Comparison of kinetic parameters of volatilization of biodiesel from babassu, palm oil and beef tallow obtained by enzymatic catalyst

Oliveira, L. E. 1; Giordani D. S. 2; Castro, H. F. 3; Silva M. L. C. P. 4 1 – Universidade de São Paulo, Brasil; 2 – Universidade de São Paulo, Brasil; 3 – Universidade de São Paulo, Brasil; 4 – Universidade de São Paulo.

Introduction

Fossil fuels have been the engines of world economy in the twentieth century; however, progress has brought new problems, the main impact, greenhouse gas emissions that contribute to the increase in greenhouse gases. The industrial energy demand and the pollution problems caused due to the widespread use of fossil fuels has made it increasingly necessary to develop alternative sources of energy. Biofuels must be acceptable, economically competitive, environmental acceptable and easily available.

With regard to catalysts, currently the homogeneous catalysis (acid or alkaline) is the predominant route technology for the production of biodiesel. However, the route by homogeneous catalyst presents difficulties in separation and the formation of soaps, high residual sodium content and high acidity. The synthesis of biodiesel using heterogeneous catalyst allows the recovery of the catalyst, thus eliminating the problems of separation, acid value and sodium found in the process with homogeneous catalyst. Furthermore, the use of heterogeneous catalyst minimizes the problems related to the final stages of purification of biodiesel; it reduces the occurrence of undesirable reactions of saponification and allows a simplification and reduction of process costs by reducing the number of associated operations.

The boiling point and volatility are important properties for biodiesel, as it is for quality control of the industry of petroleum diesel and biodiesel. In addition, through the volatility is possible to predict properties such as vapor pressure, density, latent heat, heat of vaporization, viscosity and surface tension of biodiesel.

From thermogravimetry (TG) it is possible to follow the kinetics of thermally stimulated processes, like volatilization, decomposition, oxidation, reduction, crystallization, polymerization and combustion. The aim of this study is to calculate the kinetic parameters of volatilization of biodiesel from babassu, palm oil and tallow obtained by enzymatic catalyst by thermogravimetry.

Results and Conclusions

The biodiesels were synthesized by ethanolic route and obtained using the enzyme lipase as catalyst stabilized in a support non-commercial hybrid (heterogeneous catalyst) consisting of polysiloxane-poly vinyl alcohol (POS-PVA). Table 1 shows the fisical-chemicals characterizations of biodiesels obtained.

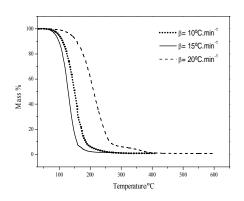
Table 1 Fisical-chemicals characterizations of biodiesels.

Biodiesel	Density	Kinematic	Acidity index	Yield (%)
	(g.cm ³)	viscosity (cSt)	mg KOH.g ⁻¹	NMR
Babassu	0.8700	3.59	0.23	100
Palm	0.8791	5.34	0.43	98
Beef tallow	0.8991	5.73	0.27	100

The diesel fuel was supplied by REVAP/Petrobras Sao Jose dos Campos unit, São Paulo state.

The thermogravimetry (TG) experiments were carried out using a thermobalance Shimadzu TGA-50 model, in the temperature range of 30–600 °C, under nitrogen atmosphere flowing in a rate of 50 mLmin⁻¹.

For the kinetic study of babassu there were used three different TG curves with different heating rates: 10, 15 and 20 ° C min-1 (Figure 1).



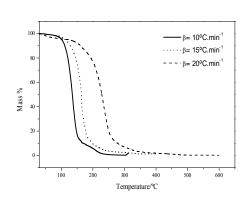
1.25 1.05 0.85 2.00 2.10 2.20 2.30 2.40 ×10⁻⁵

Fig. 2. Ozawa plot of babassu biodiesel.

Fig. 1. TG curves of babassu biodiesel at different heating rates.

From the three curves, the kinetics of volatilization of babassu biodiesel was calculated using the Ozawa method (Figure 2). The value of activation energy found is $E = 76.37 \text{ kJ.mol}^{-1}$.

The same kinetic study was conducted to palm biodiesel, using three different TG curves with different heating rates: 10, 15 and 20 ° C min-1 (Figure 3).



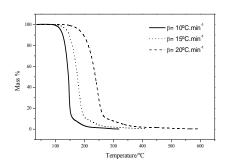
1.32 1.22 1.12 1.90 2.00 2.10 ×10⁻³

Fig. 4. Ozawa plot of palm biodiesel.

Fig. 3. TG curves of palm biodiesel at different heating rates.

From the three curves, the kinetics of volatilization of palm biodiesel was calculated using the Ozawa method (Figure 4). The value of activation energy found is $E = 87.00 \text{ KJ. mol}^{-1}$.

The same kinetic study was conducted to tallow biodiesel, using three different TG curves with different heating rates: 10, 15 and 20 ° C min-1 (Figure 5).



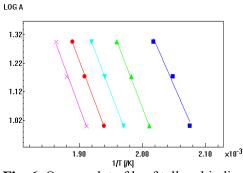
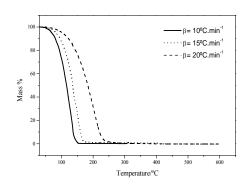


Fig. 5. TG curves of beef tallow biodiesel at different heating rates.

Fig. 6. Ozawa plot of beef tallow biodiesel.

From the three curves, the kinetics of volatilization of beef tallow biodiesel was calculated using the Ozawa method (Figure 6). The value of activation energy found is $E = 103.53 \text{ kJ.mol}^{-1}$.

It was performed the same kinetic study to petroleum diesel, thus being able to compare with the activation energy values found for babassu, palm and beef tallow biodiesel. It was used three different TG curves with different heating rates: 10, 15 and 20 ° C min-1 (Figure 7).



1.32 1.22 1.12 1.90 2.00 2.10 2.20 2.30 2.40 2.50 ×10⁻³

Fig. 7. TG curves of petroleum diesel at different heating rates.

Fig. 8. Ozawa plot of petroleum diesel

The value of activation energy found for petroleum diesel is $E = 49,38 \text{ kJ.mol}^{-1}$ (Figure 8). It is noted that biodiesel from beef tallow has a higher activation energy (103.53) compared to other biodiesels studied. So is the least volatile followed by the biodiesel from palm oil (87 kJ / mol), and biodiesel from babassu (76.37 kJ / mol).

Therefore it was concluded that the best biodiesel studied in relation to volatility, is the babassu biodiesel which has the lowest activation energy (76.38 kJ / mol). In addition it provides the activation energy closer to the mineral diesel, compared with the other two biodiesels studied.

Supported by "Conselho Nacional de Desenvolvimento Cíentifico e Tecnológico (Cnpq)"

Author publications

1. OLIVEIRA, L. E., GIORDANI, D. S., CASTRO, H. F., SILVA, M. L. C.

Estudo Cinético da degradação térmica dos biodieseis de palma, sebo bovino obtidos por rota enzimática e do diesel mineral In: IV Congresso da Rede Brasileira de Tecnologia de Biodiesel e VII Congresso Brasileiro de Plantas e Oleaginosas, Óleos, Gorduras e Biodiesel, 2010, Belo Horizonte.

Biodiesel Inovação Tecnológica e Qualidade., 2010.

2. OLIVEIRA, L. E., GIORDANI, D. S., CASTRO, H. F., SILVA, M. L. C.

Termogravimetria (TG/DTG) e calorimetria exloratória diferencial (DSC) em atmosfera oxidativa do biodiesel de sebo bovino, sebo bovino obtido por rota enzimática In: IV Congresso da Rede Brasileira de Tecnologia de Biodiesel e VII Congresso Brasileiro de Plantas e Oleaginosas, Óleos, Gorduras e Biodiesel, 2010, Belo Horizonte.

Biodiesel Inovação Tecnológica e Qualidade., 2010.

3. OLIVEIRA, L. E., GIORDANI, D. S., CASTRO, H. F., SILVA, M. L. C.

Termogravimetria (TG/DTG) e Calorimetria exploratória Diferencial (DSC) em atmosfera oxidativa do biodiesel de babaçu obtido por rota enzimática In: VII Congresso Brasileiro de Análise Térmica e Calorimetria, 2010, Águas de São Pedro.

Anais do VII Congresso Brasileiro de Análise Térmica e Calorimetria., 2010.

4. OLIVEIRA, L. E., GIORDANI, D. S., CASTRO, H. F., SILVA, M. L. C.

Termogravimetria (TG/DTG) e Calorimetria Exploratória Diferencial (DSC) em atmosfera oxidativa do biodiesel de palma obtido por rota enzimática In: VII Congresso Brasileiro de Análise Térmica e Calorimetria, 2010, Águas de São Pedro.

Anais do VII Congresso Brasileiro de Análise Térmica e Calorimetria. , 2010.

5. OLIVEIRA, L. E., GIORDANI, D. S., CASTRO, H. F., SILVA, M. L. C.

Caracterização dos Parametros Cinéticos pelo Metodo Matemático Ozawa do Biodiesel de babaçu obtido por rota enzimática In: III Congresso da Rede Brasileira de Tecnologia de Biodiesel, 2009, Brasília.

Anais do III Congresso da Rede de Tecnologia de Biodiesel., 2009.

6. OLIVEIRA, L. E., GIORDANI, D. S., CASTRO, H. F., SILVA, M. L. C.

Caracterização Térmica do Biodiesel de babaçu e Diesel mineral por termogravimetria em atmosfera de nitrogênio In: III Congresso da Rede Brasileira de Tecnologia de Biodiesel, 2009, Brasilia.

Anais do III Congresso da Rede Brasileira de Tecnologia de Biodiesel., 2009.

This document was created with Win2PDF available at http://www.win2pdf.com. The unregistered version of Win2PDF is for evaluation or non-commercial use only. This page will not be added after purchasing Win2PDF.