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Influence of Variables in the Purification Process of Castor Oil Biodiesel

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Biodiesel is a fuel alternative to petroleum diesel, usually obtained by transesterification, which is the reaction of vegetable oils or animal fat with a short chain alcohol in the presence of a catalyst. After the reaction, the biodiesel is purified through a washing process for removing impurities. The washing experiments of castor biodiesel were performed according to the complete factorial design 2^3. The variables studied were: temperature, pH of wash water, and catalyst (NaOH or KOH). The criterion used to define the best process condition was the minimum amount of water needed to wash the biodiesel. Analyzing the effects of the variables and of their interactions in the experimental procedure, the conditions that favored the minimum consumption of wash water was the acidic pH. The temperature and the catalyst type showed negligible significance for the study during the purification of biodiesel castor.

1. Introduction

The biodiesel can be obtained by transesterification of vegetables oils in the presence of mono-alcohol short chain. This reaction can be catalyzed by species that act as bases or acids of Brösnted and constitute the so-called conventional catalysts (Schuchardt et al., 1998). Best yields of the transesterification of oils or fats are obtained using sodium hydroxide or potassium as catalysts (Furuta et al., 2006).
The total or partial substitution of fossil fuels (diesel), always had a environmental appeal, since those emissions from its use generates an increase in atmospheric concentration of greenhouse gases, acid rain and reduction of the ozone layer (Mothé *et al.*, 2005; Vasconcelos, 2002).
One of the most used process to obtain biodiesel is the transesterification . It consists in the displacement of a tri-alcohol mono-alcohol by short-chain triglycerides in transforming a mixture of mono-esters of fatty acids, widely known as biodiesel, Figure 1.
In the transesterification process is commonly used alkaline homogeneous catalysis because of its greater speed, simplicity and efficiency. The main limitation is the requirement of reagents with a high degree of purity, due to the fact that the presence of water or free fatty acids under alkaline conditions promote the production of soap (saponification reaction), hindering the formation of products (Zhang *et al.*, 2003).

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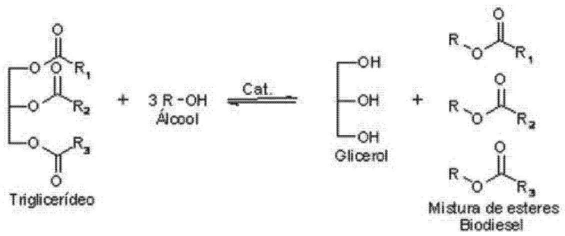

Figure 1: Global reaction of transesterification for biodiesel production.

By virtue of its reversible reaction, it is necessary to use an excess of reagents in the reaction (alcohol) to promote the formation of the desired product, in particular biodiesel (Fukuda *et al.*, 2001). However, even with excess alcohol, various intermediates are generated in parallel with the formation of ethyl esters, as well as oil, alcohol and catalyst that was not reacted.

To remove these impurities it is necessary purifying the biodiesel which basically consists of three steps: phase separation, washing and drying. The rotary evaporator was used for phase separation. Biodiesel and glycerin are separated through the evaporation of alcohol. In the washing step are removed the impurities as catalyst, excess of alcohol used in the reaction, residual free glycerin, salts of fatty acids and tri-, di-and monoglycerides. The drying step, which is the absorption of water in the biodiesel phase, was realized through adding magnesium sulfate as secant agent (Faccio et al., 2004).

This work aims to study the process extraction applied to the purification of ethyl esters of castor oil biodiesel, produced by alkaline transesterification of castor oil with anhydrous ethanol, by the washing with water at different temperatures and pH. The experiments were realized based on a full factorial experimental design 2^3, with repetition. The washing was finished when the biodiesel solution presented pH equal to 7, ensuring the neutralization of the alkaline catalyst used in the process. Then, we determined the total volume of water used in washing process

2. Methodology

In this section will be described the process of biodiesel production, the experimental design and the process of biodiesel purification.

2.1 Biodiesel production

The production of castor biodiesel was carried through the alkaline alcoholysis of castor oil, using two types of catalysts NaOH and KOH, according to the methodology Zagonel et al. (2003). The reaction was performed in the pilot plant shown in Figure 2.

For the reaction, the oil was placed in the reactor and it was heated to the desired temperature (70°C), which was maintained with the aid of a thermostat bath. Then, it was added to the reactor, a mixing of alcohol and catalyst (sodium or potassium ethoxide), the reaction temperature, starting the reaction shaken at 400 rpm, during two hours. The ethyl esters and glycerol were obtained with 98% of biodiesel conversion, been the biodiesel phase used for washing process study.

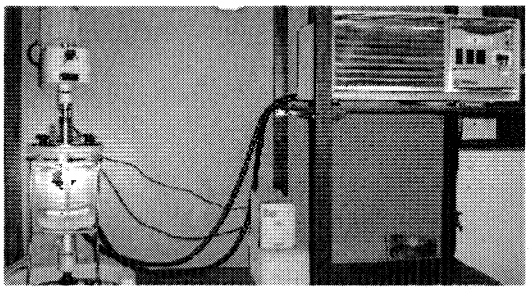

Figure 2: Pilot plant of biodiesel production.

2.2 Experimental design

It was used a complete factorial design without replications with two levels and three variables by method of Neto *et al.* (2003), to determine the experimental conditions that minimize the amount of water used in washing for biodiesel purification. The choice of the ranges of variables was determined by preliminary studies, and was adopted the following limits of ranges: temperature between 30 to 70°C; pH of the water washing between 2 and 5; and, NaOH and KOH as catalysts used in reaction.

The Table 1 presents the experimental matrix to the factorial design, where the level -1 represents lower limit, whereas the level +1 represents the upper limit of each variable.

Table 1: Experimental matrix of the factorial design 2^3 utilized in castor oil biodiesel purification

Test	pH	Temperature(°C)	Catalyst
1	2/-1	30/-1	A/NaOH
2	5/+1	30/-1	A/NaOH
3	2/-1	70/+1	A/NaOH
4	5/+1	70/+1	A/NaOH
5	2/-1	30/-1	B/KOH
6	5/+1	30/-1	B/KOH
7	2/-1	70/+1	B/KOH
8	5/+1	70/+1	B/KOH

2.3 Castor biodiesel purification

To perform the experimental matrix, it was used an initial mass of approximate 70g of castor biodiesel, for each test. After the weighing, the biodiesel was decanted in a decanting funnel. In the first wash was added acid water (pH determined on Table 1, according to the test number) at ratio of 1/4 of biodiesel mass. The mix was stirred and left to stand until the complete separation of phases.

Held separation, the pH of the lower phase (wash water) was determined. To obtain the minimum amount of water needed to neutralize the biodiesel in the next washings were used half the amount of wash water before.
After the second wash, the phase separation was performed by centrifugation at a speed of 2000 rpm for 10 minutes. When it reached the pH equal to 7, washing the biodiesel was completed and was added magnesium sulfate as drying agent. At the end, the total water quantity was computed.

3. Results and Discussions

The results obtained from the experimental matrix are shown in Table 2. In this table, V_a and M_b represent respectively the volume of water (mL) and the mass of biodiesel (g). The washing process was realized in duplicate. The results are shown in the last two columns of this table.

Table 2: Results of the purification of castor biodiesel

Test	pH	Temperature(°C)	Catalyst	V_a / M_b	
				Experiment 1	***Experiment 2***
1	2/-1	30/-1	A/NaOH	0.4416	0.4028
	5/+1	30/-1	A/NaOH	0.6383	0.6719
3	2/-1	70/+1	A/NaOH	0.3992	0.4496
4	5/+1	70/+1	A/NaOH	0.5024	0.4722
5	2/-1	30/-1	B/KOH	0.2269	0.2890
6	5/+1	30/-1	B/KOH	0.7324	0.7844
7	2/-1	70/+1	B/KOH	0.1941	0.2523
8	5/+1	70/+1	B/KOH	0.8627	0.8338

The variables effects pH, temperature, type of catalyst and the standard error are presented in Table 3. In this table, the column effect represents the percentage of increase (+) or decrease (-) of the amount of water required per gram of biodiesel to neutralize the environment, referring to the maximum and minimum range, corresponding to variable. Therefore, if the pH increase from 2 to 5, the amount of water used for washing the biodiesel will increase an average of 0.3553 mL per gram of biodiesel, being the average consumption of wash water per gram of biodiesel 0.5096.
In Table 3 the only variable that really influences the volume of wash water is pH, since the effects produced by temperature and type of catalyst are lower than the error and it is necessary at least 3 degrees of freedom for the study, Statistical effects were not considered iteration. The Pareto diagram, Figure 3 graphically represents the results obtained. It is possible to observe the greater influence pH in the process. The analyzed response (water amount) decreases when the pH decreases from 5 to 2.

Table 3: Responses from the experiments design

Factors	Variables	Effects	Standard deviation
pH	X_1	0.3553	0.116
Temperature	X_2	-0.0276	0.116
Catalyst	X_3	0.0247	0.116
pH x Temperature	$X_1 x X_2$	-0.0114	0.116
pH x Catalyst	$X_1 x X_3$	0.2074	0.116
Temperature x Catalyst	$X_2 x X_3$	0.0552	0.116

In Table 3 the variable that most influences the volume of wash water is pH, followed by the variation caused by the effect of pH *x* Catalyst, the Catalyst *x* Temperature effect shown a slight variation. The Pareto diagram, Figure 3 graphically represents the results obtained. It is possible to observe the greater influence pH in the process. The analyzed response (water amount) decreases when the pH decreases from 5 to 2.

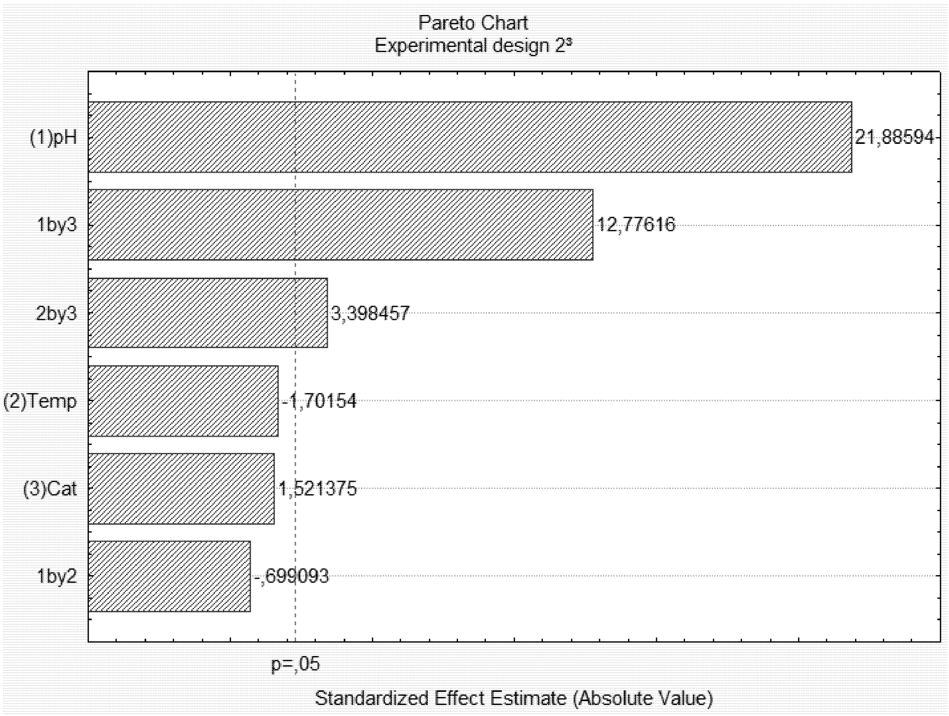

Figure 3: Responses from the design of experiments

The Equation 1 represents the model that determines the amount of water needed in the washing process of castor biodiesel using coded variables, obtained by the coefficient of the significant effect using as support the software Statistica 7.0.

$$Q = 0.5096 + 0.1777\, X_1 + 0.1037\, X_1 .\, X_3 + 0.0276\, X_2 .\, X_3 + \varepsilon_o \quad , \qquad (1)$$

Q is water amount (mL) / biodiesel mass (g); X_1, X_2 and X_3 represent pH, temperature and catalyst, respectively; and, ε_o is error (ε_o = 0.00105). The third and fourth term represent the interactions between the variables.

4. Conclusion

In this study, the most significant effect was the pH. The effects of the others variables (temperature and catalyst type) are insignificant. The pH exerts a considerable influence on the process of neutralization of the catalyst present in castor biodiesel, and the increase in pH increases the amount of wash water.

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