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Biodiesel Production from Integration Between Reaction and Separation System: Reactive Distillation Process

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Abstract 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 carbon monoxide, sulfur dioxide, and unburned hydrocarbons than petroleum-based fuel. The purpose of the present work is to present an efficient process using reactive distillation columns applied to biodiesel production. Reactive distillation is the simultaneous implementation of reaction and separation within a single unit of column. Nowadays, it is appropriately called "Intensified Process". This combined operation is especially suited for the chemical reaction limited by equilibrium constraints, since one or more of the products of the reaction are continuously separated from the reactants. This work presents the biodiesel production from soybean oil and bioethanol by reactive distillation. Different variables affect the conventional biodiesel production process such as: catalyst concentration, reaction temperature, level of agitation, ethanol/soybean oil molar ratio, reaction time, and raw material type. In this study, the experimental design was used to optimize the following process variables: the catalyst concentration (from 0.5 wt.% to 1.5 wt.%), the ethanol/soybean oil molar ratio (from 3:1 to 9:1). The reactive column reflux rate was 83 ml/min, and the reaction time was 6 min.

Keywords Biodiesel · Ethyl esters · Reactive distillation · Transesterification

Introduction

Biodiesel has become increasingly attractive due to its environmental benefits and to the fact that it is made from renewable resources. The remaining challenges are its cost and limited availability of fat and oil resources [1]. The transesterification process can be described as the triglycerides reaction with an alcohol and catalyst to obtain a fatty acid ester mixture as the main product and glycerol as by-product. The alcohols that can be used

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in the transesterification reaction are aliphatics, having only primary or secondary OH group and from one to eight carbon atoms. Methanol and ethanol are the main alcohols [2]. The catalyst employed at this process can be enzymatic (lipases: *Candida*, *Pseudomonas*), homogeneous acids (H_2SO4, HCL, H_3PO_4), heterogeneous acids (zeolites, sulfonic resins), heterogeneous bases (MgO, CaO), or homogeneous bases (KOH, NaOH), the latter being commonly used at industrial scale because it enables operation at moderate conditions and it gives a shorter reaction time. An alternative to transesterification of raw materials with higher free fatty acids is the pre-esterification with an acid catalyst followed by transesterification with a basic catalyst [3, 4].

An important alternative for making the biodiesel production process more attractive is to take advantage of the process intensification characteristics. Process intensification (PI) is defined as any chemical engineering development that leads to a substantially smaller, cleaner, and more energy- and production-efficient technology [4]. In this contribution, the PI technique is going to be applied to biodiesel production by using homogeneous reactive distillation process.

Reactive distillation (RD) is the process in which chemical reaction and distillation separation are carried out simultaneously within a fractional distillation apparatus. It may be advantageous for liquid-phase reaction systems when the reaction must be carried out with a large excess of one or more of the reactants, when a reaction can be driven to completion by removal of one or more of the products as they are formed, or when the product recovery or by-product recycle scheme is complicated or made infeasible by azeotrope formation [5].

The reactions that can participate in RD process can be thermal (non-catalyst), heterogeneous, or homogeneous catalyzed. In nearly all cases, reactions take place in the liquid phase, but reactions taking place in the gas phase and locate the catalyst in the vapor phase are conceivable. Indeed, the reaction and distillation combination is only possible if the conditions of both unit operations can be combined. This means that the reactions have to show reasonable data for conversions at pressure and temperature levels that are compatible with distillation conditions [5–7].

When this occurs, benefits can be obtained for applying reactive distillation process. Some of those are: elimination of conversion limitations by continuous removal of products from the reaction zone (for equilibrium-limited reactions) and reduction in capital investment because two process steps can be carried out in the same device. Such integration leads to lower costs in pumps, piping and instrumentation, and heat integration. If the reaction is exothermic, the heat of reaction can be used to provide the heat of vaporization and, so, the reboiler duty is reduced. Also, azeotrope formation can be avoided. Other characteristics can be described: RD conditions can allow the azeotropes to be “reacted away” in a single vessel; reactive distillation involves smaller equipments and minor number of them and, thereby, lesser number of connections between equipments. The process requires lesser safety measurements. In reactive distillation, the heat of reaction is removed by evaporation. A higher reaction rate means a higher evaporation rate, but the reaction temperature changes very little. Runaway behavior of a reactive distillation is therefore, in general, less severe than of a conventional reactor [7–9].

In recent literatures, many works about reactive distillation can be found. Chemical esterification is the major area. Wang et al. [10] studied the feasibility of reactive distillation application to the methyl acetate hydrolysis process. The results suggest that energy consumption can be reduced by 10% and the production capability can be increased by 50% compared with a conventional fixed-bed reactor. Calvar et al. [11] investigated the reaction kinetics of acetic acid esterification with ethanol, both homogeneously and heterogeneously. In addition, the influence of feed conditions and reflux ratio on the reactive column distillation was studied. Bhatia et al. [12] proposed a technically optimized reactive distillation process for the production of isopropyl palmitate by palmitic acid esterification with isopropanol based on the experimental and simulation results attaining very high conversions. Lai et al. [13] worked at experimental production of high-purity ethyl acetate using reactive distillation in a pilot-scale plant obtaining purity about 99.5 wt.%.

Steinigeweg et al. [14] developed a technically optimized reactive distillation process for the production of decanoic acid methyl esters by esterification of the fatty acid decanoic acid with methanol, based on experimental and simulation studies ensuring conversions about 100%.

He et al. [15] explored the biodiesel production by reactive distillation from canola oil and methanol using potassium hydroxide as catalyst. The results showed that a high conversion could be achieved along with a substantial decrease in production time and alcohol excess. This excess alcohol reduction is desirable because it causes reduction of downstream alcohol recovery and, therefore, reduction in equipment and operating costs.

Novel processes were proposed based on catalytic reactive distillation and reactive absorption to biodiesel production from esterification and transesterification reactions. The major benefits of this approach were: investment costs reducing about 45% energy savings compared with conventional reactive distillation, very high conversions, increased unit productivity, no excess of alcohol required, and no catalyst neutralization step [16, 17].

Experimental Procedure

Materials

The experiments were carried out with refined soybean oil obtained by supermarket (Brazil). The sodium hydroxide (Synth-Brazil) was used as catalyst. All the standards were supplied by Sigma-Aldrich Chemical Company, Inc. (St. Louis, MO, USA).

Equipment

The RD process was carried out in a semi-batch system. The equipments of RD system are listed in Fig. 1. The RD column used in this process was a packed column filled with glass rings and equipped with water condenser, temperature controller, and reflux controller. The system design was based on the relative volatilities of the raw materials and products. The reactants were lighter-than-light (LLK; ethanol) and heavier-than-heavy (HHK; soybean oil) keys, and the products were light (LK; ethyl esters) and heavy (HK; glycerol) keys. The mixture between LLK and HHK is very difficult because a large amount of reactants can hardly coexist in the liquid phase. This is the worst scenario for the forward reaction (extremely favorable for the backward reaction). This description was presented by Tung [18].

Equipment description:

1. T-01: ethanol tank of 1 l
2. T-02: soybean oil tank of 1 l
3. R-01: pre-reactor (speed of 400 rpm; reaction time of 1 min)
4. C-01: packed reactive distillation column of 2 l
5. E-09: reboiler of 2 l
6. E-08: water-cooled condenser
7. E-11: ester/glycerol separator of 2 l
8. E-12: ester (biodiesel) tank of 1 l
9. E-13: glycerol tank of 500 ml

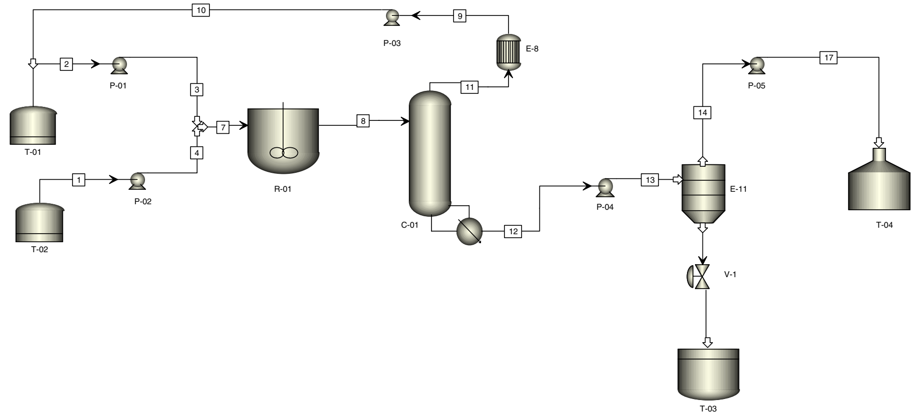

Fig. 1 Reactive distillation system

Experimental Conditions and Procedures

In the start up of RD system, the ethanol (400 ml) was fed to the reboiler (three-neck flask with mantle) by a peristaltic pump. The heating rate of reboiler was set to maintain the ethanol reflux rate at the top of the column. After, approximately 20 min, the vapor of ethanol reaching the top of the column at 78 °C is totally condensed. The resulting liquid was refluxed in order to moisten all glass rings; the reflux was maintained during 30 min. The reactions were carried out in a semi-continuous RD system equipped with water condenser. The first stage is a pre-reactor. This equipment is filled with soybean oil and heated to 50 °C. The sodium hydroxide and ethanol were mixed in a glass tank with magnetic stirrer; after that, this mixture was transferred to the pre-reactor. The pre-reactor is equipped with a water condenser to prevent the ethanol losses and a mechanic stirrer (400 rpm).

The reaction starts when the ethanol is filled in the pre-reactor by a peristaltic pump. After 1 min, the mixture is transferred to the RD by a peristaltic pump. A liquid distributor was used to guarantee the uniform RD feed. The raw material feed (Q_{feed}) is 250 ml/min, and the reflux flow rate (Q_{reflux}) is 83 ml/min. The $Q_{\text{reflux}}=1/3$ (Q_{feed}) was selected based on previous experiments. The total reaction time is 6 min, 1 min in the pre-reactor, and 5 min in the RD. After the reaction, the product mixture was withdrawn from the reboiler to the separator funnel, and two phases were formed, the ester and the glycerol layers. In order to remove the residue from raw materials and the catalyst, the ester layer was washed and dried. The glycerol layer was purified using a high vacuum distiller (through a patent process). This RD is semi-continuous because, after reaction, it is necessary to clean up each part of the system because the presence of reactant traces promotes low ester conversion.

During the reaction, samples were taken at the bottom of the column. The samples were prepared through the dilution of 0.1 g of the reaction product in 10 ml of tetrahydrofuran (THF). Then, the samples were filtered using a PTFE filter (polytetrafluorethylene) and analyzed in the high-performance size-exclusion chromatography (HPSEC).

Methods of Analyses

Gas Chromatography The raw material compositions were determined by gas chromatography equipped with a flame ionization detector and with a DB 23 column. The fatty acid compositions of the vegetable oils were determined by gas chromatography (GC), according to Hartman [19]. Injector and detector temperatures were set at 250 °C and 300 °C, respectively. The carrier gas used was helium at 46 ml/min. Air and hydrogen flow rates were 334 and 34 ml/min, respectively. Oven temperature programming was as follows: starting at 50 °C for 2 min; from 50 °C to 180 °C at 10 °C/min; 180 °C was held for 5 min; from 180 °C to 240 °C at 5 °C/min. Identification of different FAEEs were based on a reference standard (Sigma-Aldrich).

Liquid Chromatography The biodiesel compositions were determined by gel-permeation chromatography (Waters, USA) also called HPSEC. The Shoenfelder [20] methodology is specific for analyses of triglycerides (TG), diglycerides (DG), monoglycerides (MG), and glycerol (GL); nevertheless, this methodology was adapted to the analyses of esters (EE) because the ester peak appeared between the MG and the GL peak. The mobile phase was HPLC-grade THF (B&J/ACS, USA). The relative percentage of each component (x_i) was given through HPSEC, and it was determined by Eq. 1, where x_i was calculated dividing the peak area of the ester by the sum of the peak areas of all components. The x_i is the ester concentration. The ester conversion (E) was determined according to Eq. 2, C_0 is the soybean oil concentration (wt.%) at t=0 min, and C_i is the soybean oil concentration at the end of the reaction, and these results were used in the experimental design. The identification of TG, DG, MG, EE, and GL were based on reference standards (Sigma-Aldrich).

$$x_\mathrm{i} = \left(\frac{A_\mathrm{EE}}{A_\mathrm{TG}+A_\mathrm{DG}+A_\mathrm{MG}+A_\mathrm{EE}+A_\mathrm{GL}} \right) \tag{1}$$

$$E = \frac{C_0 - C_i}{C_0} \tag{2}$$

Free Fatty Acids The free fatty acid content was determined according to the AOCS official method Ca 5a-40 as oleic acid.

Experimental Design

The experimental design was chosen to study the optimization of two selected factors: ethanol/soybean oil molar ratio and catalyst concentration.

Two experimental designs were done in order to optimize the catalyst content and the ethanol/soybean oil molar ratio. The first experimental design was a 2^2 plus three central points. The second experiment sequence was a complete experimental design plus three central points and four axial points; the axial points also are called star points [21]. The first experimental design limits were: ethanol/soybean oil molar ratio: from 3:1 to 6:1; catalyst concentration level was from 0.5 to 1.5 wt.%. In order to investigate the influence of a larger ethanol excess on ester concentration, a second experimental design was done with ethanol/soybean oil molar ratio from 3:1 to 9:1. Catalyst concentration level was from 0.5 to 1.5 wt.% according to literature data for other case study [22–24]. The software Statistica (Statsoft, v.7) was used to analyze the results.

Results and Discussion

The soybean oil molar mass was 872 g/mol, according to the GC analysis. The refined soybean oil contained 0.3% of free fatty acids.

The RD column has 43 cm of height and 4 cm of inner diameter. The feed position is at 38 cm measured from column bottom.

The difference between the boiling points at 1 atm of ethanol (78 °C) and the transesterification products [25], soybean ethyl esters (355.24 °C) and glycerol (290 °C), is large. Thus, the separation section necessary to achieve a fast separation of these components is short. The section below the feed position is the reactive zone.

The pre-reactor was used because it permitted a perfect contact of the reactants and the ester conversion at the first minute of the process. This fact is very important in the transesterification reaction because the vegetable oil and ethanol are not soluble, with the exception of the castor oil that is the unique vegetable oil soluble in alcohols [24] but the ester, soluble in both components (vegetable and ethanol). Then, the ester formation permitted the increase of the mass transfer in the reaction [26] and, consequently, higher conversion in the RD system. A study of the use of a pre-reactor was done by He [15], and the best methyl ester conversion, in that study, was obtained with a pre-reactor. Other aspect is the use of a homogeneous catalyst (sodium hydroxide) in the packed column. This type of catalyst is always dissolved in alcohol. Then, if the LLK reactant, ethanol, plus catalyst were fed to the reactive column at the bottom, the alcohol should rise up in the column, but part of the catalyst would not move up because part of the catalyst would precipitate in the column bottom, and this fact leads to low biodiesel conversion.

Table 1 shows the experimental design results, and *E* (weight percent) is the ester conversion at 6 min of reaction. These results were used in the experimental design. The effect of the catalyst content and ethanol/soybean oil molar ratio on the ethyl ester conversion is presented in Fig. 2 (Pareto graph). The linear effect and the interaction between the catalyst concentration and the molar ratio were significant because these effects were shown to the right of the *p* value. This value was used as a tool to check the significance of each effect. The catalyst concentration is the most important variable as shown in Fig. 2. The confidence level was that of 95%.

The second experimental design results were listed in Table 2. Figure 3 shows the Pareto graph, the linear effect, and the interaction between the catalyst concentration and the molar ratio which were significant, because these effects were shown to the right of the *p* value, with confidence level of 90%. This value was used as a tool to check the significance of each effect. The catalyst concentration and the molar ratio had a similar effect as shown in Fig. 3. The increase in catalyst concentration was from 0.5 to 1.5, runs 5 and 6. It promotes an increase of ester concentration from 77.57 to 94.86 wt.%. The increase of molar ratio from 3:1 to 9:1 leads to an increase in ester conversion from 69.91 to 94.73 wt.%.

Table 1 First factorial design of the soybean oil transesterification.

Runs	Variables		*E* (wt.%)
	Catalyst (wt.%)	Molar ratio	
1	0.5 (−1)	3 (−1)	62.36
2	1.5 (+1)	3 (−1)	82.68
3	0.5 (−1)	6 (+1)	89.87
4	1.5 (+1)	6 (+1)	94.54
5	1 (0)	4.5 (0)	90.85
6	1 (0)	4.5 (0)	90.17
7	1 (0)	4.5 (0)	89.70

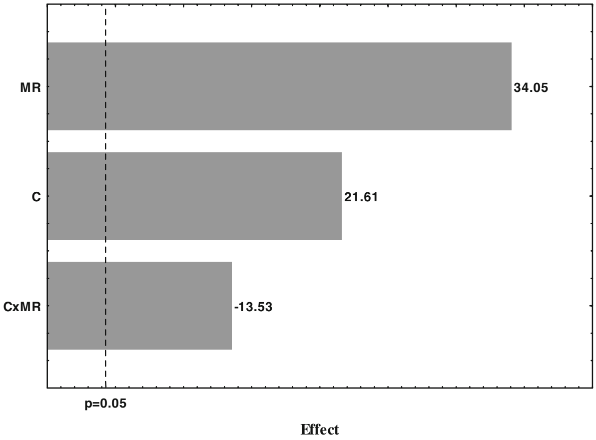

Fig. 2 Effects of catalyst concentration and ethanol/soybean oil molar ratio on soybean oil ethyl esters: first experimental design

Table 2 Second factorial design of the soybean oil transesterification.

Runs	Variables		*E* (wt.%)
	Catalyst (wt.%)	Molar ratio	
1	0.65 (−1)	3.92 (−1)	73.93
2	1.34 (+1)	3.92 (−1)	83.52
3	0.65 (−1)	8 (+1)	98.18
4	1.34 (+1)	8 (+1)	97.19
5	0.5 (−α)	6 (0)	77.57
6	1.5 (+α)	6 (0)	94.86
7	1 (0)	3 (−α)	69.91
8	1 (0)	9 (+α)	94.73
9	1 (0)	6 (0)	91.61
10	1 (0)	6 (0)	91.54
11	1 (0)	6 (0)	91.83

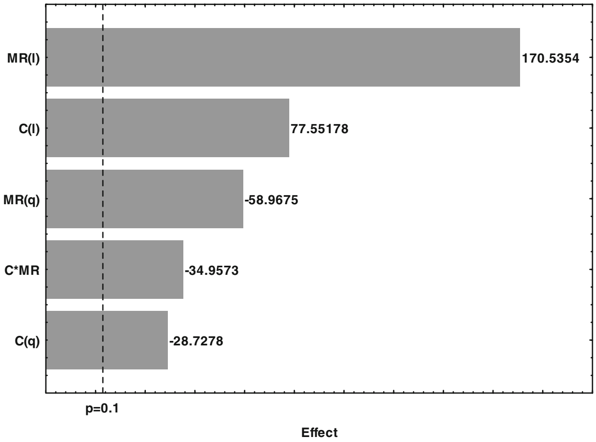

Fig. 3 Effects of catalyst concentration and ethanol/soybean oil molar ratio on soybean oil ethyl esters: second experimental design

A coded model was obtained using factorial design. This model describes the influences of the catalyst concentration and ethanol/soybean oil molar ration on soybean ethyl ester conversion (*E*), Eq. 3. The results of the second-order model fitting in form of analysis of variance (ANOVA) are given in Table 3. The ANOVA demonstrates that the model is significant as it is clear from the F_{test}. The $F_{\text{calculated}}$ and the F_{listed} ($F_{5,5}$) are 15.29 and 3.45, respectively. According to the F_{test}, a model has statistical significance when $F_{\text{calculated}}$ is larger than the F_{listed} value [21]. Figure 4 shows a comparison between the experimental results and the values predicted by the coded model. These results are very close because the experimental points are next to the line, then they represent a satisfactory adjustment of the experimental results.

$$E = 91.53 + 4.13\mathrm{C} - 1.67\mathrm{C}^2 + 9.14\mathrm{MR} - 3.63\mathrm{MR}^2 - 2.64\mathrm{C} \times \mathrm{MR} \tag{3}$$

Figure 5 shows how the catalyst concentration and the ethanol/soybean oil molar ratio affect the ethyl ester conversion. Maximum ester concentration, above 90%, can be obtained for different variables conditions such as: catalyst concentration upper to 1.0 wt.% and ethanol/soybean oil molar ratio up to 6:1 or catalyst concentration upper to 1.34 wt.% and ethanol/soybean oil molar ratio up to 5:1.

Conclusion

The analyses of the second-order coded model showed that this model can predict the ester concentration as function of the ethanol/soybean oil molar ratio and the catalyst concentration in the studied variable limits.

The reactive distillation is a process that combines the reaction and separation in single equipment. The difference between the boiling temperature of ethanol and the product mixture, ethyl esters and glycerol, is so large that the separation of the alcohol from the product mixture became easy. This behavior is in agreement with He [15], using a reactive distillation column with plates, canola oil, and methanol as raw materials.

The use of reactive distillation process to biodiesel production leads to a more efficient process than the conventional transesterification one. The results showed many advantages of the integration process as compared with the conventional biodiesel production such: decrease of the ethanol excess, of the reaction time, and of the equipments units.

The best biodiesel conversion of the first experimental design was 94.54 wt.% ethyl esters after 6 min of the reaction using a ethanol/soybean oil molar ratio of 6:1 and catalyst concentration of 1.5 wt.%. In the second experimental design, the best ester conversion was 98.18 wt.% with 0.65 wt.% of sodium hydroxide, ethanol/soybean oil molar ratio of 8:1, and reaction time of 6 min. The reaction time of 6 min means: 1 min in the pre-reactor and

Table 3 ANOVA for the full quadratic model.

Source of variation	Sum quadratic	Degree of freedom	Mean quadratic	$F_{\text{calculated}}$
Regression	914.09	5	182.8187	15.29
Residual	59.75	5	11.95	
Lack of fit	59.71	3		
Pure error	0.04	2		
Total	973.85	10		

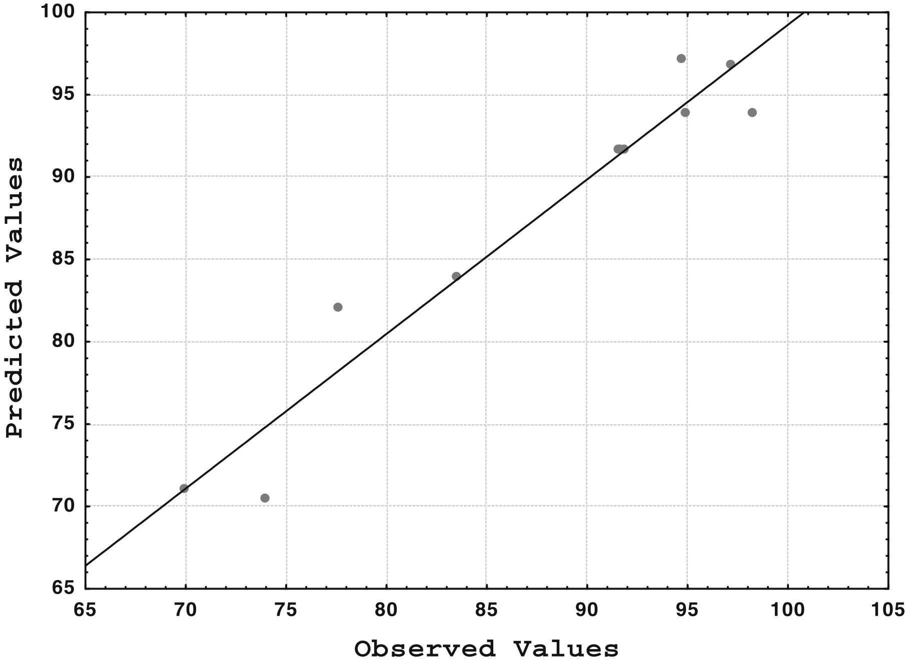

Fig. 4 Comparison between experimental results and the values predicted by the coded model

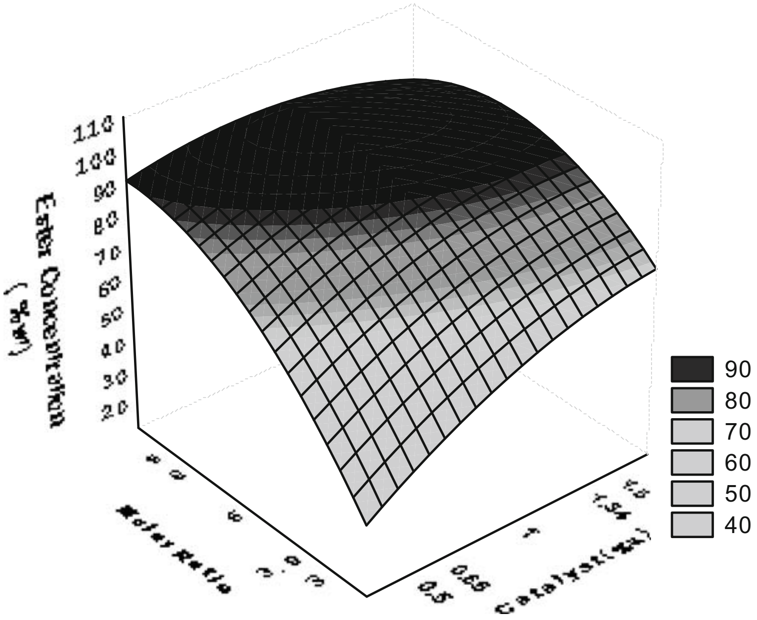

Fig. 5 Response surface of ethyl ester conversion as a function of catalyst concentration and ethanol/soybean oil molar ratio

5 min in the reactive distillation column. Then, this work showed that it is possible to achieve high biodiesel conversion with a packed reactive distillation column.

In future works of this research group, the influence of the column reflux rate will be performed and the results of the packed reactive distillation column will be compared with a tray reactive distillation column.

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