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BIODIESEL PRODUCTION FROM REACTIVE DISTILLATION PROCESS: A COMPARATIVE STUDY BETWEEN EXPERIMENTAL RESULTS AND SIMULATION

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Abstract
Biodiesel is a fuel made from vegetable oils, animal fats and microbial oil (algae, bacteria and fungi). The raw materials are converted to biodiesel through a chemical reaction involving alcohol and catalyst. 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 appropriated 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 soy oil oil and bioethanol by reactive distillation. The RD process was carried out in a semi-batch system. 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. A simulation of the reactive distillation process was carried out in Aspen Plus. Different variables affect the conventional biodiesel production process such as: catalyst concentration, reaction temperature, level of agitation, ethanol:soy oil 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), and the ethanol:soy oil oil molar ratio (from 3:1 to 9:1). The reactive column reflux rate was 83 ml/min, and the reaction time was 6 minutes.

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. 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, decrease of the reaction time, and decrease of the equipment units. The best ester conversion was 98.18%wt with 0.65%wt of sodium hydroxide, ethanol:soy oil oil molar ratio of 8:1 and reaction time of 6 minutes. The process simulation results are in agreement with the experimental ones.

Keywords: biodiesel, ethyl esters, reactive distillation, transesterification.

1. Introduction

Biodiesel has become increasingly attractive due to its environmental benefits and to the fact that it is made from renewable resources. Transesterification reaction can be catalyzed by homogeneous (alkalis and acids) and heterogeneous catalysts or without catalyst using supercritical conditions. The use of batch stirred tank reactor (BSTR) is common in this process, but some equipment has been studied in order to increase the biodiesel conversion, the reaction speed and the decreasing the process cost. 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, more energy and production efficient technology[1]. The PI technique is going to be applied to biodiesel production by 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[2]. 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 to conventional reactive distillation, very high conversions, increased unit productivity, no excess of alcohol required and no catalyst neutralization step[3-7].

This work presents the biodiesel production from soy oil oil and bioethanol by reactive distillation. A pre-reactor was used to promote the perfect contact of reactants and After 1 min, the mixture is transferred to the RD system. A study of the use of a pre-reactor was done by He (2006)[8] and the best methyl ester conversion, in that study, was obtained with a pre-reactor.

2. Experimental Procedure

2.1 Materials and Equipments

The experiments were carried out with refined soy oil oil obtained by supermarket (Brazil). The sodium hydroxide (Synth-Brazil) was used as catalyst. The standards were supplied by Sigma-Aldrich Chemical Company, Inc. (St. Louis, Mo). The RD process was carried out in a semi-batch system. The equipments of RD system are listed in Figure 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.

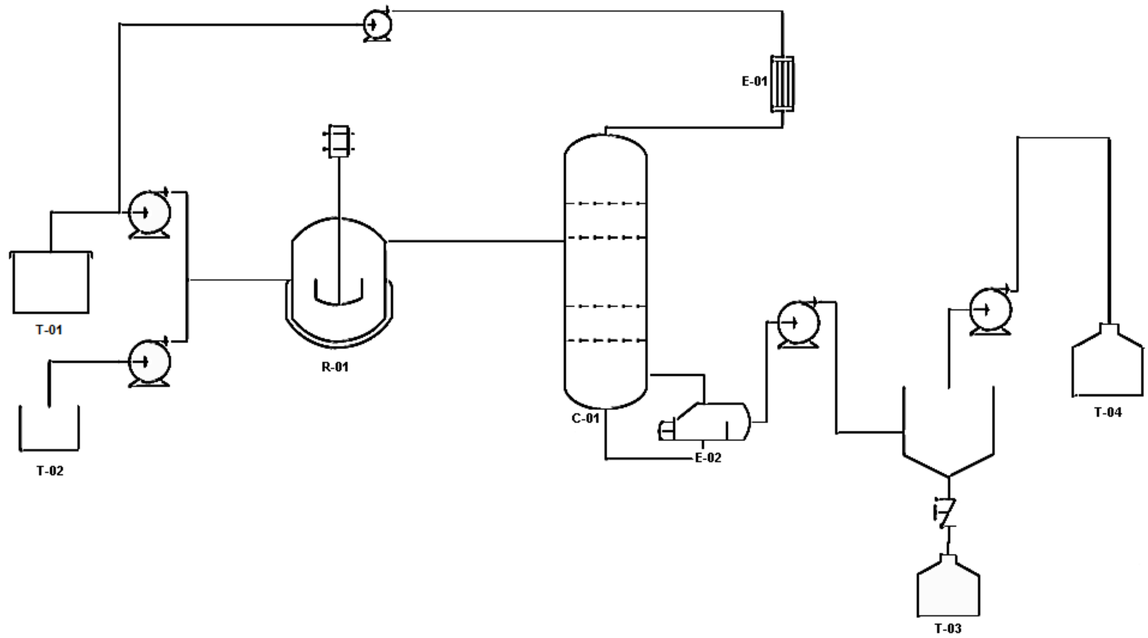

Figure 1 – Reactive distillation system

Equipment description: T-01: Ethanol tank of 1 liter; 2) T-02: Soy oil oil tank of 1 liter; 3) R-01: Pre – reactor (speed of 400 rpm; reaction time of 1 minute; 4) C-01: Packed reactive distillation column of 2 liters; 5) E-09: Reboiler of 2 liters; 6) E-08: Water - cooled condenser; 7) E-11: Ester / Glycerol separator of 2 liters; 8) E-12: Ester (biodiesel) tank of 1 liter; 9) E-13: Glycerol tank of 500 mL.

2.2 Process simulation

The process simulation software, Aspen Plus, was used in this work. The main processing units include a pre-reactor and a reactive distillation column with 7 stages. The first column stage is the condenser and the seventh stage is the reboiler. The same experimental conditions were used in the simulation process. Table 1 presents stream mass fractions of RD simulation, and Table 2 presents the stream conditions.

Table 1 - Stream mass fractions

	Ethanol	Soy oil	Feed	Ethanol1	Bio+Gly
Ethanol	1.0	0.0	0.194	1	0.035
Trilinolein	0.0	0.707	0.044	3.96e-06	0.001
Triolein	0.0	0.293	0.018	1.43e-06	4.0e-4
Ethyl linoleate	0.0	0.0	0.478	1.99e-05	0.620
Ethyl oleate	0.0	0.0	0.198	6.56e-06	0.257
Glycerol	0.0	0.0	0.068	1.74e-05	0.087

Table 2 - Stream conditions

	Ethanol	Soy oil	Feed	Ethanol1	Bio+Gly
Temperature (°C)	30	30	50	77.55	114.96
Pressure (kPa)	101.33	101.33	101.33	98.33	101.33
Mass flow (g/min)	41.83	100	141.83	22.02	119.81

2.3 Experimental conditions and Procedures

In the start up of RD system, the ethanol (400 mL) was fed to the reboiler by a peristaltic pump. The heating rate of reboiler was set to maintain the ethanol reflux rate at the top of the column. 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 soy oil oil and heated to 50°C. 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 and catalyst is filled in the pre-reactor by a peristaltic pump. After 1 min, the mixture is transferred to the RD using a peristaltic pump. The raw materials feed (Qfeed) is 250 ml/min and the reflux flow rate (Qreflux) is 83 ml/min. The Qreflux = 1/3 (Qfeed) 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 a semi-continuous process 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 analyzed in the HPSEC (high-performance size-exclusion chromatography) and the ester conversions were determined using chromatographic results.

2.4 Experimental Design

The experimental design was chosen to study the optimization of two selected factors: ethanol:soy oil oil molar ratio and catalyst concentration. Two experimental designs were done in order to optimize the catalyst content and the ethanol:soy oil 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[9]. The first experimental design limits were: ethanol:soy oil oil molar ratio: from 3:1 to 6:1; catalyst concentration level was from 0.5%wt 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 a ethanol:soy oil oil molar ratio from 3:1 to 9:1. Catalyst concentration level was from 0.5%wt to 1.5%wt, according to literature data for other case study[10,11]. The software Statistica (Statsoft, v.7) was used to analyze the results.

3. Results and Discussion

The soy oil oil molar mass was 872 g/mol, according to the GC analysis. The refined soy oil 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 transeterification products[12], soy oil 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 permitted a perfect contact of the reactants and the ester conversion at the first minute of the process and in this system was obtained an ester concentration of 10%wt. This fact is very important in the transesterification reaction, because the vegetable oil and ethanol is not soluble, exception of the castor oil that is the unique vegetable oil soluble in alcohols[13], but the ester is soluble in both components (vegetable oil and ethanol). Then, the ester formation permitted the increase of the mass transfer in the reaction[8] and, consequently, higher conversion in the RD system.

Table 3 shows the experimental design results and E (%wt) is the ester conversion at 6 minutes of reaction. These results were used in the experimental design. The effect of the catalyst content (C) and ethanol:soy oil oil molar ratio (MR) on the ethyl ester conversion is presented in Figure 3 (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 Figure 2. The confidence level was 95%.

Table 3 – First factorial design.

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

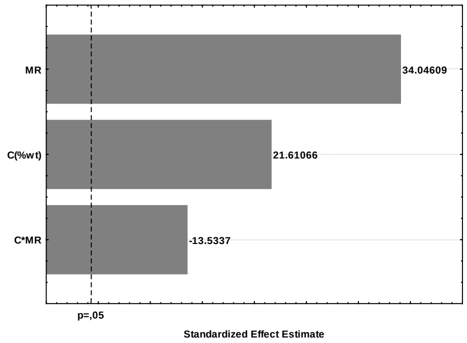

Figure 2 – Effects of catalyst concentration and ethanol:soybean oil molar ratio on soybean oil ethyl esters: first experimental design.

In order to investigate the influence of a larger ethanol excess on ester concentration, a second experimental design was done with a ethanol:soy oil oil molar ratio from 3:1 to 9:1. The second experimental design results were listed in Table 4. 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 Figure 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%wt 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.

A coded model was obtained using factorial design. This model describes the influences of the catalyst concentration and ethanol:soy oil oil molar ratio on soy oil ethyl ester conversion (E), equation 1. The results of the second order model fitting in form of ANOVA (analysis of variance) are given in Table 3. The ANOVA demonstrates that the model is significant, as it is clear from the Ftest. The Fcalculated and the Flisted (F5,5) are 15.29 and 3.45, respectively. According to the Ftest, a model has statistical significance when Fcalculated is larger than the Flisted value[9]. 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.

$$E = 91.53 + 4.13C - 1.67C^2 + 9.14MR - 3.63MR^2 - 2.64CxMR \quad (1)$$

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

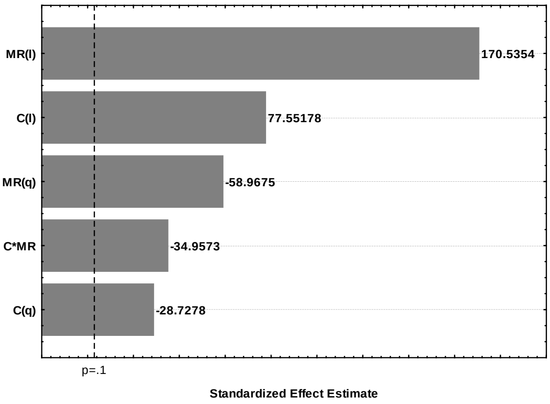

Figure 3 - Effects of catalyst concentration and ethanol:soybean oil molar ratio on soybean oil ethyl esters: second experimental design.

Table 3 - ANOVA for the full quadratic model.

Source of variation	Sum quadratic	Degree of freedom	Mean quadratic	$F_{calculated}$
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		

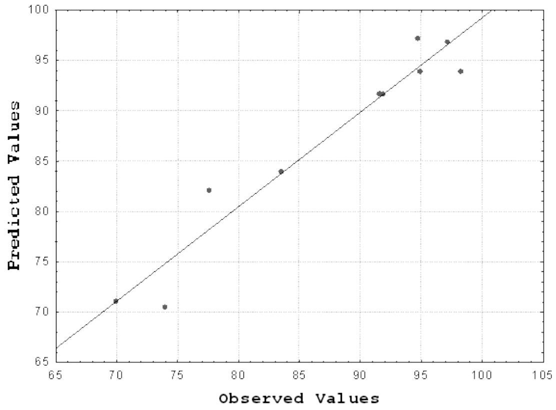

Figure 4 - Comparison between experimental results and the values predicted by the coded model.

The process simulation shows the same behavior of the experiments. The NRTL model and UNIFAC method were used to determine the thermodynamic parameters. The feed compositions were triolein and trilinolein. The simulation of run 3, (Table 2), leads to a conversion of 99.83% of ethyl esters. Figure 5 shows the mole fraction of each component present in the reactive distillation stages. The ethanol is the main component because the alcohol excess is benefic to the transesterification conversion. The first stage is the condenser and the seventh stage (reboiler) is the recovery biodiesel stage.

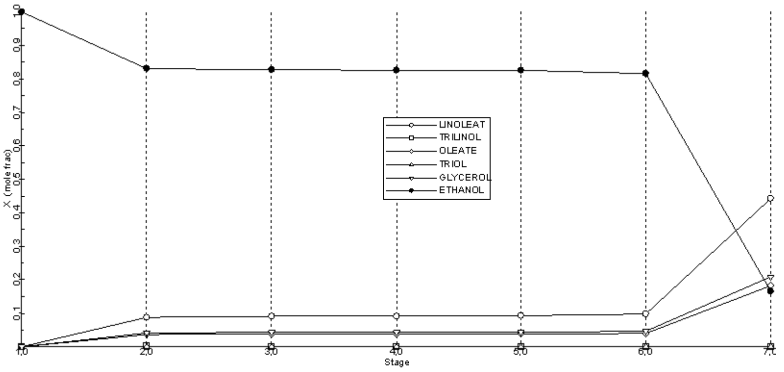

Figure 5 – Composition profile of the reactive distillation column.

4. Conclusion

The use of reactive distillation process to biodiesel production leads to a more efficient process than the conventional transesterification (BSTR reactor). 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 equipment units.

The reactive distillation is a process that combines reaction and separation in a single equipment. The difference between the boiling temperature of ethanol and of 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[8] conclusion using a reactive distillation column with plates, canola oil and methanol as raw materials.

For a biodiesel production rate of 250 mL/min, a flowsheet for continuous alkali catalyzed process using virgin soy oil oil as raw material was designed and simulated. The comparison between the simulation process and experimental results proved to be feasible for producing a high quality biodiesel product.

References

1. Stankiewicz, A.I. and Moulijn, J.A., *Chem. Eng. Prog.* 96(2000), 22–34.
2. Perry, R. H., Green, D. W. and Maloney J.O., In *Perry's Chemical Engineers Handbook*, section 13: Distillation, McGraw-Hill (1997), 7th ed, NY.
3. Kiss, A.A., Omota, F., Dimian, A.C. and Rothenberg, G., *Top. Catal.* (2006) 40, 141-150.
4. Kiss, A.A., *Sep. Purif. Technol.* 69 (2009), 280-287.
5. Diamian, A.C., Bildea, C.S., Omata, S., Kiss, A.A., *Comput. Chem. Eng.* 33(2009), 743-750.
6. Kiss, A.A., Diamian, A.C., Rothenberg, G., *Energy Fuels* 22(2007), 598-604.
7. Thotla, S., Mahajani, S., *Chem. Eng. Process.* 48(2009), 927-937.
8. He, B.B, Singh, A.P. and Thompson, J.C., *T ASABE.* 49(2006), 107-112.
9. Box, G.E. and Hunter J.S., in *Statistic for experimenters – An introduction to design, data analysis, and model building*, John Wiley & Sons (1978), New York.
10. Vicente, G., Martinez M., Aracil J. and Esteban A., *Ind. Eng. Chem. Res.* 44(2005), 5447-5454.
11. Freedman, B., Royden O.B. and Pryde E. H., *JAOCS* 63(1986), 1375 – 1380.
12. Goodrum, J.W., *Biomass Bioenerg.* 22(2002), 205-211.
13. De Lima Da Silva et.al, *Energy Fuels* 23(2009), 5636-5642.