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Production and purification of biodiesel and glycerine, since vegetal oils and kinetic of vegetal oils transesterification reaction for wasted frying oil

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This work was elaborated for biodiesel and glycerine production and purification since vegetal oils, besides it determinated the kinetic of the vegetal waste frying oils transesterification reaction, mixed with ethanol and NaOH as catalyst into a batch jacket reactor of one liter capacity, the reactor is equipped with a mechanical stirrer, which works at 400 rpm, this information was obtained from previous researches. Furthermore, the investigation was made at several temperatures like 30, 50, 70 and 80 ºC and taking samples at different times. Then, they was analyzing by HPSEC (High Performance Size-Exclusion Chromatography). The oil-ethanol molar ratio used was 1:6, this relation showed a good performance according to the esters and glycerol formation.
In the next step, excess alcohol was removed by a vacuum distillation route evaporator at 80º C, later two phases separation (esters and glycerol) is getting in a decantation funnel. After that, the esters phase was washed whit acidified water to retire catalyst traces, glycerol, alcohol and other impurities presents in biodiesel, then sodium sulfate is added to remove much water like as possible. Finally, biodiesel is distillated in a molecular distiller.

Key words: vegetal oils, ethanol, biodiesel, glycerine, kinetic of transesterification reaction

1. Introduction

The biodiesel is an alternative fuel to the diesel produced through the transesterification of vegetable oils or animal fat, with alcohol in presence of a catalyst. This fuel is defined by the American Society for Testing Materials (ASTM), as a fuel renewable and constituted by a mixture of alkyl esters of long chains fatty acids, derived from vegetable oils or animal fats.

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Biodiesel is a clean burning fuel derived from a renewable feedstock such as vegetable oil or animal fat. It is biodegradable, non-inflammable, non-toxic and produces lesser CO2, sulfur dioxide and unburned hydrocarbons than petroleum-based fuel. Biodiesel is a fuel made from fat. Either virgin vegetable oil or waste vegetable oil can be used to make quality fuel. Fats are converted to biodiesel through a chemical reaction involving alcohol and catalyst. Nowadays, due to the price of virgin oil such as canola, soybean oil, the use of low-cost feedstock, such as waste frying oils in an acid-catalyzed process, should help make biodiesel competitive in price with petroleum diesel, beyond being a suitable way to reuse waste materials Silva (2008).

2. Experimental Procedure

2.1. Materials

The frying vegetable oil was collected from local Brazilian restaurant. The frying oil contained 1, 46% of free fatty acids (determined according to the AOCS official method Ca 5a-40 as oleic acid). The sodium hydroxide and the anhydrous ethanol were obtained from Synth (São Paulo, Brazil). All the standards were supplied by Sigma-Aldrich Chemical Company, Inc. (St. Louis, Mo).

2.2. Equipments

The experiments were carried out in a batch stirred tank reaction (BSTR) of a 1 liter reactor, equipped with a reflux condenser, a mechanical stirred, and a stopper to remove samples. Prototype of molecular distiller property of LPDS

2.3. Method of analysis

Gel-permeation chromatography (Waters, USA) also called high-performance size-exclusion chromatography (HPSEC) was used for the triglycerides, diglycerides, monoglycerides, ethyl esters and glycerol analysis according to Shoenfelder (2003). The mobile phase was HPLC-grade tetrahydrofuran (JT Baker, USA). The relative percentage of each component (x_i) was give by HPSEC and it was determined by equation (1), where x_i was calculated dividing the peak area of the ester by sum of the peak area of all components.

$$x_i = \left(\frac{A_{EE}}{A_{TG} + A_{DG} + A_{MG} + A_{EE} + A_{GL}} \right) \quad (1)$$

The molar concentration was calculated using the Eq. 2, M_i was determined by dividing the product of the density (d_i) by the relative percentage x_i by the molecular weight of each component (Mw_i).

$$M_i\,(\text{mol/L}) = \left(\frac{x_i \times d_i \times 1000}{Mw_i} \right) \quad (2)$$

2.4. Experimental conditions

The system was maintained at atmospheric pressure and the experiments were carried out at constant temperature. The agitation was kept constant at 400 rpm. The reaction time was about 30 minutes. The experiments were carried out with 1% wt of sodium hydroxide, molar ratio ethanol: vegetable oil of 6:1. To examine the temperature dependency of the reaction rate constants, reactions at 30, 50, 70 and 80°C were studied.

2.5. Procedures

Initially, the reactor was loaded with 400g of frying oil, preheated to desired temperature and the agitation started. The sodium hydroxide was dissolved in ethanol and the reaction starts when the alcoholic solution was added to the vegetable oil. During the reaction, samples were prepared by dilution of 0,1g of the reaction in 10ml of THF. After dilution the samples were filtered and analyzed in the HPSEC (high-performance size-exclusion chromatography). Ten samples were collected during the course of each reaction.

3. Results and discussion

3.1. Transesterification reaction

The frying oil had a FFA content higher than 1%, then the alkaline catalyst would be destroyed because the FFA reacted with the sodium hydroxide to produce soaps and water, hence, reducing the ester conversion. Figures 1 showed the effect of the time on the frying oil transesterification. In the transesterification reaction, the reactants initially form a two-phase liquid system, because the TG and alcohol phase are not miscible [3]. This fact decreases the contact between the reactants and the reaction conversion. This fact leads to increase the mass transfer in the first stage of the reaction, and hence the ester conversion.

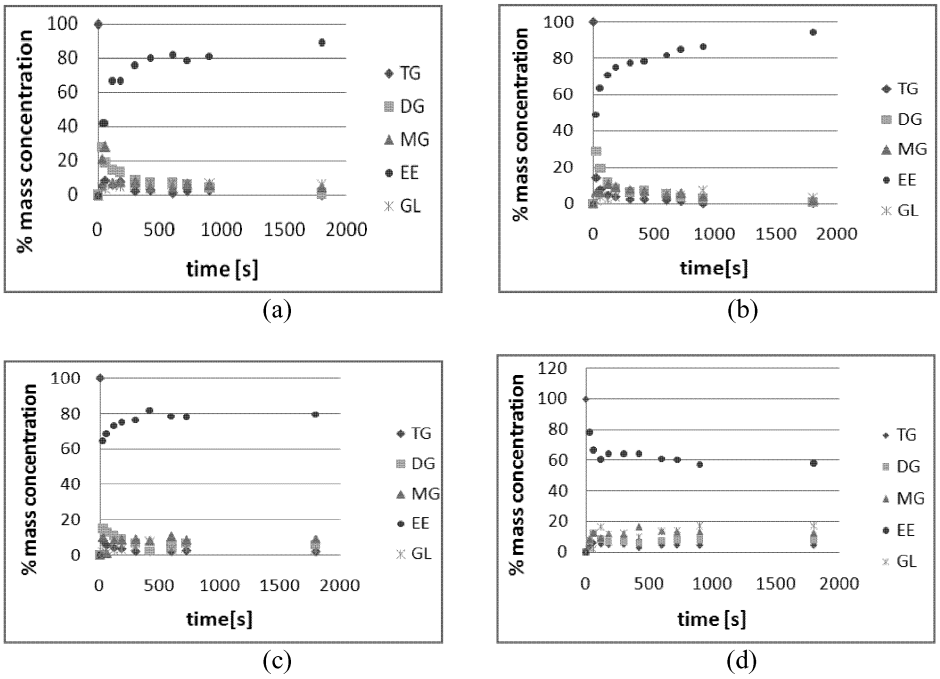

Fig.1. Experimental data for the composition of the reaction mixture during frying oil ethanolysis. Temperatures = 30°C(a)50°C(b) 70°C(c), 80°C(d) for 1% of NaOH as catalyst, impeller speed=400rpm, molar ratio 6:1.

3.2 Kinetics of frying oil to ethyl esters

The experimental results were analyzed further in terms of the kinetics of frying oil to ethyl esters. As mentioned earlier, the model is based on overall reaction. This reaction is assumed to proceed in the first order reaction as a function of the concentration of non-ethyl esters (NEE) and reaction temperature Kusdiana (2001)

$$\text{Rate} = -\frac{d[\text{NEE}]}{dt} \tag{3}$$

$$-\frac{d[\text{NEE}]}{dt} = k[\text{NEE}] \tag{4}$$

Assumed the initial concentration of NEE at time t=0 is [NEE, 0], and at t=t is [NEE, t], where [NEE, 0] > [NEE, t]. The integration gives:

$$-\int_{\text{NEE,O}}^{\text{NEE,t}} \frac{d[\text{NEE}]}{[\text{NEE}]} = k\int_{0}^{t} dt \tag{5}$$

$$-\mathrm{Ln}\frac{[\mathrm{NEE},t]}{[\mathrm{NEE},0]} = kt \qquad (6)$$

Where [UEE] include concentration triglycerides, diglycerides, and monoglycerides and unreacted free fatty acids. At the figure 2 shows the correlation between experimental data and reaction time. The experimental data were approximate to a model first order was assumed.

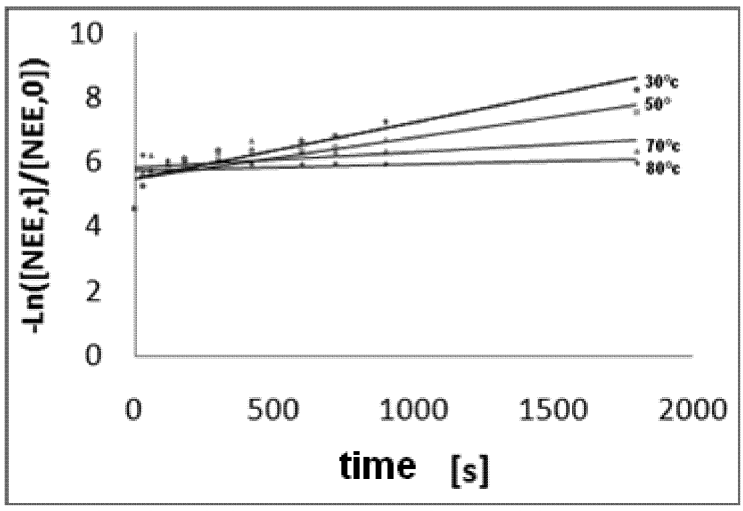

Fig. 2.Plot.of unethyl esters content in frying oil during transesterification reaction.

The rate constants values obtained in each temperature are the table 1. Can be determined the value of the global energy activation of the transesterification reaction through the equation the Arrhenius (7) for determining and Ea, in this study was obtained Ea= 57.50 kJ / mol.

$$k(t) = Ae^{-\frac{Ea}{RT}} \qquad (7)$$

Table 1. Rate constants for frying oil ethanolysis.

k (s^{-1})	T(°C)	R^2
0,00127	30	0,9809
0,00172	50	0,9444
4,95E-4	70	0,9271
2,99E-5	80	0,8598

An unusual event is observed with the values of the kinetic constants which occurs when increasing the reaction temperature (≥70°C) and is due to the presence of parallel react that occur in the transesterification reaction.

3.3. Purification biodiesel and glycerin

In the next step, excess alcohol was removed by a vacuum distillation route evaporator at 80º C, later two phases separation (esters and glycerol) is getting in a decantation funnel. After that, the esters phase was washed whit acidified water to retire catalyst traces, glycerol, alcohol and other impurities presents in biodiesel, then sodium sulfate is added to remove much water like as possible. Finally, biodiesel is distillated in a molecular distiller.
Glycerine from biodiesel production process is contaminated with water, monoglycerides, diglycerides, salt, soap, catalyst residues and some residues of esters. This product is purified by various techniques. After neutralization the product was purified using two techniques, after neutralization the product was purified using two techniques, is first passed through a column activate carbon which allows the adsorption of impurities in the glycerine and removal yellowing characteristic of neutralized glycerin. The second technique used was the vacuum distillation (molecular distillation), in which the degree of purification of glycerol is much higher reaching almost to a level of use in the pharmaceutical industry.

4. Conclusions

In reaction to higher temperatures, 70°C and 80 ° C, there was a rapid increase in the conversion of esters to TG in a short reaction time, reaching their highest values of conversion, but after that the reactions are stabilized and conversions decrease. Besides the maximum conversion at these temperatures are below those conversions were obtained at temperatures of 30°C and 50 ° C. Obtained the following equation for the reaction of biodiesel production from waste frying oil Ln(k) = 28,764 – (696,0615 / T). Equation shows that in some points a correlation factor of 0.9.

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