Biodiesel Production by an Integrated Reactive Separation System: A Comparative Study

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The aim of this work is to present an efficient process using a reactive distillation column applied to biodiesel production. Reactive distillation is characterized by simultaneous implementation of reaction and separation within a single column. In this work, the biodiesel production from soybean oil with ethanol in presence of sodium hydroxide as catalyst was studied in a tray column. The experimental design applied was a full 2^2 factorial design with three central points. Two independent variables in two levels were selected for this study: substrate molar ratio (ethanol:soybean oil) and catalyst concentration and one variable dependent was considered, the response selected was the ethyl ester conversion. The process simulation was performed using the commercial simulator Aspen Plus® 7.2. The simulation results showed a good agreement with experimental results and it can be seen that conversions above 99.84 % of ethyl esters could be achieved.

1. Introduction

Biodiesel is an alternative diesel fuel made from vegetable oils by transesterfication reaction with a short chain alcohol. The main advantages over regular diesel are that it is biodegradable, low toxicity, it produces lower emissions, it is more environmental friendly (Ma and Hanna, 1999), it has higher flash point (making it safer to handle and store) and it is a better lubricant (Kiss et al., 2007). It has similar properties compared to diesel produced from crude oil and it can be used in its pure form or as a diesel/biodiesel mixture on existing fuel engines. However, it is still more expensive than conventional diesel (Behzadi and Farid, 2009).

Biodiesel was officially introduced into the Brazil energy matrix through the Federal Law 11.097 of January 13, 2005. It was established in this law that 2 % biodiesel should be added to diesel and it was also set standard specifications for biodiesel according to the National Agency of Petroleum, Natural Gas and Biofuels (ANP). It is important to highlight that the biodiesel production and purification steps are both efficient, resulting in a biodiesel product that meets the ANP specifications. Since 1st January of 2010, the National Council of Energetic Policy (CNPE) through resolution n° 6/2009, established that 5 % of Biodiesel should be added to diesel fuel. Brazil is one of the biggest producers and consumers of biodiesel, with an annual production of 2.4 billion liters in 2010 and an installed capacity to produce $5.8 \cdot 10^9$ L that same year, according to the National Agency of Petroleum, Natural Gas and Biofuels, ANP.

In the transesterfication with reactive distillation (RD), both the reaction and separation steps take place simultaneously in one single process unit, enhancing process conditions for both unit operations, resulting in high-yield conversions at small time frames. Other benefits of RD are: less recycle streams, less need for pumping equipment and piping, less production of waste streams, which implicates into lower investment and operating costs (Singh et al., 2004). A study by (Miranda-Galindo et al., 2010) stated that in all cases where reactive distillation is used, variable cost and energy requirements are reduced by 20 % or more when compared to the classic setup of a reactor followed by distillation.

The performance of a reactive distillation column is affected by several process parameters including the sizes and location of the reaction and separation zones in the equipment, reflux ratio, feed flow rate and feed tray location. The reactive distillation unit can be a tray or packed column, tray columns are recommended for homogeneous systems because the greater holdup and the associated longer residence time (Singh et al., 2004). A study presented by (Nguyen and Demirel, 2011) showed that further reduction of energy and equipment costs is possible by thermally coupled distillation sequences, as they allow interconnecting vapor and liquid flows between the two columns to eliminate the reboiler or condenser or both in one of the columns, the thermally coupled sequence reduced the energy consumption by 13 % in the reactive distillation column and 50 % in the subsequent methanol recovery column.

The experimental design was used to optimize the process variables of biodiesel production and the best conversions (with 6 minutes of reaction time) was of 99.84 wt.% in the sieve tray reaction distillation column. Simulations of reactive distillation column were performed using commercial software Aspen Plus® 7.2 and these simulations are in good agreement with experimental data, demonstrating the role of process modeling as a useful tool to predict reactor and column performances of the biodiesel production process.

2. Materials and methods

2.1 Materials
The feedstock in this research was refined soybean oil which was purchased from supermarket, Brazil. Ethanol (99.5 % purity), and sodium hydroxide were purchased from ECIBRA and Nuclear, Brazil respectively. Tetrahydrofuran HPLC-grade (THF) was from Tedia Company Inc. OH, USA. Polytetrafluorethylene filter was supplied by Macherey-Nagel GmbH, Germany. All the standards were supplied by Sigma Aldrich Chemical Company, Inc. St. Louis, MO, USA.

2.2 Reactive distillation
The experiments were made in a tray column of FISCHER® LABODEST® (Waldbüttelbrunn, Germany) showed in Figure 1. The reactive distillation column consists on oldershaw type with 10 practical perforated plates, made in borosilicate glass. The plate distance is 30 mm with dynamic hold-up per plate 2 mL and static hold up of 0.2 mL. The column had a silvered vacuum jacket for thermal isolation. Prior to each experiment, sodium hydroxide was dissolved in ethanol until a homogeneous mixture. The feed conditions were 60 °C and 1 atm. The mixture and soybean oil were fed into a plug flow reactor with 1 min of residence time in order to carry out simultaneously mixture and reaction. The stream from plug flow pre-reactor was introduced at the 8th tray (counting from bottom to top) of the reactive distillation column and then flowed downward through the downcomer to the next tray as seen in Figure 2. The total reaction time is 6 min, 1 min in the pre-reactor and 5 min in the RD column. After the set reaction time, the product mixture was withdrawn from the last stage, the reboiler, at the bottom of the column. The transesterification reaction occurs in the liquid phase only, the upward-flowing vapour phase (ethanol) also served as an agitator in the reactant mixture and increases the miscibility of the mixture. The column pressure was fixed at 1 atm and pressure drop in each stage was assumed to be zero.
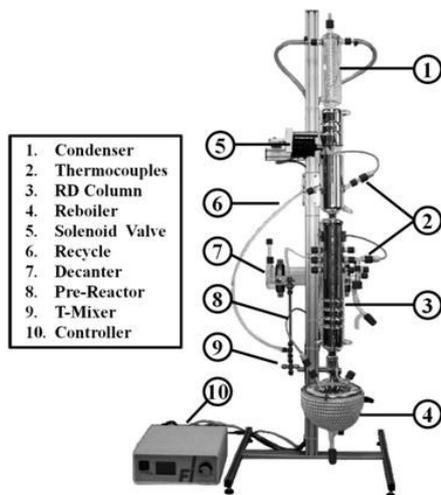
Figure 1: Reactive distillation tray column
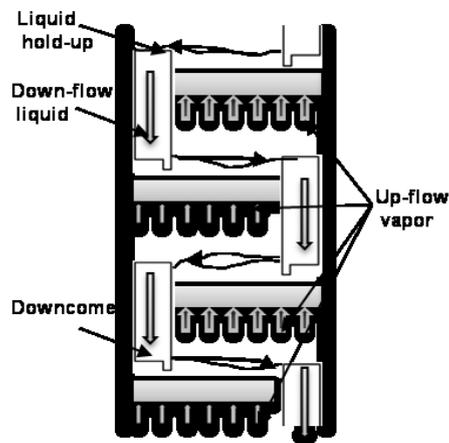
Figure 2: Liquid and vapor flows in the reactive distillation tray column

2.3 Experimental design

The experimental design applied was a full 2^2 factorial design with three central points. Two variables in two levels were initially selected for this study of biodiesel production: substrate molar ratio (3.92:1–8:1; ethanol:soybean oil) and catalyst concentration (0.65–1.34 %, by weight of soybean oil) and the response selected was the ethyl ester conversion. Additional, central points and axial points (star points) were incorporated in the two-level factorial design; a second order model was required because of the significance of curvature effect found in the linear stage. Table 1 shows this experimental design with the independent factors (coded and uncoded) and its levels.

2.4 Method of analysis

The biodiesel compositions were determined by gel-permeation chromatography (Waters, USA) also called high-performance size-exclusion chromatography (HPSEC). The methodology was described in Da Silva (2010), and it is specific for analysis of triacylglycerols (TG), diacylglycerols (DG), monoacylglycerols (MG), glycerol (GL) and esters (EE). The mobile phase was HPLC-grade THF (Tedia Company Inc., 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).

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

(1)

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

(2)

2.5 Process Simulation

A computer simulation was applied to describe the continuous biodiesel production using a reactive distillation column and a transesterification pre-reactor from soybean oil and ethanol. For this, the flow-sheet software Aspen Plus® 7.2 was used. The thermodynamic model used to simulate vapour-liquid

equilibrium was Dortmund UNIFAC model as recommended by Kuramochi et al. (2009). Sodium hydroxide was used as the reaction catalyst. The reaction steps and the general form of equations that characterizes the stepwise of catalyzed reactions used in this work can be found elsewhere (Noureddini and Zhu, 1997). The saponification reaction was assumed to be negligible because the free fatty acid content of commercial soybean oil is low (ca. 0.05-0.70 %). In addition, it was assumed that the reactions follows a first-order model with respect to the catalyst concentration, therefore, the effective reaction constants depend on the catalyst concentration and the rate constants of the catalyzed reaction (Vicente et al., 2005). The flow-sheets of both processes are shown in Figure 3. The total number of stages in the column was 12 (including condenser and reboiler) with holdup on each tray of 2 ml according to specifications of lab-scale reactive distillation column. The column pressure was fixed at 1 atm and pressure drop in each stage was assumed to be negligible.
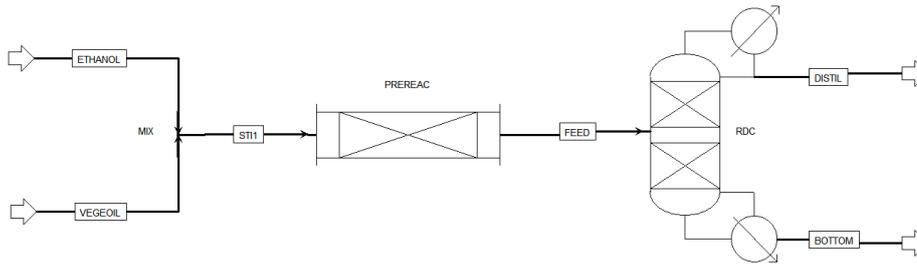
Figure 3: Process Flow-sheet to produce biodiesel from soybean oil using reactive distillation column

3. Results and discussions

3.1 Experimental analysis

The results of experimental design are shown in the fourth column of Table 1. The software Statistica (Statsoft, v.7) was used to analyze the results, the design was analyzed with a confidence level of 95 %. This analysis includes the linear (L) and quadratic (Q) effects and interactions between the linear variables. The statistical model is obtained from the real values of the variables C (catalyst concentration) and MR (substrate molar ratio) Equation (3).

A statistical analysis was performed on experimental values, and the main effects and interaction effects for two variables were calculated. The test of statistical significance, given in Table 2, shows the results of the second order model fitting in form of ANOVA (analysis of variance). The $F_{calculated}$ and the F_{listed} are 32.49 and 5.05, respectively. According to the F_{test}, a model has statistical significance when $F_{calculated}$ is larger than the F_{listed} value (Box, 1978).

$$E = -8.67 + 68.25C - 21.52C^2 + 19.42MR - 1.11MR^2 - 2.63CMR$$

(3)

Table 1: Variable level for the full factorial design

Runs	Catalyst (wt)	Molar ratio	Ethyl ester conversion (%)	
			Experimental	Simulation
1	-1 (0.65)	-1(3.92:1)	81.80	84.73
2	1 (1.34)	-1(3.92:1)	90.70	84.20
3	-1 (0.65)	1 (8:1)	98.45	99.31
4	1 (1.34)	1 (8:1)	99.84	99.40
5	-1.41 (0.5)	0 (6:1)	86.86	98.29
6	1.41 (1.5)	0 (6:1)	98.37	98.93
7	0 (1.0)	-1.41 (3:1)	76.14	56.70
8	0 (1.0)	1.41 (9:1)	99.79	99.50
9	0 (1.0)	0 (6:1)	99.22	98.99
10	0 (1.0)	0 (6:1)	98.91	98.99
11	0 (1.0)	0 (6:1)	98.61	98.99

Table 2: ANOVA for the full central composite

Source of variation	Sum quadratic	Degree of freedom	Mean quadratic	$F_{calculated}$
Regression	687.53	5	137.51	32.49
Residual	21.16	5	4.23	
Lack of fit	20.97	3	6.99	
Pure error	0.19	2	0.093	
Total	708.69	10		

3.2 Simulation analyses

The simulation results were compared with ethyl ester conversions obtained in experimental design for the lab-scale reactive distillation column (Table 1). The simulation results show a good agreement with experimental results. However, considerable differences can be found between the experimental and simulated value of runs 5 and 7.
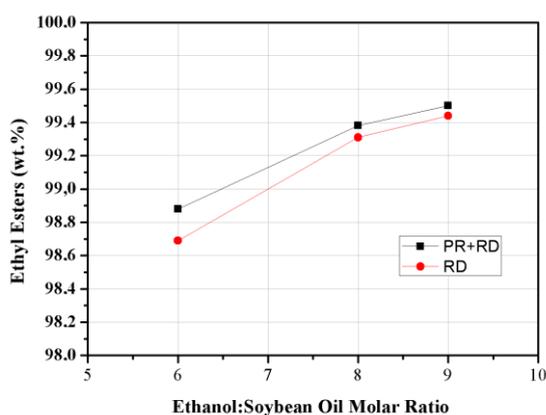
Figure 4: Effect of ethanol : vegetable oil molar ratio on ethyl esters production in a pre-reactor plus reactive distillation column (PR+RD) and a reactive distillation column (RD).
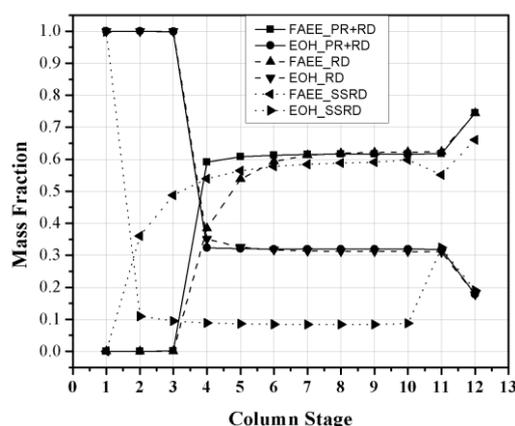
Figure 5: Comparison of biodiesel (FAEE) and ethanol (EOH) profiles (1) Pre-reactor plus RD (PR+RD); (2) Reactive distillation (RD); (3) RD with separate feeding (SSRD).

In order to evaluate the influence of pre-reactor on the continuous biodiesel production, different process configurations were simulated. Firstly, a comparison of the effect of ethanol : vegetal oil molar ratio on fatty acid ethyl ester (FAEE) production was made. As showed in Figure 4, the configuration of pre-reactor plus reactive distillation column produced higher reaction yield compared to the corresponding setup without pre-reactor. In addition, higher FAEE yields were obtained using greater ethanol:oil molar ratios, justifying the need of using alcohol excess to drive the reaction towards FAEE production. The reactive distillation column performance using two separated feed, *i.e.*, vegetable oil fed on top and ethanol fed on bottom (SSRD) was also evaluated and compared with the setup previously studied (reactive distillation column with pre-reactor (PR+RD) and without pre-reactor (RD)). Figure 5 shows the composition profiles for liquid phase within the reactive column under run 8 conditions (Table 1) where tray 1 and 12 correspond to condenser and reboiler, respectively. It is shown higher FAEE yield using PR+RD and RD process compared with SSRD setup. Using a pre-reactor favours the biodiesel production because the reaction rates of transesterification are high at the beginning and most of the reaction conversion can be achieved in the pre-reactor. This reduces the size of reactive zone and consequently the column size. In addition, Figure 5 shows that a high mass fraction of unreacted ethanol is achieved at the top of the column, whereas a large amount of biodiesel is removed as a bottom stream.

4. Conclusion

In this work, the biodiesel production from soybean oil with ethanol in presence of sodium hydroxide as catalyst was studied in a lab-scale sieve tray reactive column. Experimental and simulation study were carried out and compared. The best biodiesel conversion (99.84 wt.%) was obtained with 1.34% of catalyst and ethanol : vegetable oil molar ratio of 8:1. The experimental design was used because this methodology permitted a careful evaluation of the process variables. Despite some expected differences between process simulation and experimental results, the simulation was used to optimize other variables that were not considered in the experimental design. It was found that using a pre-reactor before the reactive column favors the biodiesel production. The simulations were in agreement with experimental results, demonstrating that process modeling software is an efficient tool for evaluating and optimizing the performance of biodiesel production processes.

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