depending mainly on the treatment of experimental data, and the rate of conversion, dα/d*t*, is a linear function of a temperature-dependent rate constant and a temperature-independent function (PEREZ-MAQUEDA et al., 2006):

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

Assuming the Arrhenius-type dependence on temperature and that the temperature of the sample is changed by a controlled and constant heating rate, β. The expression of the change in the conversion degree can be written as (GOTOR et al., 2000):

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} f(\alpha) \tag{2}$$

Integrating this equation from initial temperature, T_0, which corresponds to zero degree of conversion, to the peak temperature of the derivative thermogravimetric curve (DTG), Tp, which can affirm $\alpha = \alpha_P$, it can be written this equation (NUNEZ et al., 2001):

$$g(\alpha) = \int_0^{\alpha_P} \frac{d\alpha}{f(\alpha)} = \int_0^{T_P} e^{-E/RT} dT \tag{3}$$

Where: g(α) is the integral function of conversion degree. In thermal decomposition process several kinetic models have been proposed in order to determine the different reaction mechanisms, which g(α) assumes different expressions as described in Table 3 (FARIA; PRADO, 2007).

Table 3. Algebraic expressions for *g*(α) for the used mechanisms of solid state processes.

Functions g(α)	Solid State process
$g_1 = \alpha^2$	one-dimensional diffusion
$g_2 = \alpha + (1-\alpha)\ln(1-\alpha)$	two-dimensional diffusion
$g_3 = \left[1-(1-\alpha)^{1/3}\right]^2$	three-dimensional diffusion (Jander equation)
$g_4 = [1-\frac{2}{3}\alpha]-(1-\alpha)^{2/3}$	three-dimensional diffusion (Ginstling.Brounshtein equation)
$g_5 = -\ln(1-\alpha)$	random nucleation with one nucleus on the individual particle
$g_6 = [-\ln(1-\alpha)]^{1/2}$	nucleation and growth (Avrami equation 1)
$g_7 = [-\ln(1-\alpha)]^{1/3}$	nucleation and growth (Avrami equation 2)
$g_8 = 1-(1-\alpha)^{1/2}$	phase boundary controlled reaction (contracting área)
$g_9 = 1-(1-\alpha)^{1/3}$	phase boundary controlled reaction (contracting volume)

Several distinct methods have been developed and applied to explain the changes in thermogravimetric data by variation of the heating rate, β, in order to determine kinetic parameters as activation energy (E) and pre-exponential factor (A). One of the most used method is based on Coats-Redfern equation (COATS; REDFERN, 1964):

$$\log\left[\frac{g(\alpha)}{T^2}\right] = \log\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{2.303RT}$$

In this method, the determination of the reaction mechanism can be obtained by linear fitting, applying Coats-Redfern equation in thermal decomposition curve.

The assignment of the mechanism of thermal decomposition is based on the assumption that the form of g(α) depends on the reaction mechanism. In this investigation, nine forms of g(α) were used in order to enunciate the thermal mechanism of diesel, biodiesel and blends diesel/biodiesel. Correlation coefficients for all these forms were calculated and the form of g(α) for which the correlation has a maximum value is selected as the mechanism reaction as presented in Table 4.

Table 4. Square correlation coefficients calculated using nine forms of g(a) for diesel and diesel/biodiesel blends.

Functions g(α)	Diesel	B2	B5	B10	B20	B50	B100
g_1	0.98467	0.99443	0.99967	0.99682	0.99750	0.99830	0.99868
g_2	0.98651	0.99651	0.99980	0.99793	0.99862	0.99874	0.99888
g_3	0.99423	0.99799	0.99992	0.99871	0.99938	0.99968	0.99991
g_4	0.99819	0.99935	0.99999	0.99906	0.99948	0.99972	0.99992
g_5	0.99686	0.99738	0.99976	0.99375	0.98930	0.99629	0.99654
g_6	0.99763	0.99630	0.99969	0.99071	0.98293	0.99519	0.99590
g_7	0.99784	0.99327	0.99946	0.98389	0.96187	0.99339	0.99499
g_8	0.99652	0.99837	0.99971	0.99729	0.99580	0.99700	0.98542
g_9	0.99090	0.99769	0.99973	0.99583	0.99526	0.99526	0.98324

For all thermal analysis, the best value of correlation coefficient for materials decomposition was obtained by using the function: $[1-\frac{2}{3}\alpha]-(1-\alpha)^{2/3}$, which corresponds to a mechanism involving three-dimensional diffusion (Ginstling-Brounshtein equation). This mechanism can be explained by diffusion of fuel to vapour phase by its volatilization (GABAL, 2003).

The activation energies obtained by the application of Coats-Redfern equation were listed in Table 5 and showed in Figure 3.

Other thermal decomposition parameter, activation entropy, was determined from equation: $A = \frac{kT_S}{h} e^{\Delta S^{\neq}/R}$ (STRASZKO et al., 2000), where k is the Boltzmann constant, *h* is the Planck constant and T_S is the temperature related to DTG peak maximum value determined from Figure 1, listed in Table 1 for diesel/biodiesel blends. A third thermal degradation parameter, the activation enthalpy, was obtained from the following equation: $E = \Delta H^{\neq} - RT_S$. Finally, the activation Gibbs energy was calculated from equation: $\Delta G^{\neq} = \Delta H^{\neq} - T_S \Delta S^{\neq}$ (RODRIGUEZ et al., 2009).

Table 5. Kinetic parameters for thermal behavior diesel, biodiesel and biofuel/diesel blends.

blends	E/kJ mol^{-1}	A s^{-1}	$\Delta^{\neq}H$/kJ mol^{-1}	$-\Delta^{\neq}S$/J mol^{-1} K^{-1}	$\Delta^{\neq}G$/kJ mol^{-1}
B0	46.29	1,016	52.35	252.2	236.24
B2	48.47	1,015	54.60	252.3	240.53
B5	51.00	1,008	57.25	252.6	247.40
B10	57.54	1,020	63.95	252.7	258.91
B20	59.12	0,94	65.73	253.6	267.40
B50	91.78	0,88	98.52	254.3	304.69
B100	154.37	0,87	161.23	254.5	371.14

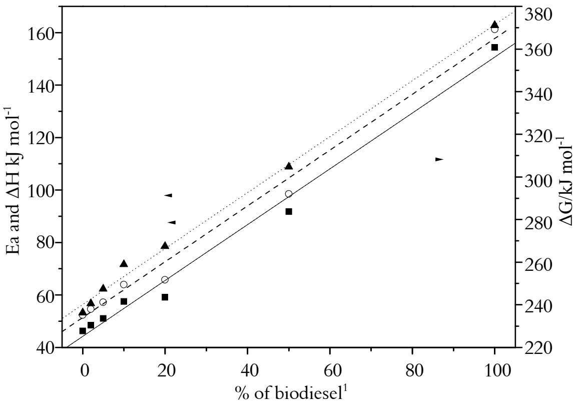

Figure 3. Effect of biodiesel amount on the thermodynamic parameters: $\Delta^{\neq}H$ (▲), $\Delta^{\neq}G$ (o) and Ea (■) of diesel/biodiesel blends.

All kinetic thermal degradation parameters for the diesel/biodiesel blends were calculated from thermogravimetric curves and the results are listed in Table 5.

Kinetic thermal analysis shows that all Ea, $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ values are positive and $\Delta S^{\ddagger}$ values are negative; consequently, all thermodynamic parameters indicate non-spontaneous processes of decomposition for diesel, biodiesel and all blends.

Activation energy, enthalpy and free Gibbs energy were plotted as function of biodiesel amount in diesel/biodiesel blends. These data show that the addition of biodiesel in blends causes a linear increase in Ea, $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ values during thermal volatilization processes of blends. This behaviour can be explained by the presence of oxygenated groups present in biodiesel, which causes more effective intermolecular interactions. In this way, volatilization processes occur by the cracking intermolecular interactions resulting in a gradual disappearance of the liquid to form the gas phase. Ability for fuel oil molecules in liquid phase to volatilize is based on the amount of kinetic energy an each individual particle may possess. Thus, the increasing temperature (as a TG assays), the fuel oil in liquid phase received thermal energy, and as consequence, the fuel oil goes to gas state. Some factors affects the temperature of phase transition such as: density, surface area, pressure, intermolecular forces etc.

In the case of diesel and biodiesel, the most of parameters are very similar. However, these fuels differs in molecular structure. The diesel is formed basically by carbon-carbon bonds and carbon-hydrogen bonds, whereas the biodiesel are methyl esters of vegetable oils. Thus, the biodiesel presents carbon-oxygen bonds of esters, resulting in a difference of polarity of molecules more accentuated than fossil diesel, and as consequence, the intermolecular interactions are more effective in biodiesel than fossil diesel. Then, the addition of biodiesel in diesel causes the increasing of volatilization temperature and the increasing in Ea, $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ values in blends, and these results in agreement of other studies with biodiesel produced from other vegetable oils (babassu, soybean and cotton) (SANTOS et al., 2007).

The heat of the combustion of diesel and the effect of the addition of those biodiesel in fossil diesel are presented in Figure 4.

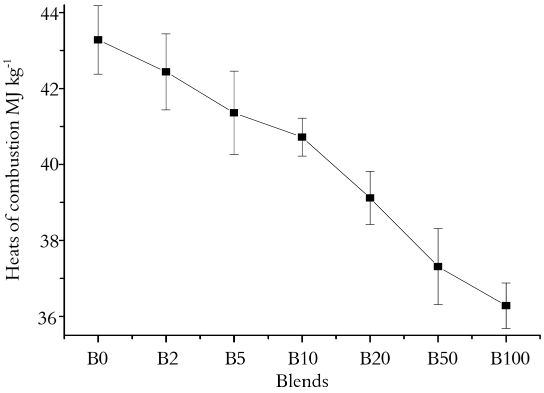

Figure 4. Heats of combustion diesel, biodiesel and biofuel/diesel blends.

These studies showed that the heat of combustion decreased with the addition of biodiesel in diesel/biodiesel blends. This fact can be explained by the presence of oxygenated groups in biodiesel, which presents enthalpy bonds lower than C=C bonds in fossil diesel (ANDRADE et al., 2011).

Conclusion

All diesel/biodiesel blends presented endothermic values for Ea and ΔH, endoergonic values for ΔG, and ΔS values were exoergonic, indicating that the volatilizations were non-spontaneous processes in all thermodynamic aspects for all blends. The present study confirmed that the incorporation of biodiesel decreased the heat of combustion of the fuel blends.

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References

ANDRADE, R. D. A.; FARIA, E. A.; SILVA, A. M.; ARAUJO, W. C.; JAIME, G. C.; COSTA, K. P.; PRADO, A. G. S. Heat of combustion of biofuels mixed with fossil diesel oil. **Journal of Thermal Analysis and Calorimetry**, v. 103, n. 3, p. 469-474, 2011.

BORSATO, D.; MOREIRA, I.; PINTO, J. P.; MOREIRA, M. B.; NOBREGA, M. M.; CONSTANTINO, L. V. Análise físico-química de diesel interior em mistura com biodiesel. **Acta Scientiarum. Technology**, v. 32, n. 2, p. 187-192, 2010.

COATS, A. W.; REDFERN, J. P. Kinetic parameters from thermogravimetric data. **Nature**, v. 201, n. 491, p. 68-72, 1964.

CONCEIÇÃO, M. M.; FERNANDES, V. J.; ANTONIO, S. J.; MIRNA, F. A.; SANTOS, M. G.; SOUZA, A. G. Thermal and oxidative degradation of castor oil biodiesel. **Energy and Fuels**, v. 21, n. 3, p. 1522-1527, 2007.

CRUZ, A. D.; KULKARNI, M. G.; MEHER, L. C.; DALAI, A. Synthesis of biodiesel from canola oil using heterogeneous base catalyst. **Journal of the American Oil Chemists' Society**, v. 84, n. 10, p. 937-943, 2007.

DEOLIVEIRA, E.; QUIRINO, R. L.; SUAREZ, P. A. Z.; PRADO, A. G. S. Heats of combustion of biofuels obtained by pyrolysis and by transesterification and of biofuel/diesel blends. **Thermochimica Acta**, v. 450, n. 1-2, p. 87-90, 2006.

FARIA, E. A.; PRADO, A. G. S. Kinetic studies of the thermal degradation of cellulose acetate/niobium and chitosan/niobium composites. **Reactive and Functional Polymers**, v. 67, n. 7, p. 655-661, 2007.

FARIA, E. A.; MARQUES, J. M.; DIAS, I. M.; ANDRADE, R. D. A.; SUAREZ, P. A. Z.; PRADO, A. G. S. Nanosized and reusable SiO_2/ZrO_2 catalyst for highly efficient biodiesel production by soybean transesterification. **Journal of the Brazilian Chemical Society**, v. 20, n. 9, p. 1732-1737, 2009.

FERNANDO, S.; HALL, C.; JHA, S. NOx reduction from biodiesel fuels. **Energy and Fuels**, v. 20, n. 1, p. 376-382, 2006.

GABAL, M. A. Kinetics of the thermal decomposition of CuC_2O_4–ZnC_2O_4 mixture in air. **Thermochimica Acta**, v. 402, n. 1-2, p. 199-208, 2003.

GARCIA, C. C.; FRANCO, P. I. B. M.; ZUPPA, T. O.; FILHO, N. R. A.; LELES, I. M. G. Thermal stability studies of some cerrado plant oils. **Journal of Thermal Analysis and Calorimetry**, v. 87, n. 3, p. 645-648, 2007.

GOMES, L. F. S.; SOUZA, S. N. M.; BARICATTI, R. A. Biodiesel produzido com óleo de frango. **Acta Scientiarum. Technology**, v. 32, n. 1, p. 57-62, 2008.

GOTOR, F. J.; CRIADO, J. M.; MALEK, J.; KOGA, N. Kinetic analysis of solid-state reactions: the universality of master plots for analyzing isothermal and nonisothermal experiments. **Journal of Physical Chemistry**, v. 104, n. 46, p. 10777-10782, 2000.

HRIBERNIK, A.; KEGL, B. Influence of biodiesel fuel on the combustion and emission formation in a Direct Injection (DI) diesel engine. **Energy and Fuels**, v. 21, n. 3, p. 1760-1767, 2007.

KROUMOV, A. D.; MODENES, A. N.; WENZEL, B. M. Desenvolvimento de um modelo da cinética enzimática da transesterificação de óleos vegetais para produção de biodiesel. **Acta Scientiarum. Technology**, v. 29, n. 1, p. 9-16, 2007.

LECLERCQ, E.; FINNIELS, A.; MOREAU, C. Transesterification of rapeseed oil in the presence of basic zeolites and related solid catalysts. **Journal of the American Oil Chemists' Society**, v. 78, n. 11, p. 1161-1165, 2001.

MEHER, L. C.; SAGAR, D. V.; NAIK, S. N. Technical aspects of biodiesel production by transesterification a review. **Energy Review**, v. 10, n. 3, p. 248-268, 2006.

MOURA, A. O.; PRADO, A. G. S. Effect of thermal dehydration and rehydration on Na-magadiite structure. **Journal of Colloid and Interface Science**, v. 330, n. 2, p. 392-398, 2009.

NETO, B. A. S.; ALVES, M. B.; LAPIS, A. A. M.; NACHTIGALL, F. M.; EBERLIN, M. N.; DUPONT, J.; SUAREZ, P. A. Z. 1-n-Butyl-3-methylimidazolium tetrachloro-indate (BMIdot operatorInCl_4) as a media for the synthesis of biodiesel from vegetable oils. **Journal of Catalysis**, v. 249, n. 2, p. 154-161, 2007.

NUNEZ, M. R.; VILLANUEVA, M.; RIAL, B.; NUNEZ, B. L. Comparative study of the thermal stability of the epoxy systems BADGE n=0/1, 2 DCH and BADGE n=0/1, 2 DCH/$CaCO_3$. **Journal of Thermal Analysis and Calorimetry**, v. 66, n. 1, p. 209-221, 2001.

PEREZ-MAQUEDA, L. A.; CRIADO, J. M.; SANCHEZ-JIMENEZ, P. E. Combined kinetic analysis of solid-state reactions: a powerful tool for the simultaneous determination of kinetic parameters and the kinetic model without previous assumptions on the reaction mechanism. **Journal of Physical Chemistry**, v. 110, n. 45, p. 12456-12462, 2006.

PRASAD, R.; SRIVASTAVA, A. Triglycerides-based diesel fuels. **Energy Review**, v. 4, n. 2, p. 111-133, 2000.

RODRIGUEZ, R. P.; SIERENS, R.; VERHELST, S. Thermal and kinetic evaluation of biodiesel derived from soybean oil and higuereta oil. **Journal of Thermal Analysis and Calorimetry**, v. 96, n. 3, p. 897-901, 2009.

SANTOS, N. A.; TAVARES, M. L. A.; ROSENHAIM, R.; SILVA, F. C.; FERNANDES, V. J. J.; SANTOS, I. M. G.; SOUZA, A. G. Thermogravimetric and calorimetric evaluation of babassu biodiesel obtained by the methanol route. **Journal of Thermal Analysis and Calorimetry**, v. 87, n. 3, p. 649-652, 2007.

STRASZKO, J.; OLSZAK-HUMIENIK, M.; MOZEJKO, M. J. Study of the mechanism and kinetic parameters of the thermal decomposition of cobalt sulphate hexahydrate. **Journal of Thermal Analysis and Calorimetry**, v. 59, n. 3, p. 935-942, 2000.

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