ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

Optimization of Biodiesel production in Spinning disc Reactor using Response Surface Methodology

***Vishnu Ashroba Gite [1], and Y.C. Bhattacharyulu [2]**

1. Department of chemical Engineering, MGM'S Jawaharlal Nehru Engineering College, Aurangabad (M.S.), India
2. Department of chemical Engineering, Anuradha Engineering College Chikhli Dist Buldana, Maharashtra, India

Manuscript Info

Manuscript History:

Received: 19 April 2015
Final Accepted: 22 May 2015
Published Online: June 2015

Key words:

Biodiesel, Spinning Disc Reactor,Transesterification, response surface methodology (RSM**).**

****Corresponding Author***

Vishnu Ashroba Gite

Abstract

An experiment was performed to study Transesterification in spinning disc reactor using response surface methodology. Spinning disc reactor have been fabricated and used for continuous alkali-catalyzed transesterification biodiesel production. The reactor was designed with a 110 mm diameter circular disc made of stainless steel as a static disc and another disc of same dimension made up of high density polyethylene to serve as rotating disc, enclosed on cylindrical vessel made of plexi-glass. The small gap sizes about 1 millimeter between static disc and rotating disc were maintained. The parameters for biodiesel preparation are studied with a response surface methodology (RSM) in this, central composite design (CCD) was used. This method is suitable for fitting the quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments, and also to analyze the interaction between the parameters. The variables studied 1) A: reaction temperature 2) B: Flow Rate of oil and 3) C: catalyst concentration. Mole ratio of oil to methanol was fixed 1:6 by carrying various experiments.

INTRODUCTION

Transesterification is a common method for biodiesel production from vegetable oils and animal fats and usually preferred instead of direct esterification [1]. In transesterification or alcoholysis, fats or oils react with alcohol in presence of a catalyst to form alky esters and glycerol [2]. The transesterification process reduces the viscosity of oils which is higher than petro-diesel [3]. Selecting a suitable alcohol and catalyst is important for transesterification method. Various alcohols such as methanol, butanol, ethanol, propanol and amyl alcohol can be used for transesterification. Methanol is used widely because it is relatively cheaper than other alcohols and has chemical and physical advantages over other alcohols [4]. In theory 3 moles of alcohols are required to neutralize 1 mole of triglyceride to produce 3 moles of fatty acid methyl ester (FAME) and 1 mole of glycerin [5]. A good catalyst is also needed to obtain a reasonable rate for transesterification of triglycerides and its conversion to biodiesel [6]. Acid and alkaline catalysts can be used in the form of homogeneous or heterogeneous catalysts for transesterification process [7]. Research and industry prefer alkali catalysts, such as NaOH and KOH because alkali catalysts react faster and are less corrosive than acidic compounds [8]. High water and free fatty acid in oil reduce the effectiveness of catalysts, produce soap and require considerable amounts of catalysts. Free fatty acids (FFAs) and water in oil needs to be removed before applying base catalysis process. Acid catalyst was used to eliminate the above-mentioned problems. acid catalysts act better than base catalysts, because acid catalysts are able to convert higher percentage of free fatty acids (FFAs) to triglyceride. The first choice for acid catalysts is sulfuric acid which was used by several researchers [9]. In addition to the acid and base catalysts, enzyme catalysts are also considered for biodiesel production. The enzyme catalysts are gaining more interest in recent years because they don't constitute soap and

their process is simple to complete. Enzymatic catalysts are currently not feasible for commercial productions since they have higher cost and need longer reaction time [5].

The current conventional techniques involve long residence time, high molar ratio of alcohol to oil and catalyst concentration, and most of them are run in a batch mode and thus do not gain some of the advantages of continuous operation. Long residence times and downstream processing time incur low production efficiency. High cost and energy consumption are involved in order to recover excess amounts of alcohol and catalyst, and to deal with the resulting significant amounts of toxic waste water during downstream processing. In recent years, some process intensification technologies have been developed and applied to improve mixing and mass/heat transfer between the two liquid phases. These technologies either utilize novel reactors or coupled reaction/separation processes. Reaction rate is greatly enhanced and thus residence time may be reduced

Spinning disc reactors (SDR) are one of process intensification technologies employing high gravity field. It is mainly aimed at fast and very fast liquid/liquid reactions involving large heat effects, such as nitrations, sulfonations, and polymerizations [10]. Ramshaw's group designed spinning disc reactor at Newcastle University (Newcastle, U.K.) High gravity field–centrifugal force is created by rotation of a disc surface in spinning disc reactors. When a liquid is introduced onto the disc surface at or adjacent to the spin axis, the liquid flows radially outward under the centrifugal force in the form of a thin film. At up to approximately 1,000 rpm, these films are less than 100 microns thick and so offer a short diffusion path length [11]. The film is unstable and forms waves at the gas-liquid interface. Unsteady film surface waves on the disc surface, coupled with the shearing action of the rotating surface, ensure that micro mixing and excellent mass and heat transfer are achieved. Extensive mass and heat transfer studies using this technology have shown that convective heat transfer coefficients as high as 14kWm-2 K and mass transfer coefficients, KL values as high as 30×10-5 ms-1 and KG values as high as 12×10-8 ms-1, can be achieved whilst providing micro-mixing and an appropriate fluid dynamic environment for achieving faster reaction kinetics [12]. Residence times on the spinning disc range from a few seconds down to fractions of a second, and it is therefore well suited to fast processes where the inherent reaction kinetics are of the same order or faster than the mixing kinetics [13]. The SDR has the characteristics: Intense mixing in the thin liquid film; High heat and mass transfer coefficients; Short residence time; and Plug flow characteristics.

A central composite design of the RSM is the most commonly used in optimization experiments. The method includes a full or fractional factorial design with center points that are augmented with a group of star points. As the distance from the center of the design space to a factorial point is defined as ±1 unit for each factor, the distance from the center of the design space to a star point is ±α with |α|>1. In this study, the central composite design was used to optimize operating variables (temperature, catalyst concentration and oil flow rate) to achieve high value of biodiesel yield. The coded values of the variables were determined by the following equation.

$$xi = \frac{xi - xo}{\Delta x} \qquad (1)$$

Where x_i is the coded value of the i^{th} variable, Xi is the encoded value of the ith test variable and $X0$ is the encoded value of the i^{th} test variable at center point. The range and levels of individual variables were given in Table 2. The experiment design was given in Table 3. The value of biodiesel yield is the response.

The regression analysis was performed to estimate the response function as a second order polynomial.

$$Y = \beta o + \sum_{i=1}^{n} \beta i x i + \sum_{i=i}^{n} \sum_{j=1}^{i-1} \beta i j x i x j \qquad (2)$$

Where Y is the predicted response, βi and βij are coefficients estimated from regression, they represent the linear, quadratic and cubical effect of $x1$, $x2$, $x3$... on response. All results are expressed as mean ± SD for six mice in each group. To determine the effect of treatment, data were analyzed using one way analysis of variance (ANOVA) repeated measures. *P*-Values of less than 0.05 were regarded as significant. Significant values were assessed with Duncan's multiple range tests. Data were analyzed using the statistical package "Design Expert 8.0".

the objectives of our work were to evaluate the effects of the reaction parameters of temperature, catalyst concentration and oil flow rate on the biodiesel yield and to optimize the reaction conditions using RSM. The properties of produced methyl ester were analyzed and the quality of biodiesel was compared with petro-diesel.

Material and Methods

Design of spinning disc reactor

The reactor was designed with a 110 mm diameter circular disc made of stainless steel as a static disc and another disc of same dimension made up of high density polyethylene to serve as rotating disc, enclosed in a cylindrical vessel made of plexi-glass(ID = 165 mm, L = 200 mm) as shown in Fig.1. The cylindrical vessel serves to collect liquid mixture sprayed from the gap between two discs. The rotating disc mounted on a hollow shaft. The stainless steel shaft is supported by a ball bearing (15mm×28mm×7mm, 6902 ZZ) assembly and a plexi-glass cover sitting above the cylindrical vessel. The rotation of the top disc can be achieved when the shaft is driven by a DC motor via a pulley and a belt. The rotational speed is adjustable to 1000 rpm. The oil can be pumped at the centre of the rotating disc through a steel tube coaxially installed through a bearing. The stationary disc also mounted on a hollow shaft. The small gap sizes about 1 millimetre between static disc and rotating disc were maintained. A circular

copper coil (2 mm ID) was welded to the bottom side of the stationary disc through which hot water from constant temperature bath was circulated, to facilitated carry out reaction at different temperature. Another stainless steel tube was connected at the centre of the bottom disc to allow potassium methoxide to be introduced into the reaction zone.

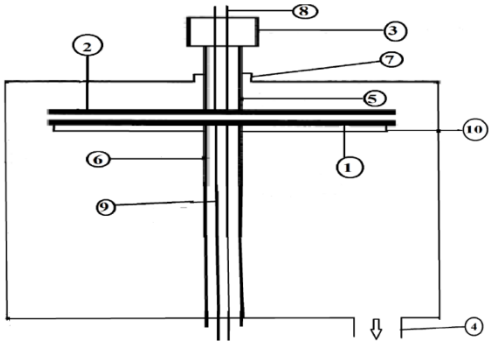

Figure 1. Design of the Spinning Disc Reactor (1- static diec;2- rotating disc; 3-pully;4-product drain;5&6- hollow stainless steel shaft; 7- bearing; 8&9- stainless steel tube for oil and potassium methoxide inlet;10- heating arrangement)

Chemicals Required

Soybean oil was obtained from local market. The physical properties are as follows: acid value of 1.97 mg KOH/g, Saponification value of 193 mg KOH/g, density of 0.920 g/ml, and viscosity of 30 cSt. Methanol and potassium hydroxide were purchased form Merck (Mumbai India). Potassium methoxide were prepared by mixing methanol and potassium hydroxide (1% weight of oil). Methanol (analytical grade) and potassium hydroxide (purity >87.9% wt) was obtained from Merck (Mumbai India).

Procedure

At the beginning of each experiment, the gap between two discs was adjusted to be 1 millimeter value and the hot water from the temperature bath circulated through copper coil fitted to the bottom side of the stationary disc, and When the temperature in circulator reached the set point, DC motor was started and the rotational speed was adjusted to set point (1000 rpm) by the power controller and measured using a digital tachometer. Both oil and sodium methoxide were pumped into reactor by peristaltic pump under preheated to reaction temperature by passing through coil housed in the constant temperature bath. Oil and potassium methoxide were continuously charged into the upper inlet and lower inlet of the spinning disc reactor at fixed flow rates and product streams was collected continuously. The flow rates of these two phases were determined based on the desired molar ratio of methanol to oil. A mercury thermometer was used to record the temperature of the product stream from the reaction zone. Every five minutes, the samples were continuously collected at the sampling point located at the bottom of reactor into a separating funnel the reaction mixture was then left for 1 hour to settle in a separating funnel .After settling, the mixture separated into two phases, the lower part being glycerin rich phase and the upper large part ester layer. After separating the glycerin layer, the ester layer was washed with warm water (50^oC) with equal volume of ester layer. This was done until the wash water did not turn pink on addition of phenolphthalein indicator, indicating that the catalyst was washed out. The ester layer was dried after washing by heating the layer at 100^0C in a beaker until the layer changed from being cloudy to clear indicating that the water had been evaporated. Parameters measured for the biodiesel were viscosity, density, acid value and yield. All the determinations were done in triplicate and average values were recorded.

Biodiesel analysis

The transesterification of soybean oil and methanol has been optimized using RSM for the maximization of soybean biodiesel yield which was calculated using the following equation

$$\text{yield of biodiesel}\,(\%) = \frac{\text{Total weight of methyl esters}}{\text{Total weight of oil in the sample}} \times 100 \qquad (3)$$

Physical properties of the biodiesel which were produced in the optimum conditions were measured in the lab and shown in Table 1. These results are tabulated and compared with ASTM standard and petro-diesel. It is found which results are drawn on the ASTM standard and compared well with petro-diesel.

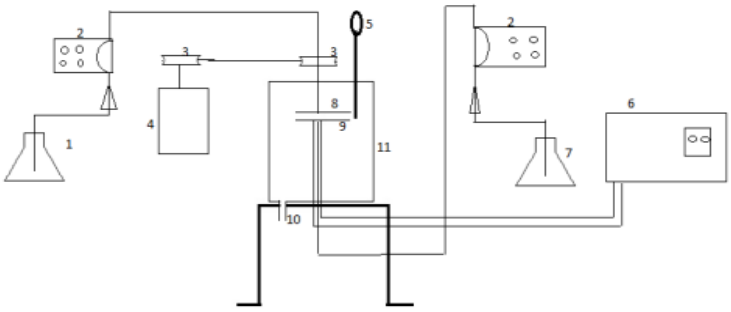

Figure 2.Schematic diagram of the experimental setup for biodiesel production in spinning disc Reactor. (1-Soybean oil vessel, 2- peristaltic pump, 3-pulley, 4- dc motor, 5-thermameter,6-constant temperature bath, 7- potassium methoxide vessel, 8- rotating disc, 9- stationary disc,10- product drain, 11 cylindrical vessel.)

Table 1: **Physical properties of the Biodiesel**

Test	Method	Unit	Biodiesel	ASTM	Petro-Diesel
Flash point	D93	°C	170	130 min	54 min
Kinematics Viscosity 40°C	D445	cSt.	4.5	1.9-6.0	2.0-5.5
Acid Number	D974	mg KOH/g	0.267	0.8	0.002
Specific gravity	D1298	-	0.881	N/A	0.835

Result and Discussion

20 experiments were performed to get the experimental values of soybean biodiesel yield. Experimental and predicted values for soybean biodiesel yield responses at the design points are given in Table 2.The regression equation in Terms of Coded Factors for the determination of predicted values of output parameter (i.e. soybean biodiesel yield) is given as follows:

$$yield = +88.32 - 6.01 * A + 11.72 * B + 15.32 * C + 3.25 * A * B - 3.00 * A * C - 7.00 * B * C - 1.37 * A2 - 23.47 * B2 - 12.68 * C2 \quad (4)$$

Table 2: **Codes, ranges and levels of independent variables in RSM design**

Symbols	Independent variables	Coded level				
		- α	- 1	0	+1	+ α
A	flow rate of oil (ml/min)	3.64	5	7	9	10.37
B	Temperature(^{0}C)	14.78	25	40	55	65.23
C	Catalyst concentration. (%wt)	0.46	0.8	1.3	1.8	2.15

The analysis of variance (ANOVA) for response surface second order model is given in table 3. The p –value showed that all of linear coeficent were more highly significant han their quadratic and cross product term The Model F-value of 18.12 implies the model is significant. P-vaue is less than 0.0001,i.e. there is 0.01% chance that error is caused by noise. This implies a vey high significance of the regression model. This fit of the model was checked with the coefficient of determination R2, which was culated to be 0.9422, indicating that 94.22% of the response variability. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, B^2, C^2 are significant model terms.The "Lack of Fit F-value" of 60.83 implies the Lack of Fit is significant. There is only a 0.02% chance that a "Lack of Fit F-value" this large could occur due to noise. This study indicates that the model can be considered statistically significant. The Model F-value of 6.09 implies the model is significant. There is only a 0.46% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case B, C, B^2, C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those

required to support hierarchy), model reduction may improve your model. The "Lack of Fit F-value" of 118.14 implies the Lack of Fit is significant. There is only a 0.01% chance that a "Lack of Fit F-value" this large could occur due to noise.

Table 3: CCD arrangement and responses for soybean biodiesel yield

Exp No	Flow Rate of oil (ml/min)	Temp. (deg C)	Cat Conc. (Wt %)	Experimental Yield (%)	Predicted Yield (%)
1	0	0	0	90	88.31
2	0	0	0	85	88.31
3	- 1	- 1	- 1	25	31
4	0	0	+ 1.68	70	23
5	- 1	+ 1	+ 1	92	76.6
6	- 1	+ 1	- 1	70	54
7	+ 1	- 1	- 1	12	10.5
8	0	0	0	91	88.31
9	- 1.68	0	0	85	94.54
10	+ 1	+ 1	- 1	75	54
11	0	0	0	90	88.31
12	0	0	0	90	88.31
13	0	+ 1.68	0	10	41.63
14	+ 1	+ 1	+ 1	80	65.07
15	+ 1.68	0	0	60	74.3
16	0	- 1.68	0	10	2.28
17	7	0	0	88	88.31
18	0	0	- 1.68	11	26.78
19	- 1	- 1	+ 1	70	73.66
20	+ 1	- 1	+ 1	50	49.14

Response surface plots were drawn to observe the effect of catalyst concentration, temperature and 0il flow rate on biodiesel yield. RSM can be illustrated with three-dimensional plots by presenting the response in function of two factors and keeping the other constant. It is visualized by the yield of biodiesel in relation to the catalyst concentration, temperature and 0il flow rate in Figure 3 to 5. Figure 3 denotes the surface plot of the Transesterification reaction yield as a function of temperature and oil flow rate at Catalyst concentration of 1.3%wt. This figure show that temperature and oil flow rate have a direct effect on the yield of methyl ester but until the near boiling temperature of alcohol and 7 oil flow rate, then yield of biodiesel decreased with increasing the temperature and oil flow rate. Temperature has an important influence on speed of reaction and led to higher conversion of ester. With increasing temperature of reaction, yield of biodiesel increased quickly to near the boiling point of alcohol. At low temperatures, relatively low conversion to methyl ester evident due to the subcritical state of methanol. At higher temperature than boiling point of methanol, alcohol evaporates and the yield was decreased. Also oil flow rate had a significant effect which yield decrease dramatically in high value of those with increasing oil flow rate,

Figure 4 denotes the surface plot of transesterification reaction yield as a function of catalyst concentration and flow rate at temperature of 40 ^{0}C. Yield of biodiesel reduced when concentration of catalyst increased than 1.3 wt%, as shown in Figure 4, because with increasing concentration of catalyst, soap was formed exponentially with catalyst concentration and lower amount of biodiesel can separate from glycerol. The resulting soaps do not only lower the conversion of ester, but also cause other problems associated with phase separation. Figure 5 denotes the surface plot of transesterification reaction yield as a function of catalyst concentration and temperature at oil flow rate of 7 ml/min. The elliptical shape of the curves indicated a strong interaction between the variables.

Table 4: ANOVA for response surface quadratic model

Source	Sum of Squares	Mean df	F Square	F Value	p-value Prob > F	
Model	15668.78	9	1740.98	6.09	0.0046	significant
A-flow rate	492.89	1	492.89	1.72	0.2185	
B-temperature	1874.52	1	1874.52	6.56	0.0284	
C-cat. conc.	3205.38	1	3205.38	11.21	0.0074	
AB	84.5	1	84.5	0.3	0.5986	
AC	72	1	72	0.25	0.6267	
BC	392	1	392	1.37	0.2688	
A2	26.97	1	26.97	0.094	0.7651	
B2	7935.01	1	7935.01	27.75	0.0004	
C2	2317.71	1	2317.71	8.11	0.0173	
Residual	2859.42	10	285.94			
Lack of Fit	2835.42	5	567.08	118.14	< 0.0001	significant
Pure Error	24	5	4.8			
Cor Total	18528.2	19				

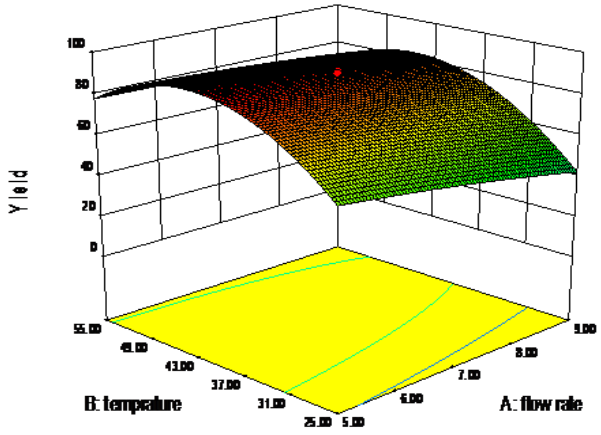

Figure 3. effect of temperature and flow rate

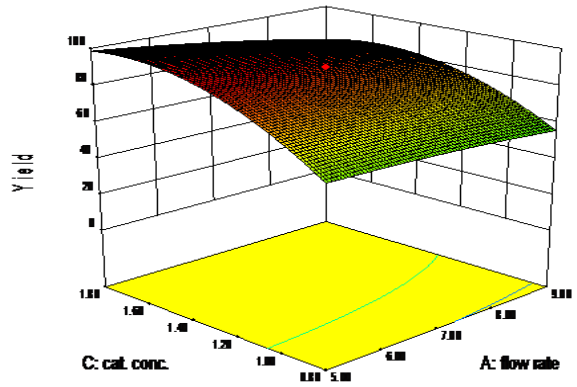

Figure 4. effect of catalyst concentration and flow rate

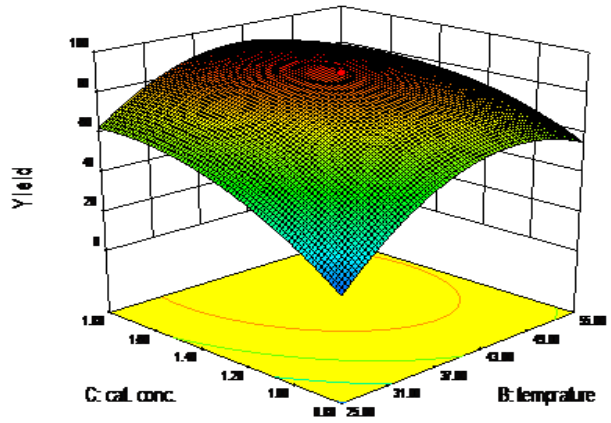

Figure 5. effect of catalyst concentration and temperature

Conclusion

Response surface methodology was successfully applied for transesterification of methanol. The high regression coefficients of the second-order polynomial showed that the model was well fitted to the experimental data. The ANOVA implied that oil flow rate, reaction temperature and concentration of catalyst have the great significant factor affecting the yield of biodiesel. It was predicted that the optimum reaction condition within the experimental range would be the oil flow rate 7 ml/min and temperature of 40°C and concentration of NaOH equal to 1.3wt%. At the optimum condition we can reach to yield of 92%. The methyl ester which produced at optimum conditions meets the ASTM standards and compared well with petro-diesel. A Spinning Disc Reactor has significant potential for enhancement of biodiesel production and for continuous production. Hence higher conversion yields are possible, under milder conditions and involving reduced lower reaction temperature and catalyst concentration than conventional stirred reactors

References

1. **Abreu, F., Lima, D., Hamú, E., Einloft, S., Rubim, J., Suarez**, "New metal catalysts for soybean oil transesterification". *Journal of the American Oil Chemists' Society*, P. 2003. 80(6), 601-604.

2. **Meher, L.C., Vidya Sagar, D., Naik, S.N**. 2006. "Technical aspects of biodiesel production by transesterification--a review". *Renewable and Sustainable Energy Reviews*, 10(3), 248-268.

3. **Stavarache, C., Vinatoru, M., Nishimura, R., Maeda, Y**. 2005. "Fatty acids methyl esters from vegetable oil by means of ultrasonic energy". *Ultrasonics Sonochemistry*, 12(5), 367-372.
4. **Ma, F., Hanna, M.A**. 1999. "Biodiesel production: a review". *Bioresource Technology*, 70(1), 1-15.

5. **Leung, D.Y.C., Wu, X., Leung, M.K.H**. 2010. "A review on biodiesel production using catalyzed transesterification". *Applied Energy*, 87(4), 1083-1095.

6. **Lotero, E., Liu, Y., Lopez, D.E., Suwannakarn, K., Bruce, D.A., Goodwin, J.G**. 2005. "Synthesis of Biodiesel via Acid Catalysis". *Industrial & Engineering Chemistry Research*, 44(14), 5353-5363.

7. **Pereira, R.G., Oliveira, C.D., Oliveira, J.L., Oliveira, P.C.P., Fellows, C.E., Piamba, O.E**. 2007. "Exhaust emissions and electric energy generation in a stationary engine using blends of diesel and soybean biodiesel". *Renewable Energy*, 32(14), 2453-2460.

8. **Pinto, A.C., Guarieiro, L.L.N., Rezende, M.J.C., Ribeiro, N.M., Torres, E.A., Lopes, W.A., De Pereira, P.A.P., De Andrade, J.B**. 2005. "Biodiesel: An overview". *Journal of the Brazilian Chemical Society*, 16(6 B), 1313-1330.

9. **Marchetti, J.M., Errazu, A.F**. 2008. "Esterification of free fatty acids using sulfuric acid as catalyst in the presence of triglycerides". *Biomass and Bioenergy*, 32(9), 892-895.

10. **A Stankiewicz and A.A..H. Drinkenburg**, Process intensification: History, philosophy, principles, in: Re- engineering the chemical processing plant process intensification, edited by A. Stankiewicz and J.A. Moulijn, Marcel Dekker, Inc., 2004.

11. **I. Stankiewicz, J.A. Moulijn**, "Process intensification: transforming chemical engineering", Chem. Eng. Pro., 96 (2000) 22-34.

12. **R. Jachuck**, Process intensification for responsive processing, Trans IChemE, 80 (2002) 233-238.

13. **R.A. Holl**, Methods of operating surface reactors and reactors employing such methods, Patent US 7,125,527 B2, 2006.