Eclética Química
ISSN: 0100-4670
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Universidade Estadual Paulista Júlio de Mesquita Filho
Brasil

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Production of biodiesel from babassu oil using methanol-ethanol blends
Eclética Química, vol. 35, núm. 1, 2010, pp. 47-54
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Resumo: Um método "spot-test" qualitativo e seqüencialmente quantitativo é proposto para análise de dipirona em fármaco "puro" e em preparações farmacêuticas. A formação de coloração vermelho-violeta indica um resultado qualitativo positivo. Na seqüência, um procedimento quantitativo pode ser realizado no mesmo frasco. Os resultados quantitativos obtidos foram comparados estatisticamente com os resultados obtidos pelo método indicado pela Farmacopéia Brasileira, utilizando o teste ***t*** de Student e o teste ***F***. Considerando a concentração em uma alíquota de 100 µL, o limite qualitativo visual de detecção foi de cerca 5×10^{-6} g; instrumentalmente o limite de detecção foi de LOD $\cong$ 1.4×10^{-4} mol L^{-1} e o limite de quantificação de LOQ $\cong$ 4.5×10^{-4} mol L^{-1}.

Palavras-chave: dipirona, spot-test, análise, qualitativa, quantitativa

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phic location and agricultural tradition. A big part of such production can be transformed in the biodiesel fuel.

Biodiesel is defined as a fuel composed of alkyl esters of long chain fatty acids, derived from vegetable oils or animal fats [7,8]. This fuel can be used in any diesel cycle engine, without the need of adaptations.

Owed to technical and economic reasons, the industries use more often methanol (MeOH) in the biodiesel production process. However, this alcohol presents several drawbacks, such as its high toxicity, being synthesized from non renewable sources, besides the fact that Brazil is not auto-sufficient in its production [9].

Although ethanol has a higher cost per ton, the biodiesel production by means of the ethanol route is attractive under the strategic standpoint, as Brazil is the biggest ethanol producer in the world. As for the environmental aspects, ethanol is not toxic and since it is produced from renewable sources, the whole biodiesel is 100% renewable [10,11].

One of the ways of combining the technical and economic advantages of methanol with the environmental advantages of ethanol is to obtain biodiesel from a blend of these alcohols. Therefore, the proposal of this work was the improvement of the transesterification process of degummed, neutralized and clarified babassu oil, using blends of different proportions of these alcohols with homogeneous catalysis [12].

II. Experimental

The reagents utilized were: commercial clarified babassu oil (OLEAMA), anhydrous ethanol (Petrobrás Distribuidora), methanol P.A. (Quimis) and potassium hydroxide 85 % (Quimis) as catalyst. The raw materials were analyzed following the Standard Methods for the Analysis of Oils, Fats and Derivatives (SMAOFD). For the characterization of the methyl/ethyl biodiesel from babassu were utilized the standards from the Brazilian Association of Technical Standards (ABNT) and the American Society for Testing and Materials (ASTM), indicated in the Resolution number 42 of the Brazilian National Petroleum Agency (ANP) [7].

In the experiments, were utilized a pHmeter Quimis model Q400M2, a mechanical stirrer and a gas chromatograph VARIAN CP 3800.

The procedure for the transesterification reaction starts by dissolving KOH in the methanol/ethanol blend, under stirring at room temperature. Next, add to this solution 100 g of oil under stirring and allow the reaction up to the phase separation. Remove the alcohol excess by distillation under reduced pressure. Transfer the mixture of esters and glycerin to a separatory funnel and allow settling for 12 hours. Afterwards, separate and weigh both phases and wash the biodiesel, using the air bubbling technique. For the first washing, utilize a 0.1 M HCl solution, followed by washings with water until reaching the pH 7.0. Dry the biodiesel in an oven at 100 ºC for 3 hours, allow cooling and weigh, for further physico-chemical tests.

III. Results and discussion

The best reaction conditions to obtain methyl and ethyl babassu biodiesel were determined by Silva and Brandão: oil/methanol molar ratio of 1:4.6, KOH content of 1.5 %, 30 min of reaction time, stirring of 1760 rpm and room temperature [13]. Using the methanol mass as reference, several MeOH:EtOH ratios were investigated, aiming at the optimization of the babassu oil transesterification process. Table 1 presents the percentages and volumes of the alcohols used in the babassu oil transesterification reactions.

Table 2. Influence of the ethanol/methanol ratio on the yield and ester percentages of babassu biodiesel

$\%_{EtOH}$	$\%_{MeOH}$	$t_{reaction}$	$\%_{mBP}$	$\%_{E}$
0	100	30 min	95.32	98.84
10	90		91.70	97.17
$_{2}0$	80		95.32	98.70
30	70		93.70	98.18
$_{4}0$	60		92.29	98.44
50	50		84.26	96.77

PB: Pure biodiesel
m_{PB}: Mass yield of pure biodiesel
E: $Ester_{s}$
m_{E}: Ester content

The separation of the biodiesel/glycerin mixture does not occur spontaneously using ethanol percentages higher than 50%, even with the removal of the alcohol excess by means of distillation under reduced pressure. It was observed that the mass yield of pure biodiesel tends to diminish with the increase of the ethanol proportion in the blend, due to the difficulty of the biodiesel/glycerin separation.

In Figure 2 shows the influence of the ethanol percentage of the methanol/ethanol blends on the ester content and the mass yield of pure biodiesel, for a fixed reaction time of 30 min.

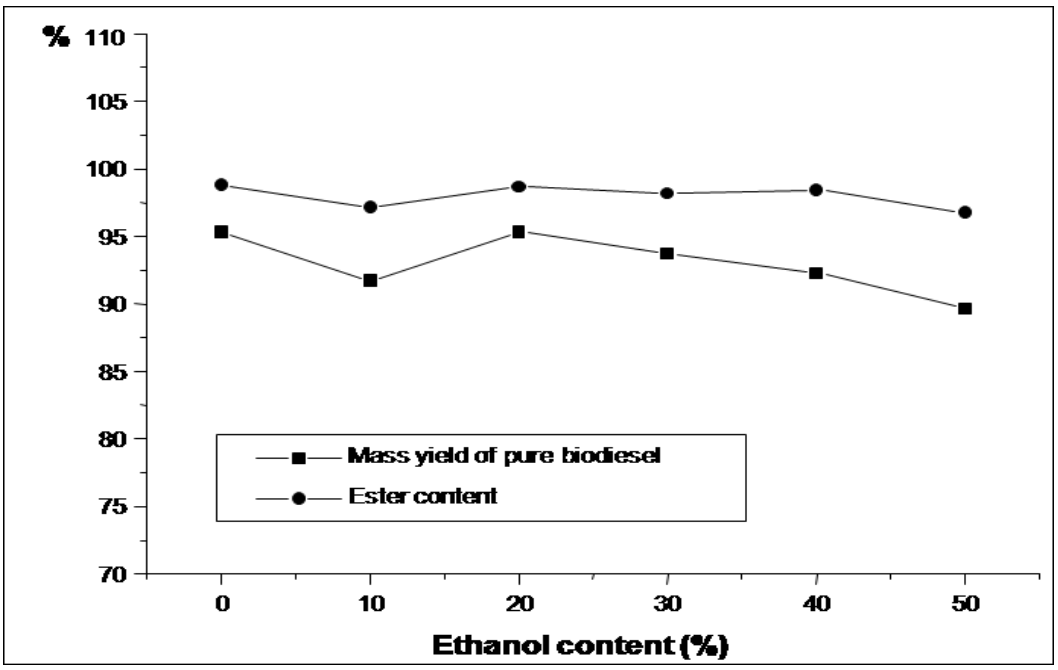

Figure 2. Influence of the MeOH:EtOH ratio on the ester content and on the mass yield of pure biodiesel, for a reaction time of 30 min.

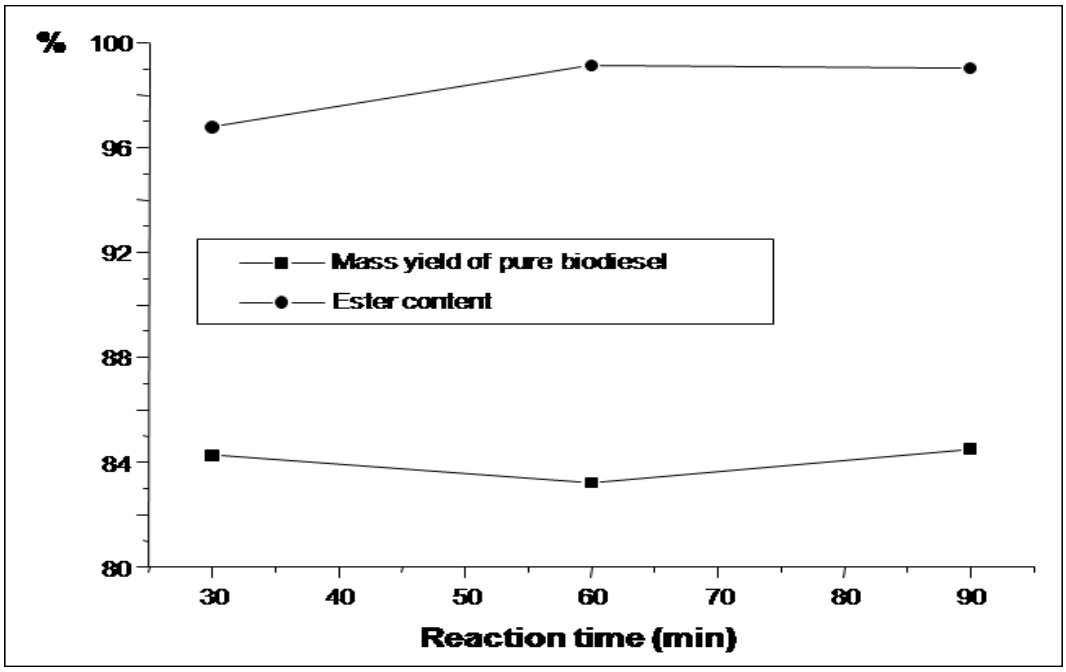

Figure 3. Influence of the reaction time on the mass yield of pure biodiesel and the ester content.

As for the physico-chemical properties, the babassu oil was analyzed utilizing SMAOFD [14] methods and the methyl/ethyl biodiesel analyses employed ASTM and ABNT standards. Table 4 shows the results of some physico-chemical tests of the biodiesel sample obtained with the 80:20 methanol/ethanol blend, as well as the specification limits of the standards.

IV. Conclusions

The following reaction conditions were shown to optimize the biodiesel production from the transesterification of babassu oil with a blend of alcohols: methanol/ethanol ratio of 80% MeOH : 20% EtOH and 30 minutes of reaction time. With these conditions, a biodiesel mass yield equal or higher than 95.32 % was obtained and also an ester content of 98.70 % was achieved, thus meeting the specification of the ANP. It was also observed that it is possible to utilize an ethanol/methanol mass ratio of 50:50, provided that the reaction time is of 60 minutes, in order to obtain satisfactory ester contents (98.13 %). The samples of biodiesel produced with the 80% MeOH:20%EtOH blend meet the specifications required by ANP, taking into account the physico-chemical tests listed in Table 4.

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