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Optimization of Third Generation Biofuels Production: Biodiesel from Microalgae Oil by Homogeneous Transesterification

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Competing between foods and biofuels production, the world food crisis and high oil prices have ignite attention in algaculture for making biofuels. Among algae biodiesel positive characteristics are: it can be produced using sea water and wastewater without affecting fresh water resources, is biodegradable and relatively harmless to the environment if spilled. This work represents the first attempt of optimizing third-generation biodiesel production by homogeneous transesterification. It was used a synthetic algae oil based on *Chorella vulgaris* fatty acid composition. The first step of this research was the experimentation based on a central composite design and second was the optimization of process conditions by using response surface methodology. Three process variables were evaluated at two levels: methanol/oil molar ratio, reaction temperature and amount of catalyst. A second-order model was obtained to predict yield of fatty acid methyl esters as a function of the three evaluated variables with high statistical significance (p-value=0.0146). The best combination of process variables are 14:1 methanol/oil molar ratio, 0.42 wt% of NaOH and 43 °C.

1. Introduction

Global warming is arguably one of the major concerns of mankind today. Its primary cause is greenhouse gases emission. As a possible solution, the use of biofuels was proposed. However, first-generation biofuels have produced controversy by the effect on food prices associated with some of them. This soon led to the development of second-generation biofuels from non-food crops. These include waste biomass, the stalks of wheat, corn, wood, and special-energy-or-biomass crops. But one of the most important disadvantages of second-generation biofuels is low energy efficiency of production processes. There is currently widespread interest in cultivation of different microalgae species, whose oil can be used as feedstock in the production of biodiesel. This algae biodiesel is also called third-generation biodiesel. Microalgae capture carbon from atmospheric CO2 (Schenk et al, 2008), have high growth rates, doubling its population within 24 hours (Rittmann, 2008), can grow in salty or waste water (Schenk et al, 2008), their oil production per unit of cultivated area can be up to 300 times

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greater than that of oil plants (Chisti, 2007). Despite these benefits, the studies reported so far on algae oil transesterification are limited (Wu and Miao, 2006; Ehimenet al, 2010).

Estimation of the main and interaction effects of some factors on a given response variable are usually accomplished through studies based on experimental designs. 2^k factorial designs, with k factors evaluated at two levels (maximum and minimum), are most frequently used. A polynomial equation is obtained in terms of the test factors to predict the value of response variable. This model can be employed to generate a response surface and to calculate the optimal combination of conditions which provide the best response. Several authors have studied the influence of the main process variables on the transesterification applying response surface methodology (RSM) (Domingos et al, 2008; Yuan et al, 2008).

This paper presents the optimization of a synthetic algae oil methanolysis. This synthetic algae oil simulates the fatty acid composition of *Chlorella vulgaris* oil and was used because of the limitations in obtaining the pure *Chlorella vulgaris* oil in the amounts needed for a complete study. This work was sponsored in the framework of projects supported by the Colombian Ministry of Agriculture and Rural Development, the Colombian Petroleum Institute and the Ibero-American Program on Science and Technology for Development (CYTED).

2, Materials and methods

2.1 Preparation of synthetic algae oil

The fatty acids in *Chlorella vulgaris* oil reported by Petkov y García (2006) for outdoor cultivation were grouped according to their degree of unsaturation. Thus, 14:0, 16:0 and 18:0 were grouped as saturated fatty acids and their percentage in the mixture was calculated equal to 13%. Similarly, 16:1 and 18:1 were grouped as mono-unsaturated, 16:2 and 18:2 as di-unsaturated, and 16:3 and α-18:3 as tri-unsaturated. The percentages calculated for each group are reported in Table1.

After testing different combinations of oils, it was found that the mixture of linseed oil, sunflower oil, olive oil and palm superstearin fulfills the math requirement expressed by the system of linear equations formed by Equations 1, 2, 3 and 4; these equations represent the mass balance of saturated, mono-unsaturated, di-unsaturated and tri-unsaturated fatty acids in an ideal mixing unit, where the oils are entering and the mixture is leaving.

$$W_BC_{B1}+W_CC_{C1}+W_DC_{D1}+W_EC_{E1}=W_AC_{A1} \quad (1)$$
$$W_BC_{B2}+W_CC_{C2}+W_DC_{D2}+W_EC_{E2}=W_AC_{A2} \quad (2)$$
$$W_BC_{B3}+W_CC_{C3}+W_DC_{D3}+W_EC_{E3}=W_AC_{A3} \quad (3)$$
$$W_BC_{B4}+W_CC_{C4}+W_DC_{D4}+W_EC_{E4}=W_AC_{A4} \quad (4)$$

W is the mass of oil, Cij the mass composition in the oil i of the fatty acid j, A microalgae oil, B linseed oil, C sunflower oil, D olive oil, E palm superstearin, 1 saturated , 2 mono-unsaturated, 3 di-unsaturated and 4 tri-unsaturated fatty acids. The amounts required to prepare 1 kg of synthetic algae oil were 729.33 g of linseed oil, 240.09 g of sunflower oil, 8.76 g of olive oil and 21.92 g of palm superstearin.

Table 1 Fatty acid composition of Chlorella vulgaris oil according to their unsaturation degree

Fatty acid	%
Saturated	13
mono–unsaturated	20
di–unsaturated	28
tri–unsaturated	39

2.2 Analytical method of the synthetic algae oil

Analysis of the synthetic algae oil fatty acid composition was carried out by Gas Chromatography (GC) with Flame Ionization Detector (FID). The column employed was a DB-23 (50%-cyanopropyl-poly(methylsiloxane), 60mx0.25mmx0.25mm). Helium was used as the carrier gas at a flow of 2μL/min.

2.3 Experimental design

The range and levels of the factors investigated are listed in Table 3. Studies accomplished for several authors confirmed that a linear model can not describe the relationship that existed among this factors and the yield (*Y*) of the ester layer, which was choosen as the response variable, since to low regression coefficient and statistically unacceptable *p*-value of the regression variance of the model (Domingos et al, 2008). A Central Composite Design (CCD) was then carried out in order to examine the non linear behavior of the response variable into the experimental domain. The CCD comprises a typical 2^3 factorial design augmented with six axial points and three center points. The Statgraphics 5.0 Plus software was used for regression analysis of the experimental data, statistical significance assessment of the model and optimization of the transesterification of the synthetic algae oil by RSM.

2.4 Transesterification

For achieving the experiments, it was employed a sealed 2 L glass reactor equipped with a reflux condenser, a temperature controller and a magnetic stirrer, which was set at 600 rpm. The reactor was filled with 250 g of synthetic algae oil and heated. When the reactor reached to the temperature established for the test. The sodium hydroxide and the methanol were added to oil in the amounts established for each experiment, which was prolonged for 90 min. After cooling, two layers were separated by sedimentation. The upper layer was purified by distilling the residual methanol. The remaining catalyst was extracted by successive rinses with distilled water. Finally, the water present was eliminated by heating.

2.5 Analytical method of the biodiesel

Gel Permeation Chromatography (GPC) was used for quantifying methyl esters and unreacted glycerides. This analysis was performed with two columns: a PLgel MIXED Gel (MIXED-E 300x7.5x3μm) and a TSK-Gel (G1000HXL 300x7.8x5μm) operated at 40 °C in tandem with tetrahydrofuran (THF) as the mobile phase at 1 mL/min and a Refractive Index Detector (RID).

Table 2 Fatty acid composition of synthetic algae oil according to their unsaturation degree

Fatty acid	%
Saturated	12.5
mono–unsaturated	24.6
di–unsaturated	27.6
tri–unsaturated	35.3

Table 3 Experimental range and levels of the factors

Variables	Symbol coded	Range and levels				
		-1.682	-1	0	1	1.682
Methanol/oil molar ratio	X_1	4:1	6:1	9:1	12:1	14:1
Catalyst concentration (%)	X_2	0.42	0.7	1.1	1.5	1.77
Reaction temperature (ºC)	X_3	38	45	55	64	72

3. Results and discussion

The experiments were carried out according to the CCD experimental plan shown in Table 4. The following second-order polynomial equation was obtained from multiple regression analysis of the experimental data:

$$Y=98{,}0982+3{,}95078X_1+2{,}30503X_2+0{,}886048X_3-2{,}07287X_1^2-0{,}664306X_2^2-0{,}755302X_3^2-3{,}15X_1X_2-1{,}22X_1X_3-1{,}7875X_2X_3 \quad (5)$$

Table 4 Central composite design matrix and responses for synthetic oil methanolysis

Methanol/oil molar ratio	Catalyst concentration (% w/w)	Temperature (ºC)	X_1	X_2	X_3	Yield (%)
6:1	0.7	45	-1	-1	-1	77.01
12:1	0.7	45	1	-1	-1	97.88
6:1	1.5	45	-1	1	-1	96.89
12:1	1.5	45	1	1	-1	98.88
6:1	0.7	64	-1	-1	1	88.92
12:1	0.7	64	1	-1	1	98.63
6:1	1.5	64	-1	1	1	95.37
12:1	1.5	64	1	1	1	98.76
9:1	1.1	55	0	0	0	97.89
9:1	1.1	55	0	0	0	97.85
9:1	1.1	55	0	0	0	98.28
4:1	1.1	55	-1.682	0	0	87.68
14:1	1.1	55	1.682	0	0	98.38
9:1	0.42	55	0	-1.682	0	95.82
9:1	1.77	55	0	1.682	0	98.21
9:1	1.1	38	0	0	-1.682	96.44
9:1	1.1	72	0	0	1.682	97.08

To evaluate the statistical significance of the regression model, the analysis of the variance (ANOVA) was performed. For a given model, the smaller the *p*-value, the significance for the model is higher (Yuan et al, 2008).

Table 5 Analysis of variance (ANOVA) for the regression model and coefficients

Source	Sum of squares	Degrees of freedom	Mean of squares	F-test	*p*-value
Model	462.004	9	51.3337	5.88	0.0146
Residual	61.1382	7	8.73408		
X_1	213.165	1	213.165	24.41	0.0017
X_2	72.5613	1	72.5613	8.31	0.0236
X_3	10.7142	1	10.7142	1.23	0.3047
X_1^2	48.4584	1	48.4584	5.55	0.0507
X_2^2	4.97583	1	4.97583	0.57	0.4750
X_3^2	6.41794	1	6.41794	0.73	0.4197
X_1X_2	79.38	1	79.38	9.09	0.0195
X_1X_3	11.9072	1	11.9072	1.36	0.2812
X_2X_3	25.5612	1	25.5612	2.93	0.1309
Total	523.142	16			

The *p*-value of the model shows high significance (*p*-value=0.0146<0.05). The determination coefficient (R^2=88.3132) confirms the fit of the model: only 11.6868 % of the total variance are not attributed to the independent variables.
From Table 5 it could be concluded that molar ratio has the largest effect on the response variable (due to the smaller *p*-value) followed by catalyst concentration, whereas temperature has insignificant effect. The interaction between molar ratio and catalyst concentration was also significant. This fact reveals that the effect of increasing molar ratio depends on the level where the catalyst concentration is and inversely. Figure 1 shows that the yield is significantly positive affected by rising the catalyst concentration at 6:1 molar ratio (-1 in coded value), whereas increasing the amount of catalyst has a negative effect on the yield at 12:1 molar ratio (+1 in coded value). However this effect is not considerably. Therefore, the operating conditions of small molar ratio should be avoided.

Based on its statistical significance, the model was used to calculate the conditions under which synthetic oil methanolysis lead to the highest ester yield. The RSM indicated that the optimal conditions are 14:1 methanol/oil molar ratio, 0.42 wt% of NaOH and 43 °C.

4. Conclusions

This work represents the first attempt of optimizing third-generation biodiesel production by homogeneous transesterification using synthetic algae oil based on *Chorella vulgaris* fatty acid composition. The use of this synthetic algae oil gives the possibility to evaluate the effect of the methanol/oil molar ratio, catalyst concentration and reaction temperature on the production of third-generation biodiesel. A second-order model was obtained to predict yield of fatty acid methyl esters as a function of the three evaluated variables with high statistical significance (p-value=0.0146). The optimization of the process was successfully performed using the response surface methodology. The best combination of conditions are 14:1 methanol/oil molar ratio, 0.42 wt% of NaOH and 43 °C.

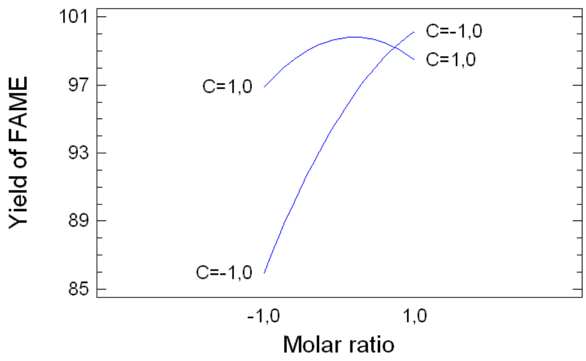

Figure 1: Interaction effect between molar ratio and catalyst concentration

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