STUDY OF BIODIESEL PRODUCTION FROM WASTE COOKING OIL APPLYING THE SURFACE RESPONSE

K. QUIJADA†, F. MILLÁN‡ and S. DI SCIPIO§

† *Coordinación de Ing. Química, Universidad Simón Bolívar, AP. 89000 Caracas, Venezuela.*
quijadakarina@yahoo.com
‡ *Dpto. de Tecnología de Procesos Biológicos y Bioquímicos, Universidad Simón Bolívar, AP. 89000 Caracas, Venezuela.*
fmillan@usb.ve
§*Dpto. de Termodinámica y Fenómenos de Transferencia, Universidad Simón Bolívar, AP. 89000 Caracas, Venezuela.*
sdiscipio@usb.ve

***Abstract*— Two ways of synthesis to produce biodiesel from waste cooking oil were compared: 1) Transesterification of fatty acids with basic catalyst (KOH) and 2) Esterification with H_2SO_4 followed by the transesterification evaluated previously, using factorial designs 2^3 with central points and the Surface Response Methodology (RSM). Raw material was characterized through its acid value and moisture content. In synthesis (1) the factorial design factors were: reaction temperature, catalyst wt%/ weight of processed oil and, methanol:oil molar ratio, and response variables were: yield of reaction, density and, kinematic viscosity, with 75 minutes as reaction time. Yields around 88% were achieved. In synthesis (2) the factorial design was applied only for esterification reaction, using two of the preceding factors and reaction time instead of temperature (fixed at 60ºC). The best conditions determined for synthesis (1) were applied and yield of reaction increased to 97%. The kinematic viscosities and densities satisfied the standards.**

***Keywords*— biodiesel, waste cooking oil, transesterification, esterification, surface response methodology.**

I. INTRODUCTION

The need to guarantee the supply of sustainable energy, with reasonable prices, has promoted the active research of renewable sources through chemical processes more profitable, with highest yields. The biodiesel of second generation obtained from waste vegetable cooking oil, is an energetic product which reduces the highly contaminant oil spills in water bodies.

In order to improve the production of biodiesel, several researches of its obtainment from residual cooking oil has been developed, considering the molecular changes that triglycerides can experiment at high temperatures and humidity related with the food frying processes. As consequence of the degradation process experimented by the residual oil, Canakci (2007) concluded that the process required to obtain the biodiesel has to be robust, to tolerate the wide variations in moisture (0.01 to 1.42 wt%) and free fatty acids (0.7 to 41.8 wt%) content.

The most conventional process to obtain biodiesel is transesterification, which consist in the conversion of the free fatty acids (FFA) from vegetable triglycerides in esters, using short chain alcohols as methanol or ethanol, and basic catalyst (KOH or NaOH). Some authors agree that the most adequate molar ratio for methanol and oil is 6:1 (Noureddini and Zhu, 1997; Darnoko and Cheryan, 2000; Issatiyakul and Dalai, 2009; Tomasevic and Siler-Marinkovic, 2003). While Phan and Phan (2008) proposed ratios in the range 7:1 to 8:1, similar to Giracol *et al*. (2011) that used 7:1. Enciner *et al*. (2002) used ethanol and reported molar ratios in the range 3:1 to 15:1, the best properties were obtained at 12:1 ratio.

When residual cooking oils are used, transesterification process produces low yields due to free fatty acids neutralization by the base catalyst. The free fatty acid content and moisture contribute to the occurrence of saponification process, which produces fatty acid salts (commonly named soap), as secondary product (Banerjee and Chakraborty, 2009). Soap increases the kinematic viscosity, and in some cases, gels can be produced making difficult the separation process step between esters and glycerol (secondary product of transesterification process).

The fatty acids esterification with a strong acid (i.e. H_2SO_4) is also used to produce biodiesel. The kinetics of that reaction is slower than the transesterification reaction; in consequence, considerable high time reaction is required (until 96h) to achieve yields close to 90% (Canakci and Van Gerpen, 1999).

Another alternative for the biodiesel synthesis is a combination of an acid esterification to reduce the content of FFA in the oil, followed by a transesterification reaction. Canakci and Van Gerpen (2001) reduced the acid level in samples of soybean enriched with palmitic acid using H_2SO_4 (0, 5, 15 and, 25 wt%) as catalyst, 1h as reaction time, a methanol:oil or ethanol:oil ratio equal to 9:1 and, temperature between 60 and 75°C. With methanol the initial acid value, was reduced from 41.33 mgKOH/g to 1.77 mgKOH/g at 5 wt% H_2SO_4 and until to 0.54 mgKOH/g at 25 wt% H_2SO_4. Additionally, they applied this process to yellow and brown greases, decreasing the acidity with a multistage acid esterification, using 6:1 as methanol:oil molar ratio and different types of base catalyst and, obtaining yields in the range 74.8 to 82.2% for yellow greases and, 56.4 to 75.1% for brown greases.

The surface response methodology (RSM) has been

used to describe biodiesel production reaction systems by Chin *et al.* (2008) and Vicente *et al.* (1998).

The objective of the present work was the study of biodiesel production through two different ways of synthesis, transesterification and the combined process of acid esterification and transesterification, applying a factorial design 2^3 with central points, with the corresponding variance analysis and the RSM in each case.

II. METHODS

A. Raw Material and Characterization

The raw material (waste cooking palm oil) was obtained from cafeteria in the Simon Bolivar University, Caracas, Venezuela. It was characterized through its acid value by titration and moisture content by weight difference. The oil moisture content oscillated between 0.45 and 0.69% and the acid value was 1.5±0.3 mgKOH/g. These results fit into the range studied by Canakci (2007).

B. Experimental procedure

- *Method 1: Transesterification*

100 g of filtered waste cooking palm oil samples were used for each assay and heated till treatment temperature. Previously, KOH and methanol were mixed to incorporate them in the main reaction. When the oil reached the assay temperature, methoxide formed was mixed with oil. Time of reaction was timed as soon as methoxide was added to oil and carried on for 75 min.

After 75 min, the mixture was cooled at room temperature, washed with 5 vol% aqueous H_2SO_4 solution and separated by gravity in two layers: glycerol (white and heavier layer) and methyl ester (brown and lighter layer). Glycerol layer was removed and 3 g to Na_2SO_4 were added to methyl ester layer to eliminate remaining moisture.

- *Method 2: Acid esterification with transesterification*

H_2SO_4 was used as catalyst. 100 g of filtered waste cooking palm oil samples were used for each assay and heated till 60°C. When this temperature was reached, methanol was added to oil and mixed for 5 minutes with a magnetic stirrer. After that, H_2SO_4 was added to mixture and the reaction carried on. Time of reaction depended on the factorial design treatment and temperature was maintained at 60°C.

After reaction time the mixture was allowed to cool at room temperature, decanted into a funnel and washed with water and separated by gravity in two layers: glycerol (white and heavier layer) and methyl ester (brown and lighter layer). The methyl ester layer was used like a raw material to the transesterification reaction, described previously.

In both procedures, the response variables measured were: yield of reaction in wt%, specific mass at 15°C using a pycnometer and, kinematic viscosity using a Cannon viscometer number 100 at constant temperature (40°C), inside a glycerin bath.

C. Factorial design and statistics analysis

Similar to Vicente *et al.* (1998), which used a 2^2 factorial design to optimize reaction temperature and catalyst concentration for a transesterification reaction, in this study a 2^3 factorial design with central points was developed for each reaction, to determine the influence of the variables temperature of reaction (A_1), methanol: oil molar ratio (B_1) and base catalyst mass percentage (C_1) for transesterification (Eqs. 1, 2 and 3). For acid esterification reaction (Eqs. 4, 5 and 6) the variables were time of reaction (A_2), methanol: oil molar ratio (B_2) and catalyst mass percentage (C_2). It was necessary to define the coded variables in two levels, minimum (-1) and maximum (+1). The treatments for each reaction were performed per triplicate to verify the reproducibility, except central points (coded variable is zero). The analysis of variance (ANOVA) was developed with Statgraphics Centurion XVI program and the model's assumptions of normality, independence and homoscedasticity were checked. Probability of Type I error (α=0.05) was considered. The linear effects and the studied factor interactions were considered statistically significant when the probabilities associated with the F-statistics were lower than 0.05 (P<0.05). Tables 1 and 2 shown the combination of variables in each treatment.

$$A_1 = \frac{T(^oC) - 50^oC}{10^oC}, \quad (1)$$

$$B_1 = \frac{CH_3OH : ac(molar) - 8:1}{4:1}, \quad (2)$$

$$C_1 = \frac{KOH(wt\%) - 1.5(wt\%)}{0.5(wt\%)}, \quad (3)$$

$$A_2 = \frac{t(h) - 6h}{3h}, \quad (4)$$

$$B_2 = \frac{CH_3OH : ac(molar) - 30:1}{10:1}, \quad (5)$$

Table 1. 2^3 Factorial design with central points corresponding to the synthesis 1.

	Coded Factors			Natural Factors		
Treatment	A_1	B_1	C_1	A_1	B_1	C_1
1	-1	-1	-1	40	4:1	1%
2	+1	-1	-1	60	4:1	1%
3	-1	+1	-1	40	12:1	1%
4	-1	-1	+1	40	4:1	2%
5	+1	+1	-1	60	12:1	1%
6	+1	-1	+1	60	4:1	2%
7	-1	+1	+1	40	12:1	2%
8	+1	+1	+1	60	12:1	2%
Central Points	0	0	0	50	8:1	1.5%

Table 2. 2^3 Factorial design with central points corresponding to the synthesis 2.

	Coded Factors			Natural Factors		
Treatment	A_2	B_2	C_2	A_2	B_2	C_2
1	-1	-1	-1	2	20:1	5%
2	+1	-1	-1	8	20:1	5%
3	-1	+1	-1	2	40:1	5%
4	-1	-1	+1	2	20:1	25%
5	+1	+1	-1	8	40:1	5%
6	+1	-1	+1	8	20:1	25%
7	-1	+1	+1	2	40:1	25%
8	+1	+1	+1	8	40:1	25%
Central Points	0	0	0	5	30:1	15%

$$C_2 = \frac{H_2SO_4(wt\%) - 15(wt\%)}{10(wt\%)}, \quad (6)$$

In the combined process the temperature was fixed at 60°C and the factors varied were reaction time, methanol molar ratio and catalyst weight percentage from acid esterification process. For transesterification process, the best technical conditions from the first factorial design were used.

D. Quality properties measurement

Cetane number, heat of combustion and flash point were measured for biodiesel produced from each of the best technical reaction condition from each process considered in this work (Transesterification called synthesis 1 and combined process called synthesis 2). Some ASTM standards were considered as reference (Cetane number ASTM D-613-10a and heat of combustion ASTM D240), flash point employing a calorimeter.

III. CONCLUSIONS

A. Synthesis 1: Transesterification

In Table 3 are shown the response variables corresponding to biodiesel production through synthesis 1. For all treatments of transesterification reaction, except number 6, the yields were close to 90% wt%, similar to Darnoko and Cheryan (2000); it was expected due to the low catalyst concentration. The ANOVA of transesterification reaction results for yield, density and kinematic viscosity are shown in Table 4, where bold numbers represent statistical significant results. All main effects (A, B and, C) were statistically significant ($P<0.05$) for yield, but lack of fit was insignificant ($P=0.0654$). The significant interaction A1B1 response surface is shown in Fig. 1.

The ANOVA results for density and kinematic viscosity can be observed in Table 4. Lack of fit for density was statistically significant, with a correlation coefficient R^2=76.93% and $R^2_{adjusted}$=66.37%. The difference between R^2 and $R^2_{adjusted}$ suggests the presence of outlayers. Outlayers were produced by treatments 1 and 2. However, they fit in normal range of densities values accepted (860-890 kg/m^3). About kinematic viscosity, the treatments 1 and 2 have viscosity values above 8 cSt (see on Table 3) and 5 to 6 cSt are the higher value accepted according to the standards (EN14214:2008 or ASTM D6751-10), in consequence, these treatments were not considered valid.

The temperature-methanol combination was the most important system interaction. The increase of temperature at the lower methanol quantity promotes the production of free fatty acids; in consequence, reaction of saponification is favored. Better yields were obtained in two surface zones: 1) lowest temperature for all methanol molar ratios and, 2) highest methanol molar ratio for all temperatures.

Nevertheless, at lowest temperature and methanol molar ratio, densities are similar to the oil and kinematic viscosities and greater than values established in the standards (ν=8 cSt), therefore, the triglycerides conversion in esters was considered poor and the main product obtained was non converted oil. In the second zone,yield was 88% (average value), which is a satisfactory result. Similar results were obtained at B_1C_1 interaction analysis (Fig. 2). Highest methanol molar ratio

Table 3. Response variables results corresponding to the synthesis 1

Treatment	Yield (wt%)	Density (kg/m3)	Kinematic viscosity (cSt)
1	87	895	8.39
2	87	894	8.10
3	91	886	5.15
4	86	890	6.40
5	89	886	5.11
6	70	886	5.67
7	87	887	5.05
8	86	887	5.17
Central Points	89	886	5.13

Table 4. ANOVA for the synthesis 1 factorial design.

	Yield		Density		Kinem. Visc.	
Parameter	F Value	P Value	F Value	P Value	F Value	P Value
A_1:Temp. of reaction	33.75	0.0000	17.63	0.0009	17.13	0.0010
B_1: CH_3OH:oil molar ratio	23.76	0.0002	93.47	0.0000	402.64	0.0000
C_1: KOH wt.%	22.60	0.0003	18.79	0.0007	79.47	0.0000
A_1 B_1	22.64	0.0003	19.70	0.0006	26.59	0.0001
A_1 C_1	1.33	0.2688	2.96	0.1074	0.05	0.8230
B_1 C_1	2.86	0.1131	53.94	0.0000	81.96	0.0000
Lack of fit	3.34	0.0654	16.66	0.0002	62.34	0.0000

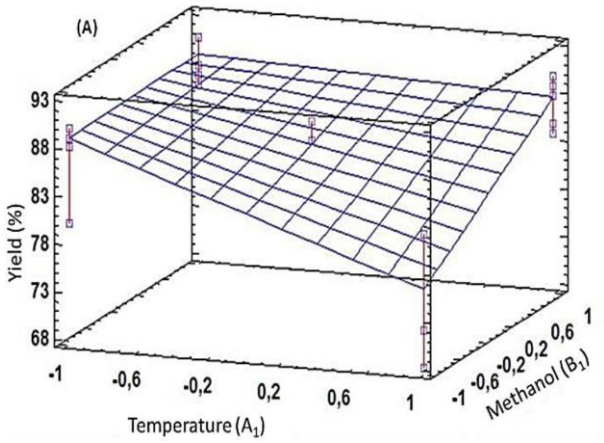

Figure 1. Yield response surface for A_1B_1 interaction.

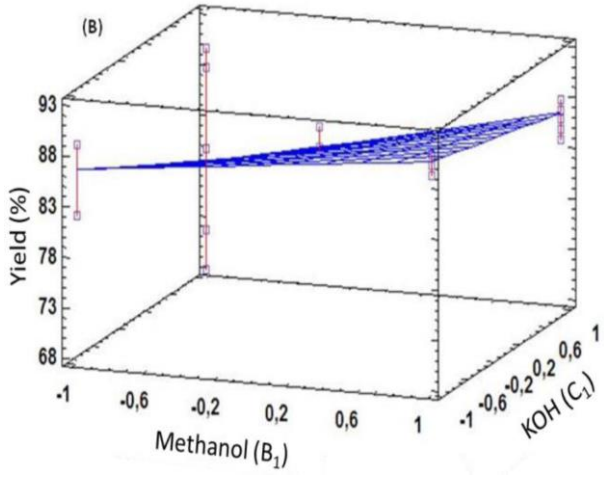

Figure 2. Yield response surface for B_1C_1 interaction (synthesis 1).

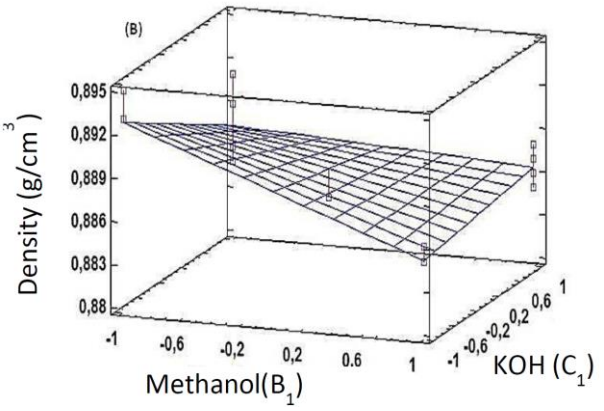

Figure 3. Density response surface for B_1C_1 interaction (synthesis 1).

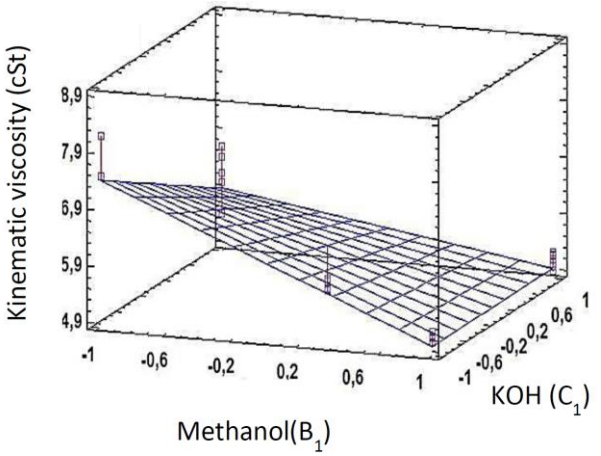

Figure 4. Kinematic viscosity response surface for B_1C_1 interaction (synthesis 1).

produced better yields, independent on mass percentage of KOH. Stoichiometry methanol molar ratio to molar triglycerides processed is 3:1 however, as can be observed at Fig. 2, a real transesterification system needs higher molar methanol ratios like 3:1 (more than 6:1) to produce satisfactory yields. If methanol excess is enough, the effect caused by KOH as a saponification reagent is very low.

Figure 3 shows density response surface for B_1C_1 interaction and Fig. 4 shows kinematic viscosity response surface for B_1C_1 interaction. The highest densities values were at lowest methanol molar ratio value and KOH mass percentage. On the other hand, Fig. 4 shows kinematic viscosity values outside the expected range (6 cSt maximum) produced by the same conditions mentioned above. Both of them, similar to Fig. 2, show that excess of methanol above stoichiometry value improves yield of reaction and other biodiesel properties.

The best operation condition correspond to the central point treatments, considering that higher yields and normal product properties could be obtained with lower catalyst and methanol molar ratio compared with the top levels, favouring the possibility of cost reduction (T=60°C, t= 75 min, CH_3OH:oil = 8:1, wt.%KOH=1.5). The difference between top levels' yields and central point's yields was around 3 or 4%. Beside this, quality standards (88% of yield, ρ=885 kg/m^3, ν=4.92 cSt) fulfill expected values. The lack of fit from ANOVA for the yield variable was no significant while the viscosity and density lack of fit were significant, due to the presence of outlayers corresponding to experimental treatments which produced biodiesel that no satisfy the ASTM standards used as a reference.

B. Synthesis 2: Acid esterification with transesterification (combined process)

In Table 5 are shown the response variables corresponding to biodiesel production through synthesis 2. Compared to the yields reached with the oils studied by Canakci and Van Gerpen (2001), in this work better results were obtained (more than 90% for all treatments). The ANOVA results of yield, density and, kinematic viscosity for acid esterification with transesteri-fication process are shown in Table 6. A yield reaction increase from 4 to 9 % comparing with synthesis 1 was observed. The density and kinematic viscosity of these samples were lower than the previous ones produced by transesterification.

In the yield statistical analysis, main factors A_2, B_2 and all interactions were significant, except lack of fit. Fig. 5 represents the response surface for interaction A_2 B_2. As the time reaction increased, the yield de-creased till 92% (lowest yield value with synthesis 2). A combination of higher time reactions and higher methanol molar ratio with unsaturated fatty acid and heat promotes the breakdown of triglycerides, generating more FFA and the free radical oxidation reaction; in consequence, low yields were generated. All response surfaces shown highest yields around lower acid weight percentages, time reaction and methanol molar ratio, which represents an operational advantage for a pre-treatment step to the biodiesel industrial production process, compared with times obtained by Canakci and Van Gerpen (2001),

Table 5. Response variables results corresponding to the synthesis 2

Treatment	Yield (wt%)	Density (kg/m3)	Kinematic viscosity (cSt)
1	97	889	5.06
2	97	885	4.94
3	95	885	4.90
4	97	887	4.88
5	96	886	4.95
6	90	891	5.02
7	96	885	4.71
8	92	885	4.92
Central Points	84	888	4.85

Table 6. ANOVA for the synthesis 2 factorial design.

	Yield		Density		Kinem. Visc.	
Parameter	F Value	P Value	F Value	P Value	F Value	P Value
A_2:Temp. of reaction	52.14	0.0000	15.13	0.0011	14.14	0.0570
B_2: CH_3OH:oil molar ratio	60.15	0.0000	0.13	0.7278	3.02	0.0995
C_2: H_2SO_4 wt.%	0.35	0.5636	136.13	0.0000	7.12	0.0156
A_2 B_2	94.76	0.0000	45.13	0.0000	0.81	0.0403
A_2 C_2	5.54	0.0302	45.13	0.0000	0.72	0.4079

B_2 C_2	5.05	0.0375	0.13	0.7278	2.46	0.1344
Lack of fit	1.86	0.1841	52.24	0.0000	0.76	0.4816

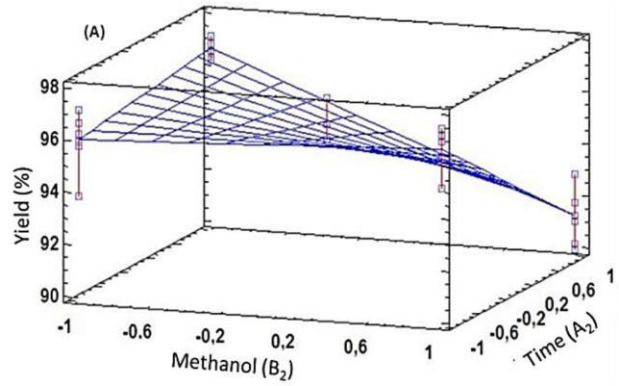

Figure 5. Yield response surface for A_2B_2 interaction (synthesis 2).

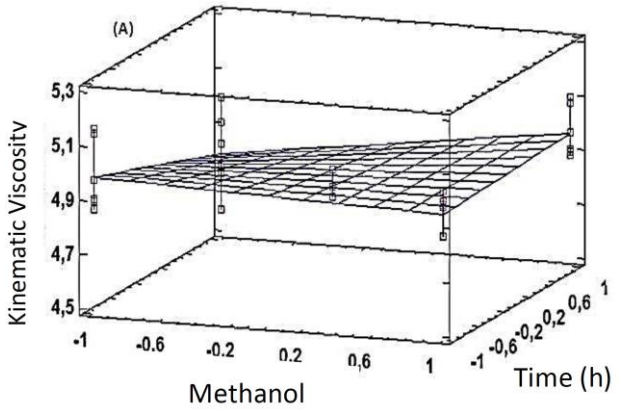

Figure 6. Kinematic Viscosity response surface for A_2B_2 interaction (synthesis 2).

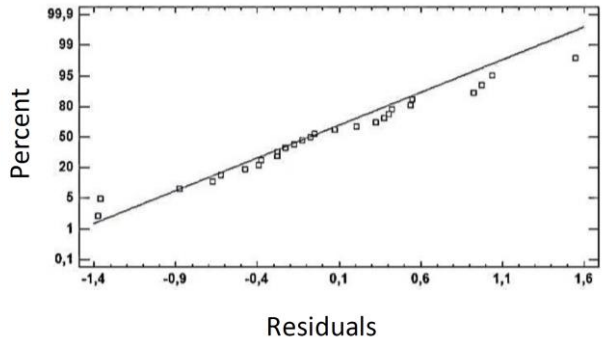

Figure 7. Normal probability plot of the residuals for synthesis 2 yield response.

who produced biodiesel from waste oil by acid esterifcation. Yield's difference between lowest and highest time points (Δt=6h) for lowest methanol molar ratio represents around 1% more, which is a few product increment compared with increment in time and energy using 8h as reaction time.

For density response, all of main factors and lack of fit were significant. However, density values were similar between them and within normal ranges. This result produced a flat response surface due to all density values were closer to 888 kg/m^3.

For kinematic viscosity, H_2SO_4 weight percentage and A_2B_2 interaction were statistically significant, but the values were within the expected value comparing them with standards (results could be seen in Table 5). Kinematic viscosity response surface is shown in Fig. 6. Lack of fit of main factors was negligible; the correlation coefficient R^2 for the yield response variable was 90.94%. The operational conditions most favorable for acid esterification were methanol:oil ratio 20:1, 120 min and 5%$w_{catalyst}/w_{oil}$; this operation point combined with transesterification process, produce biodiesel with satisfactory yield quality properties.

Figures 7 to 9 shown three specific plots to examine the assumptions underlying the ANOVA for yield response corresponding to Method 2. Graphics for all response variables are similar than the graphics presented below. Assumptions were satisfied in all cases.

C. Quality Properties

Flash point measured for synthesis 1 was 173°C and 171°C for synthesis 2. Comparing with the Flash Points standards (ASTM 93 °C and ISO 101 °C, minimum) the results were satisfactory. The heat of combustion obtained for both process was between 38.59 and 39.97 MJ/kg, into the standard range (37.5 MJ/kg and 40 MJ/kg). The values for cetane number were similar to results obtained in previous studies related to biodiesel production from palm oil, who reported the following values: 58.3 (Schwab *et al.*, 1987), 62.4 (Liang *et al.*, 2006) and 62.0 (Marchetti *et al.*, 2005). As can be seen in Fig. 10, biodiesel cetane number fit between minimum and maximum cetane numbers reported by others researchers, for synthesis 1 was 61.8 and, 59.9 for synthesis 2.

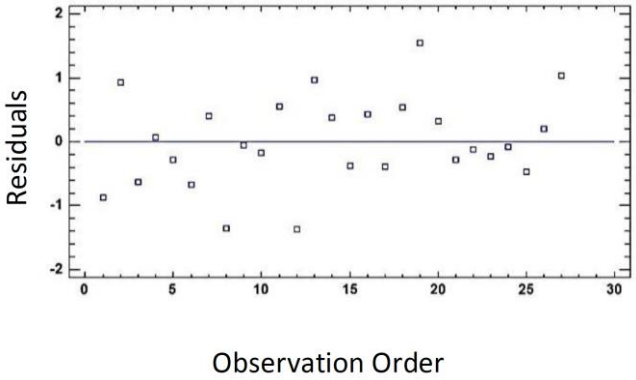

Figure 8. Observation Order vs. Residuals for synthesis 2 yield response.

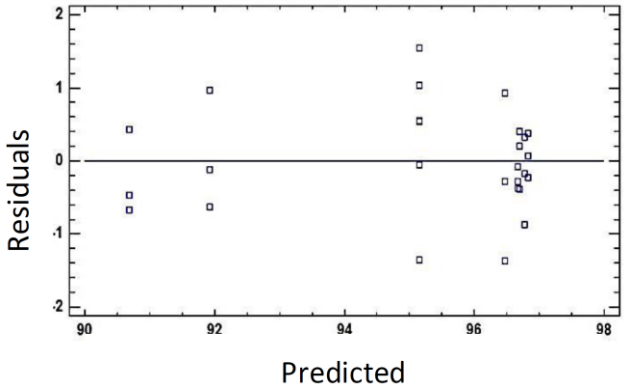

Figure 9. Predicted vs. Residuals for Method 2 yield response.

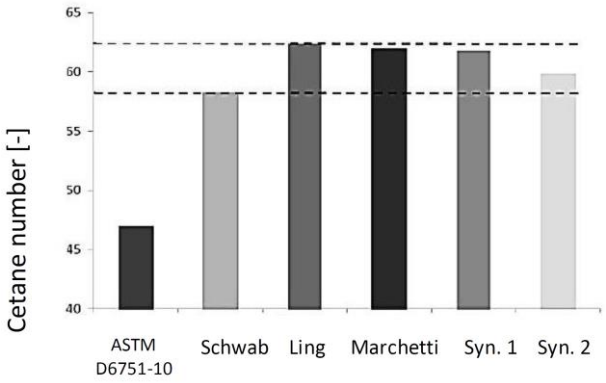

Figure 10. Cetane number comparison from palm oil biodiesel with ASTM standard

REFERENCES

Banerjee, A. and R. Chakraborty, "Parametric sensitivity in transesterification of waste cooking oil for biodiesel production-A review," *Resour. Conserv. Recy*., **53**, 490-497 (2009).

Canakci, M., and J. Van Gerpen, "Biodiesel produc-tion via acid catalysis," *Trans. ASAE*, **42**, 1203-1210 (1999).

Canakci, M. and J. Van Gerpen, "Biodiesel production from oils and fats with high free fatty acids," *Trans. ASAE*, **44**, 1429-1436 (2001).

Canakci, M., "The potential of restaurant waste lipids as biodiesel feedstock," *Bioresource Technol*., **98**, 183-190 (2007).

Chin, L., B. Hameed and A. Ahmad, "Process Optimization for Biodiesel Production from Waste Cooking Palm Oil (Elaeis guineensis) Using Response Surface Methodology," *Energ. Fuel*, **23**, 1040-1044 (2009).

Darnoko, D. and M. Cheryan, "Kinetics of palm oil transesterification in a batch reactor," *JAOCS*, **77**, 1263-1267 (2000).

Enciner, J., J. González, J. Rodríguez and A. Tajedor, "Biodiesel fuels from vegetable oils: transesterification of Cynara Cardunculus L. oils with etanol," *Energy Fuels*, **16**, 443-450 (2002).

Giracol, J., K.C. Passarini, S. Catureba, F. Araújo, E. Tambourgi and J.C. Curvelo, "Reduction in ecological cost through biofuel production from cooking oils: an ecological solution for the city of Campinas, Brazil," *J. Clean. Prod*., **19**, 1324-1329 (2011).

Issariyakul, T., and A. Dalai, "Utilization of used cooling oil, canola oil and greenside canola oil for biodiesel production," *8th World Cong. Chem. Eng*., Montreal, Canada (2009).

Liang, Y., C. May, C. Foon, M. Ngan, C. Hock and Y. Bariron, "The effect of natural and synthetic antioxidants on the oxidative stability of palm diesel," *Fuel*, **85**, 867-870 (2006).

Marchetti, J., V. Miguel and A. Errazu, "Possible methods for Biodiesel production," *Renew. Sust. Energ. Rev.*, **11**, 1300-1311 (2005).

Noureddini, H., and D. Zhu, "Kinetics of transesterfication of soybean," *JAOCS*, **74**, 1263-1267 (1997).

Phan, A. and T. Phan, "Biodiesel production from waste cooking oils," *Fuel*, **87**, 3400-3496 (2008).

Schwab, A., M. Bagby and B. Freedman, "Preparation and properties of diesel fuels from vegetable oils," *Fuel*, **66**, 1372-1378 (1987).

Tomasevic, A. and S. Siler-Marinkovic, "Methanolysis of used frying oil: optimization for biodiesel production," *Fuel Process. Technol*., **81**, 1-6 (2003).

Vicente, G., A. Coteron, M. Martinez and J. Aracil, "Application of the factorial design of experiments and response surface methodology to optimize biodiesel production," *Ind. Crop Prod*., **8**, 29-35 (1998).

Received: April 12, 2015.
Sent to Subject Editor: November 30, 2015.
Accepted: August 9, 2016.
Recommended by Subject Editor:
Marcelo Seckler