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Evaluation of the Potential of Ethyl Esterification Reaction Catalyzed by the Enzyme to Improvement the Quality of Bio-Oil

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INTRODUCTION

The National Agency of Petroleum, Natural Gas and Biofuels (ANP) in Brazil prioritizes seven segments, including biofuels, with emphasis on the development of new fuel products. Bio-oil is a renewable liquid fuel obtained by thermal cracking of biomass at high temperature. Its properties vary according to processing conditions, ad it resembles petroleum. To determine its quality, the commonly investigated properties are specific mass, viscosity, calorific value, iodine value and acid value. The acid number can be reduced by several processes, including the addition of antioxidants and esterification with enzyme catalysts such as immobilized lipases. This last process has not yet been reported in the literature.

METHODOLOGY

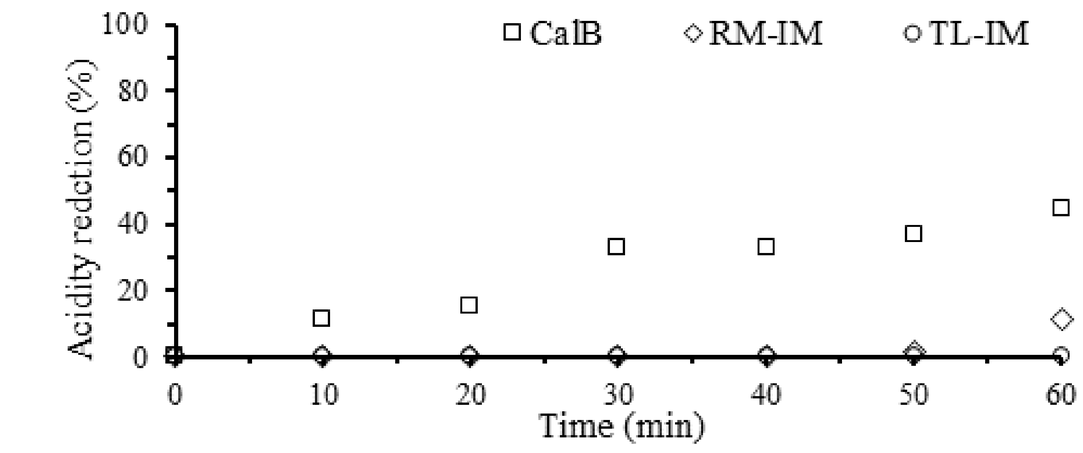
Esterification reactions were conducted in 10 mL screw-capped flasks containing 5% by mass in relation to the bio-oil, 5 g of de bio-oil and 1.5 g of ethanol mass ratio 3:1 (bio-oil to ethanol). In these experiments, we evaluated three different enzymes: Novozym 435 (CalB), *Rhizomucor miehei* (RM-IM) and *Thermomyces lanuginosus* (TL-IM). The reaction medium was incubated on a rotary shaker at 200 rpm and 40 °C at 60 min. At fixed intervals of 10 min, 100 µL samples of the mixture were removed and analyzed for acidity index (AI). The AI of bio-oil was performed according to ASTM D 974

The lipase that stood out in the previous step was used as catalysts. The independent variables evaluated were the concentration of commercial immobilized lipase (E), the Novozym 435 (1%, 3%, 5% by mass in relation to the bio-oil), mass ratio (RM) (a bio-oil to ethanol - 1:3, 1:6, 1:9) and time (t) (2 h, 4 h, 6 h), the response variable was the percentage AI reduction at the end of the esterification reaction.

RESULTS AND DISCUSSION

The bio-oil obtained from thermal cracking of soybean oil present an updated acid index of 139.6 mg KOH/g. Lipases were used to the reduction of AI of bio-oil on the ethylic esterification reaction. The results of AI of bio-oil obtained of its esterification catalyzed whit three different immobilized enzymes, Novozym 435, *Rhizomucor miehei* (RM-IM) and *Thermomyces lanuginosus* (TL-IM) as shown in Figure 1.

Figure 1. Profile of acid index of bio-oil catalyzed by the lipases on the ethyl esterification reactions. Reaction conditions: 5% of enzyme (wt.%: wt.%) (250 mg) in 5 g of bio-oil and 1.5 of ethanol mass ratio 3:1 (bio-oil to ethanol, at 40°C and 200 rpm.



The bio-oil with the best result used Novozym 435 as catalysts and presented reduction AI of 44% at 1 h reaction. At time zero, the AI of the reaction medium containing lipase Novozym 435 was 75.75 mg of KOH/g of sample and at the end of the reaction this value decrease to 41.92 mg of KOH/g of sample. Meanwhile, the RM-IM enzyme showed a reduction of only 11%, lowering its acid value from 91.93 to 81.64 mg KOH/g of sample, and the TL-IM showed no reduction. The Table 1 shows the real and coded values of the independent variables and the experimental percentage index acidity reduction.

Table 1. Experimental conditions and results according to 2^3 factorial design experiment used for improvement of the esterification of the bio-oil.

Run	Conditions			AI reduction (%)
	E[a] (wt %)	RM[b]	t[c] (h)	
1	1 (-1)	1:3 (-1)	2 (-1)	22.1
2	1 (-1)	1:9 (+1)	2 (-1)	3.7
3	5 (+1)	1:3 (-1)	2 (-1)	58.3
4	5 (+1)	1:9 (+1)	2 (-1)	21.2
5	1 (-1)	1:3 (-1)	6 (+1)	28.9
6	1 (-1)	1:9 (+1)	6 (+1)	46.4
7	5 (+1)	1:3 (-1)	6 (+1)	59.6
8	5 (+1)	1:9 (+1)	6 (+1)	29.8
9	3% (0)	1:6 (0)	4 (0)	43.7
10	3% (0)	1:6 (0)	4 (0)	36.0
11	3% (0)	1:6 (0)	4 (0)	36.0

a: enzyme concentration (Novozym 435); b: mass ratio (bio-oil:ethanol); c: time of the esterification.

The difference obtained between runs 7 (greater reduction in acidity) and experiment 2 (lesser reduction in acidity) was 93%, which confirms the relevance of the factors chosen for analysis.

CONCLUSION

With the ethyl enzymatic esterification reaction was possible to reduce the acidity index. Novozym 435 lipase was the enzyme that presented the best performance in the esterification reactions. With the 2^3 factorial design, it was possible to identify that the condition that most contributed to the reduction of the acidity index was ethyl esterification at 40°C with a catalyst concentration of 5% and mass ratio (1:3), with reduction of AI 60% of the initial acid value after 6 h reaction.

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