Version of Record: https://www.sciencedirect.com/science/article/pii/S2213343720301962
Manuscript_f7693fd35d951f7d8f3ab3e4cefaeb48

Biodiesel Fuel Production from Brown Grease Produced by Wastewater Treatment Plant: Optimization of Acid Catalyzed Reaction Conditions

Mohammed J K Bashir[1*], Wong Lai Peng[1], Dickens St. Hilaire[2], Jihyun Kim[3], Oluwaseun Salako[4], Mith Jennifer Jean[4], Remi Adeyemi[4], Serena James[4], Tia Foster[4], Lawrence M. Pratt[4]

[1]Department of Environmental Engineering, Faculty of Engineering and Green Technology (FEGT), University Tunku Abdul Rahman, 31900 Kampar, Perak, Malaysia

[2] Department of Chemistry and Chemical Technology, Bronx Community College, 2155 University Avenue, Bronx, New York 10453 United States.

[3] Stella and Charles Guttman Community College-CUNY, 50 W, 40th St. New York, NY 10018

[4] Department of Chemistry and Environmental Science, Medgar Evers College, The City University of New York, 1638 Bedford Ave, Brooklyn, New York 11225, United States

*Corresponding Author: jkbashir@utar.edu.my

Abstract

Periodic spikes in crude oil prices have led to a need in alternative energy sources. A major potential source of biodiesel feedstocks is brown grease, a byproduct of wastewater treatment. A recent brown grease sample from this contained 60% FOG (fats, oils, and greases), 25% water, and 15% biosolids by mass. This study is focused optimizing the reaction conditions (i.e., quantities of Methanol, Sulfuric Acid, $Fe_2(SO_4)_3$, and time) to maximize the yield of esters, with minimal residual free fatty acid (FFA), in the shortest residence time. Response Surface

Methodology (RSM) was used to evaluate the correlation between the process variable and the response. The significance of quadratic model of each response was determined by analysis of variance, where all models indicated sufficient significance with p-value < 0.0001. Using a basis of 40 g brown grease, optimized conditions were 35 ml MeOH, 1.3 ml H_2SO_4, 0 g $Fe_2(SO_4)_3$ and reaction time of 120 min, resulting in a biodiesel yield of 99.70%. The results showed efficient biodiesel production under the optimum conditions.

Keywords: Biodiesel; Renewable energy; Waste; Fatty acids; Process optimization; Catalyst

1.0 Introduction

Brown grease is the oily material that accumulates in sewer lines and sewage treatment plants. It is an attractive raw material for making biofuels due to its very low cost and abundant supply. For instant, a typical wastewater plant in Torrington, Connecticut, USA produces between 10,000 and 50,000 gallons (40,000-200,000 L) of brown grease per week. The raw brown grease consists of fats, oils, and greases (FOG), as well as water, trash, and biosolids. This is the fraction that can be converted to biodiesel by esterification, or hydrocarbon green diesel by pyrolysis. The raw brown grease is pre-treated by screening to remove the large pieces of trash and the coarser biosolids, which are retained on the screen. Finer biosolids remain suspended in the aqueous layer when the water is gravity-separated from the FOG. Pyrolysis of brown grease has been used to make a hydrocarbon fuel chemically similar to diesel fuel or kerosene, and the distribution of products depends on the reaction conditions [1-4]. That process is relatively energy intensive, and lowvalue byproducts may be formed in addition to the diesel and kerosene. As an alternative for lowcost fuel production, production of biodiesel was investigated. Biodiesel consists of the methyl esters of fatty acids. It is most often synthesized by a base catalyzed process from virgin or used vegetable oils. Due to high demand for biodiesel, the starting materials are expensive and in short supply, thus limiting the growth of the biodiesel industry. For these reasons, a quest for sustainable and renewable biofuels has been gaining momentum on development of a scheme for continuous biodiesel production from brown grease in the near future. This scheme will enable to solve two problems: energetic and environmental, as brown grease, a low-value material that often incurs disposal costs, is a valuable in huge quantities. In general, biodiesel can be better for the environment than petroleum diesel because it tends to generate fewer toxins and greenhouse gasses. Unlike fossil fuels dug up from underground, biodiesel doesn't release long-stored carbon as carbon dioxide into the atmosphere when burned. Nevertheless, the best benefit of grease trap waste is that it's a renewable resource [5].

Brown grease consists primarily of fatty acids and their calcium salts [6, 7]. As such, an acid rather than a base catalyzed process is required for esterification of brown grease. The acid catalyst may be a mineral acid or a Lewis acid, as illustrated by several studies of ferric sulfate catalysis of carboxylic and fatty acid esterification [8-10]. Sulfuric acid is cheap and convenient to use. Eventual conversion to a continuous process must be considered in designing this system. Ferric sulfate is also sparingly soluble in methanol, thus limiting the option of adding it via a methanol solution. In this study, the reactions were performed in batch mode to optimize the ratios of brown grease, acid catalyst, and methanol, and to determine the required reaction time. The goal is to optimize the parameters to maximize the yield of esters, with minimal residual free fatty acid (FFA), in the shortest residence time. The most widely exploited module of RSM, i.e. CCD, was used to evaluate the correlation between the process variable and the response. Typically, RSM utilizes the combination of statistical and mathematical workings to optimize and design an experiment based on numerous independent variables with minimum amount of experiment runs and analyze the relationship between the dependent and independent variables [11, 12].

2.0 Materials and methods

2.1 Sample preparation and analysis

Samples of brown grease were obtained from wastewater plant in Torrington, Connecticut, USA. The oily material was separated from the water, biosolids, and debris by heating in a hot water bath and decanting the oil from the surface. Alternatively, the crude brown grease was screened to remove the large debris, melted to separate the water and most of the biosolids, which settled to the bottom, and screened again to remove the remaining biosolids, as described above. This brown grease still contained significant amounts of water, which was removed by azeotropic distillation with toluene. The molten grease (approximately 500 mL) was placed in batches in a 1-L round bottom flask with about 50 mL toluene, and the flask was fitted with a Dean-Stark trap for azeotropic water removal. The remaining toluene was distilled off under vacuum, so that the toluene content of the brown grease generally did not exceed 5%. All esterification reactions were calculated on the basis of 40 g of brown grease. Forty grams of brown grease was placed in a 100 mL round bottom flask fitted with a stir bar, and the flask was fitted with a reflux condenser and placed in a stirring heating mantle. The appropriate amount of methanol, concentrated sulfuric acid catalyst, and in some cases, a ferric sulfate co-catalyst was added, and the mixture refluxed for the required time period. To ensure consistent reaction times, the brown grease-methanol mixture was brought to reflux, and the catalyst then added, which was taken as the reaction starting time. The temperature was fixed at 65 ^{o}C/min, the temperature of refluxing methanol. This does not vary during the experiments because at atmospheric pressure, the boiling point of methanol is constant. Samples for GCMS analysis were taken periodically, typically at 30 or 60 minute intervals. The GCMS analysis was performed on a Shimadzu model QP2010S machine equipped with a Restek Rxi-5Sil MS fused silica column with a length of 30 m, inner diameter of 0.25 mm, and phase thickness of 0.25 µm. The carrier gas was helium with a flow rate of 1.2 mL/min. The column temperature profile was initial temperature 30 ^{o}C, hold for 3 min., increase to 300 at 12 ^{o}C/min., and hold for 10 minutes. Samples were prepared by adding 4-5 drops of the reaction mixture to 1.5 mL dichloromethane in standard GC vials. The percentage of each compound was determined from the peak areas, and the percentage of esters, free fatty acids (FFA), residual toluene, hydrocarbons, and other compounds were reported for each reaction at the specified time intervals. Traces of hydrocarbons (other than toluene) were occasionally detected from slight brown grease pyrolysis during the drying process. The "other" compound category generally included traces of alcohols, aldehydes, ketones, amines, or siloxane products from the breakdown of silicone joint grease.

2.2 Experimental design and statistical analysis

Design-Expert® Version 10.0 (Stat-Ease, Inc., Minneapolis, MN, USA) software is a Windows®¬based program that provides many powerful statistical tools such as RSM developed by Stat-Ease, Inc. In this study, RSM was used to determine the optimum operational condition for ECP. RSM is a collection of mathematical and statistical techniques for empirical model building. By careful design of experiments, the objective is to optimize a response (output variable) which is influenced by several input variables. In this study, four operational parameters were ultimately optimized, including methanol dosage (A), sulfuric acid dosage (B), co-catalyst dosage ($Fe_2(SO_4)_3$) (C) and contact time (D) with each process variable was numerically varied from -1 to +1 coded value as illustrated in Table 1. The respective range of the operational variables were

32 - 64 mL, 0.1 – 2.4 mL, 0 – 1.2 g and 60 – 180 min which they were selected based on literature [12-15]. In overall, 5 responses (dependent variables) were investigated including ester, and FFA yield (%). However, the residual toluene, hydrocarbons, and other compounds are functions of the brown grease pre-treatment, and do not reflect the esterification conditions.

Table 1: The independent variables code and the range of actual values based on 40 g brown grease.

Code	**Factor**	**Range of actual independent variables**				
		-1 (low)	**-0.5**	**0**	**+0.5**	**+1(high)**
A	Methanol, mL	32	40	48	56	64
B	Sulfuric Acid, mL	0.1	0.675	1.25	1.825	2.4
C	$Fe_2(SO_4)_3$ dosage, g	0.0	0.3	0.6	0.9	1.2
D	Time, min	60	90	120	150	180

A total of 30 sets of experiment with varying operational conditions were generated after respective ranges were filled into the software. Subsequently, 30 experiments were conducted and the corresponding recovery results for all of the 30 sets of experiments were recorded.

Subsequently, the experiment outcome was completely evaluated and analyzed using an ANOVA analysis to determine the competency and significance of the response surface quadratic model as represented in Equation (1):

$$= + \qquad + \qquad + \qquad + \qquad\qquad (1)$$

where is the response, and are the operational variables, is the constant coefficient, , and are the interaction coefficients of linear, quadratic and second-order terms respectively, is the number of operational variable and is the random error [13]. The fitness of experimental data was then verified with percentage of the sample variation that perfectly fit the model's estimated data point through value of coefficient of determination, R^2 and the statistical significance of quadratic model of each responses was tested by ANOVA based on the probability (p-value) of 95% confidence level. Models that described the respective response's interaction were then used to predict the optimum operational parameters targeted on maximum ester yield.

3.0 Results and discussion

The collected sample was characterized and it was found to contain 60% FOG, 25% water, and 15% biosolids by mass. A total of 30 experiments were conducted and the corresponding removal results for all of the 30 set of experiments were recorded as shown in Table 2. The monitored responses were the simultaneous percentage of ester, FFA, toluene residue, hydrocarbon and other compounds yield at the end of each run. The results show ester yields to be from 89.24% to 99.81%, and FFA yield from 0% to 8.96. It is the ester yield and residual FFA that are crucial to the process design, as the other variables are largely determined by variation in the drying time, temperature, and other drying conditions.

Table 2: Experimental run and results

Run	Operational Variables				Responses	
	MeOH	H_2SO_4	$Fe_2(SO_4)_3$	Time	Ester	FFA
	mL	mL	g	min	%	%
1	64	0.1	0	180	92.96	2.9
2	56	1.25	0.6	120	95.97	0.33
3	64	2.4	1.2	60	94.21	2.43
4	48	1.25	0.9	120	95.99	0
5	48	1.25	0.6	120	95.31	0.52
6	48	1.25	0.6	120	97.02	1.48
7	64	2.4	1.2	180	89.24	0
8	32	2.4	0	60	100	0
9	48	1.25	0.6	150	94.56	1.22
10	48	1.25	0.3	120	94.45	0.42
11	48	1.25	0.6	90	93.84	2.17
12	32	0.1	1.2	180	96.44	1.98
13	48	1.25	0.6	120	98.49	0
14	32	0.1	0	60	90.72	8.96
15	48	1.25	0.6	120	95.77	0.44
16	64	2.4	0	180	94.7	0.81
17	48	0.675	0.6	120	95.07	0.25
18	64	0.1	1.2	180	94.32	0
19	48	1.25	0.6	120	99.07	0.24
20	32	2.4	1.2	60	99.81	0
21	32	0.1	1.2	60	94.99	4.79
22	48	1.825	0.6	120	95.73	0.14
23	40	1.25	0.6	120	96.55	2.39
24	64	0.1	1.2	60	95.29	1.48
25	64	2.4	0	60	96.09	0.14
26	64	0.1	0	60	88.38	7.37

27	32	2.4	1.2	180	99.78	0
28	32	2.4	0	180	99.58	0
29	48	1.25	0.6	120	99.11	0.27
30	32	0.1	0	180	95.82	3.76

3.1 Statistical significance of responses' models

The experiment outcome was completely evaluated and analyzed using an ANOVA analysis to determine the competency and significance of the response surface quadratic model, and the results were tabulated in Table 3. All of the F values are large enough to produce low pvalue of < 0.05 that suggests that all models are statistically significant. Only p-value for FFA yield model is less than 0.0001. The fitness on experimental data of each parameter was further verified by high R^2 values. R^2 value for FFA yield model >90% but for Ester yield model is 0.82. The model for Ester yield can be accepted because the p-value of lack of fit < 0.05. R^2 value of higher than 0.90 for all models are indicative of a good agreement between the experimental and predicted value generated based on the developed model. As the R^2 approach toward unity, it is illustrated that predicted values of responses given by the model are proximate to experimental value and hence it will be a better fit model [16] Equation 2 and 3 are the suggested model to predict the ester and FFA yield.

$$\text{ester yield (\%)} = 96.28 - 1.95*A + 1.50*B + 0.40*C + 0.22*D - 1.12*A*B - 0.25*A*C - 0.55*A*D - 1.28*B*C - 1.06*B*D - 0.77*C*D + 3.67*A2 + 0.23*B2 - 0.49*C2 - 4.57*D2 \quad (2)$$

$$\text{FFA yield (\%)} = 0.06 - 0.033*A - 1.69*B - 0.82*C - 0.98*D + 0.70*A*B - 0.019*A*C + 0.019*A*D + 1.01*B*C + 0.76*B*D + 0.14*C*D + 2.36\,A^2 - 2.30*B^2 - 2.24*C^2 + 3.70*D^2 \quad (3)$$

where A, B, C, and D correspondingly represent operational variables in this model which are methanol dosage (mL), sulfuric acid dosage (mL), $Fe_2(SO_4)_3$ dosage (g), and contact time (min).

Table 3: Analysis of variance (ANOVA) for response surface quadratic model for ester and FFA, yield

	Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Ester yield (%)	**Model**	197.35	14	14.10	4.80	0.0023	Significant
	A-MeOH	63.00	1	63.00	21.46	0.0003	
	B-H_2SO_4	37.34	1	37.34	12.72	0.0028	
	C-$Fe_2(SO_4)_3$	2.64	1	2.64	0.90	0.3580	
	D-Time	0.83	1	0.83	0.28	0.6018	
	AB	20.05	1	20.05	6.83	0.0196	
	AC	0.99	1	0.99	0.34	0.5710	
	AD	4.90	1	4.90	1.67	0.2161	
	BC	26.24	1	26.24	8.94	0.0092	
	BD	18.00	1	18.00	6.13	0.0257	
	CD	9.59	1	9.59	3.27	0.0907	
	A^2	2.24	1	2.24	0.76	0.3962	
	B^2	8.643E-003	1	8.643E-003	2.944E-003	0.9574	
	C^2	0.040	1	0.040	0.014	0.9083	
	D^2	3.48	1	3.48	1.19	0.2935	
	Residual	44.03	15	2.94			
	Lack of Fit	29.98	10	3.00	1.07	0.5027	
	Pure Error	14.05	5	2.81			
F-value: 4.8; R^2: 0.8176; Adequate precision: 9.06; Standard deviation (%): 1.71							
	Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**	
FFA yield (%)	Model	129.52	14	9.25	11.25	< 0.0001	Significant
	A-MeOH	1.76	1	1.76	2.14	0.1641	
	B-H_2SO_4	47.23	1	47.23	57.41	< 0.0001	
	C-$Fe_2(SO_4)_3$	11.00	1	11.00	13.37	0.0023	
	D-Time	15.90	1	15.90	19.32	0.0005	
	AB	7.73	1	7.73	9.39	0.0079	
	AC	0.12	1	0.12	0.14	0.7130	
	AD	5.625E-003	1	5.625E-003	6.837E-003	0.9352	
	BC	16.44	1	16.44	19.99	0.0004	
	BD	9.30	1	9.30	11.31	0.0043	
	CD	0.32	1	0.32	0.39	0.5392	
	A^2	0.93	1	0.93	1.13	0.3052	
	B^2	0.88	1	0.88	1.07	0.3174	

C^2	0.83	1	0.83	1.01	0.3298
D^2	2.28	1	2.28	2.77	0.1168
Residual	12.34	15	0.82		
Lack of Fit	11.01	10	1.10	4.12	0.0657
Pure Error	1.33	5	0.27		
F-value: 11.25; R^2: 0.9130; Adequate precision: 14.51; Standard deviation (%): 0.91					

In this study, a ratio greater than 4 for adequate precision which observed in all model validates that the model has adequate signal which indicating that the model can be used to navigate the design space [17, 18]. Small standard deviation for ester and FFA yield revealed that data points were dispersed proximate to their respective expected outcome. This was further supported by Figure 1 that shows all the experimental values were scattered around the predicted values. As shown in Figure 1, the predicted values of ester and FFA yield obtained from the model and the actual experimental data were in good agreement.

3.2 Effect of the operational variables on ester yield

Figures 2 and 3 show the relationship between the independent variables to the dependent variables. From Fig 2, dosage of $Fe_2(SO_4)_3$ used as a co-catalyst has minor effects to the ester yield which can be confirmed by Figure 4 as well. As indicated in Table 3, the effect of factor $CFe_2(SO_4)_3$ on ester yield is less important comparing with other factors A and B with p value of 0.3580. However, there were a considerable effect via the interaction between factor B (H_2SO_4) & C ($Fe_2(SO_4)_3$) on ester yield with a significant p value of 0.0092.

Nevertheless, to save cost, minimum dosage of catalyst used is suggested. As indicated in Figures 3, ester production increased when the operational variables of sulfuric acid dosage increased from 0.1 mL to 2.4 mL. However, ester yield was observed to be higher when a 32 ml of MeOH was applied. Thus, optimized MeOH dosage is critical to obtain maximum ester yield. Other than that, contact time which is one of the operational variables has great impact on ester production. With an increase in contact time, an upward movement of the graph's surface was observed will maximize the ester yield, however, prolonged contact time will give adverse effect to the production of ester. Thus, optimized contact time is important for maximum ester yield.

With the best experimental condition at contact time of 120 min, higher ester yield was achieved.

Figure 4 presented the perturbation plot of the operational variables to ester yield. The perturbation plot supports to compare the effects of all the factors at a particular point in the design space. A steep slope or curvature in a factor shows that the response is sensitive to that factor. A relatively flat line shows insensitivity to change in that particular factor. From the plot, operational variable A (MeOH), B (H_2SO_4) and D (contact time) have the most significant influence on the ester yield which indicated by the curvet of the curve. Increasing the amount of sulfuric acid variable B (H_2SO_4) increased the ester yield. However, variable C ($Fe_2(SO_4)_3$) cocatalyst dosage showed minimal effect to the ester yield, although it can catalyze the reaction in the absence of sulfuric acid.

3.3 Effect of operational variables on residual FFA yield

As presented in Figure 5, optimum contact time up to 120 min and optimum volume of sulfuric acid used up to 1.83 mL significantly resulted in lower residual FFA. However, the amount of residual FFA was insignificant for low contact time (60 min) and prolong contact time (180 min). Over and above that, prolonged contact time is not favorable due to high energy consumption which will eventually increase treatment cost [19]. Figure 6 presents the perturbation chart for FFA yield. From the chart, all operational variables (A, B, C and D) showed equally effect to FFA yield.

3.5 Optimization of experimental conditions and verification

Analysis of operational variables interaction and impact on ester yield was performed and optimized using a multiple response optimization tools vis RSM. For optimization purpose, the range of operational variables were selected. As such, MeOH, H_2SO_4, catalyst ($Fe_2(SO_4)_3$ and time were selected within the ranges, while the ester yield was maximized. On another note, Ester production was targeted at maximum. Fig. 7 shows the overlay plot for optimum conditions. The As seen from the box in Fig. 7, the optimized conditions occurred at 35 ml MeOH, 1.3 ml H_2SO_4, 0 g $Fe_2(SO_4)_3$ and reaction time 120 min. These optimum operational conditions, according to the model, should be able to achieve 99.40 % ester production. An experiment was then conducted to compare actual and predicted outputs. Table 4 shows the responses obtained from model prediction and laboratory experiment to be in good agreement.

Table 4: Optimum response results from overlay plot and laboratory (Operational conditions of 35 ml MeOH, 1.3 ml H_2SO_4, 0 g $Fe_2(SO_4)_3$ and reaction time 120 min)

Response	**Predicted value**	**Actual value**
Ester yield (%)	99.4	99.7
FFA yield (%)	0.8	0

4.0 Conclusions

In this study, the response statistical models showing significant terms of interactive operational variables were tested and confirmed by ANOVA with p-value < 0.0001. The goodness of fit on experimental data of responses was also verified by higher values of closer to 1 that indicated each quadratic model was statistically desirable and better fit. The RSM was used to simultaneously optimize the operational variables required in the biodiesel production from brown grease (40 g basis), where the 35 ml MeOH, 1.3 ml H_2SO_4, 0 g $Fe_2(SO_4)_3$ and reaction time of 120 min were obtained. Upon on these conditions, 99.70 % of ester yield was achieved. The results exhibited the promising of brown grease as a renewable and environmentally friendly source for biodiesel production. Brown grease is renewable because it is constantly forming in the sewer lines and sewage treatment plants. Turning brown grease into a fuel is more environmentally friendly than dumping it in a landfill, where it will form methane and CO2, but without producing any useful work in the process.

Acknowledgments

This work was supported in part by NSF grant # CBET 1802524. Also we would like to thanks Roy Matthews, Alonzo Toney, MiAsia Burns, and Michelle Noel for their technical assistance.

References

1. Pratt, L. M.; Pinnock, T.; Amoa, K.;Akther, K.; Domond, J.; Gordon, R.; Loriston, K.; Strothers, J.; Toney, A.;Rizvi, H.; Gunasekaran, M.; Noshadi, I.; Parnas, R.; Provatas, A. NEWEA Journal **2014**, *48(2)*, 44-53, Beneficial Use Brown Grease—A Green Source of Petroleum Derived Hydrocarbons.

2. Pratt, L. M.; Parnas, R. U. S. Patent #9,701,911 Issued 11 July, **2017** Process for converting fats, oils, and greases into fuels.

3. Sim, Y-L; Meyappan, N.; Yen, N. S.; Subramaniam, S. K.; Khoo, C. H.; Cheah, W. L.; St. Hilaire, D.; Pinnock, T.; Bacolod, B.; Cai, Z. B.; Gurung, D.;Hasnat, R.;J Strothers,J.; Remy,C. T.; Gentles, P. K.; Groveman, S.;Vittadello, M.; Kim, J.; Pratt. L. M. *Fuel* **2017**, *207*, 274-282 Chemical Reactions in the Pyrolysis of Brown Grease.

4. Strothers, J.; Matthews, R. B.; Toney, A.; Cobham, M. R.; Cox, S.; Ford, W.; Joseph, S.; Joyette, W.; Khadka, S.; Pinnock, S.; Burns, M.; Noel, M.; Tamang, M. G.; St. Hilaire, D.; Kim, J-H.; Pratt, L. M. Hydrocarbon Fuel from Brown Grease: Effects of Reaction Temperature Profile on Yields and Product Distribution. *Fuel* **2019**, *239*, 573-578

5. M. Tosczak. How Grease Interceptors Can Reduce Greenhouse Gases. Thermaco 2016 https://thermaco.com/blog/role-of-grease-traps-in-reducing-greenhouse-gas-emissions/

6. Williams, J. B; Clarkson, C.; Mant, C.; Drinkwater, A.; May, E. Fat, Oil and Grease Deposits in Sewers: Characterization of Deposits and Fornation Mechanisms. *Water Res.* **2012**, *46*, 63196328

7. He, X.; de los Reyes III, F. L.; Leming, M. L.; Dean, L. O.; Lappi, S. E.; Ducoste, J. J. Mechanisms of Fat, Oil, and Grease (FOG) deposit formation in sewer lines. *Water Research* **2013**, *47*, 4451- 4459

8. Maheshika G. N., Wijerathna J. A. R. H, Gunawardena S. H. P. Ferric Sulphate Catalyzed Esterification of High Free Fatty Acids Content Waste Coconut Oil for Biodiesel Synthesis *Int. J. Sci. Res.* **2014**, *3*, 2068-2072

9. Guana, G., Kusakabe, K. biodiesel production from waste oily sludge by acid-catalyzed esterification Int. J. Biomass and Renewables 2012, *1*, 1-5

10. Gan, S., Ng, H. K., Ooi, C. W.; Motala, N. O.; Ismail, M. A. F. Ferric sulphate catalyzed esterification of free fatty acids in waste cooking oil *Bioresource Technology* **2010**, *101*, 73387343

11. Azmi, N.B., Bashir, M.J.K. Sethupathi, S., Lim, J.W., Ng, C.A., 2015. Stabilized landfill leachate treatment by sugarcane bagasse derived activated carbon for removal of color, COD and NH_3-N – Optimization of preparation conditions by RSM. J. Environ. Chem. Eng., 3, 1287-1294

12. Bashir, M., Tham, M., Lim, J., Ng, C., Abu Amr, S., 2016. Polishing of treated palm oil mill effluent (POME) from ponding system by electrocoagulation process. Wat. Sci. Tech. 73, 2704-2712.

13. Lin, C. K., Bashir, M.J.K., Abu Amr, S.S., Sim L.C., 2017. Post treatment of palm oil mill effluent (POME) using combined persulphate with hydrogen peroxide ($S_2O_8^{2-}/H_2O_2$) oxidation. Wat. Sci. Tech.74, 2675-2682

14. Bashir, M.J.K., Chong, J.W., Abu Amr. S. S., Ng, C.A., 2017. Electro persulphate oxidation for polishing of biologically treated palm oil mill effluent (POME). J. Environ. Manag. 193, 458-469.

15. Barrera-Díaz, C., Frontana-Uribe, B., Bilyeu, B., 2014. Removal of organic pollutants in industrial wastewater with an integrated system of copper electrocoagulation and electrogenerated H_2O_2. Chemosphere, 105, 160-164.

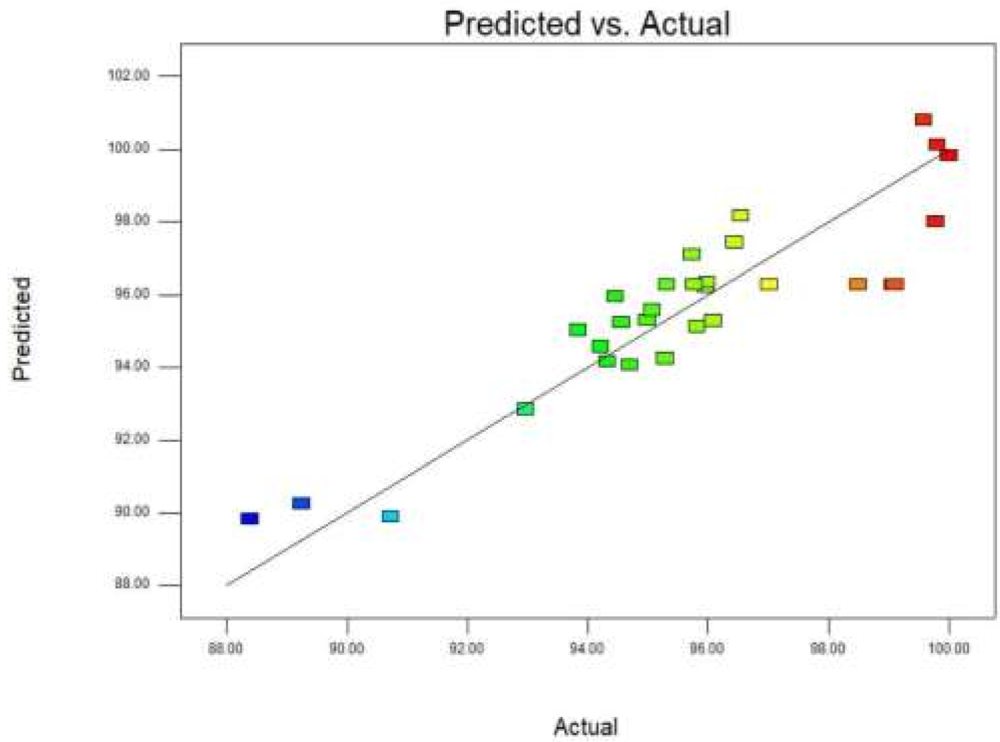
16. Jami, M., Rosli, N., Amosa, M., 2015. Optimization of Manganese Reduction in Biotreated POME onto 3A Molecular Sieve and Clinoptilolite Zeolites. Wat. Environ. Res. 87, 1-12.

17. Mohajeri, S., Aziz, H.A., Isa, M.H., Zahed, M.A., Bashir, M.J.K., Adlan, M.N., 2010. Application of the central composite design for condition optimization for semi-aerobic landfill leachate treatment using electrochemical oxidation. Wat. Sci. Technol. 61, 1257–1266.

18. Wong, L.P., Isa, M.H., Bashir, M.J.K., 2018. Disintegration of palm oil mill effluent organic solids by ultrasonication: Optimization by response surface methodology. Process Saf. Environ. Prot. 1 1 4, 123–132.

19. An, C., Huang, G., Yao, Y., Zhao, S., 2017. Emerging usage of electrocoagulation technology for oil removal from wastewater: A review. Sci. Total Environ. 579. 537-556.

a)



b)

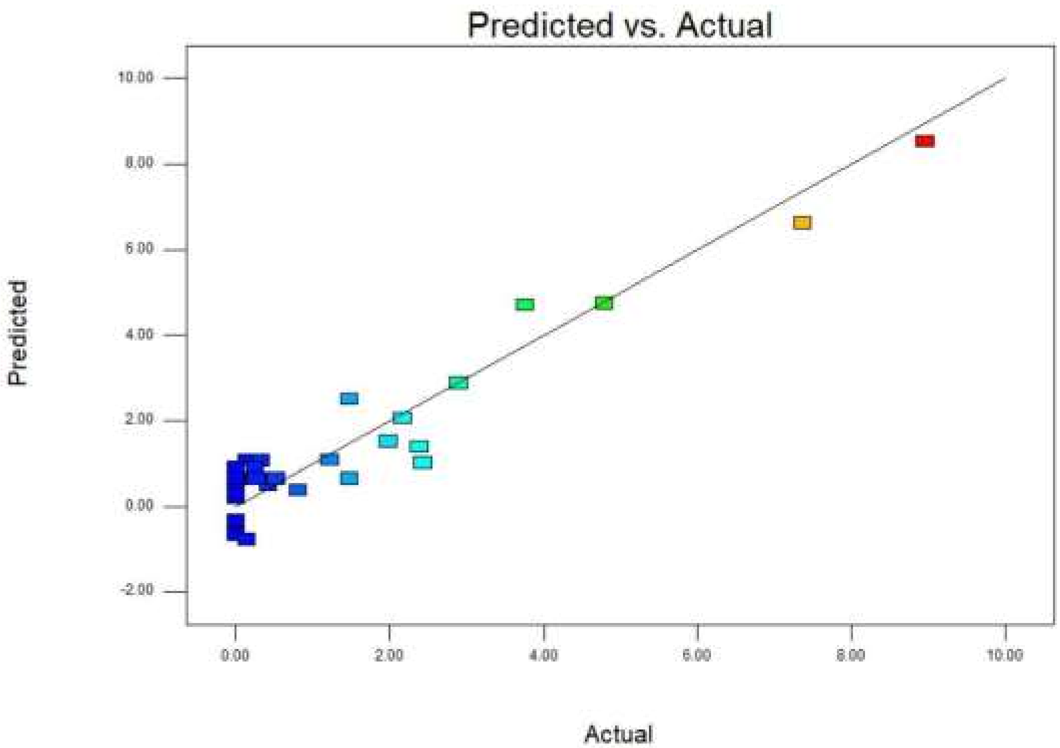


Figure 1: Correlation of actual and predicted values for (a) ester and (b) FFA yield

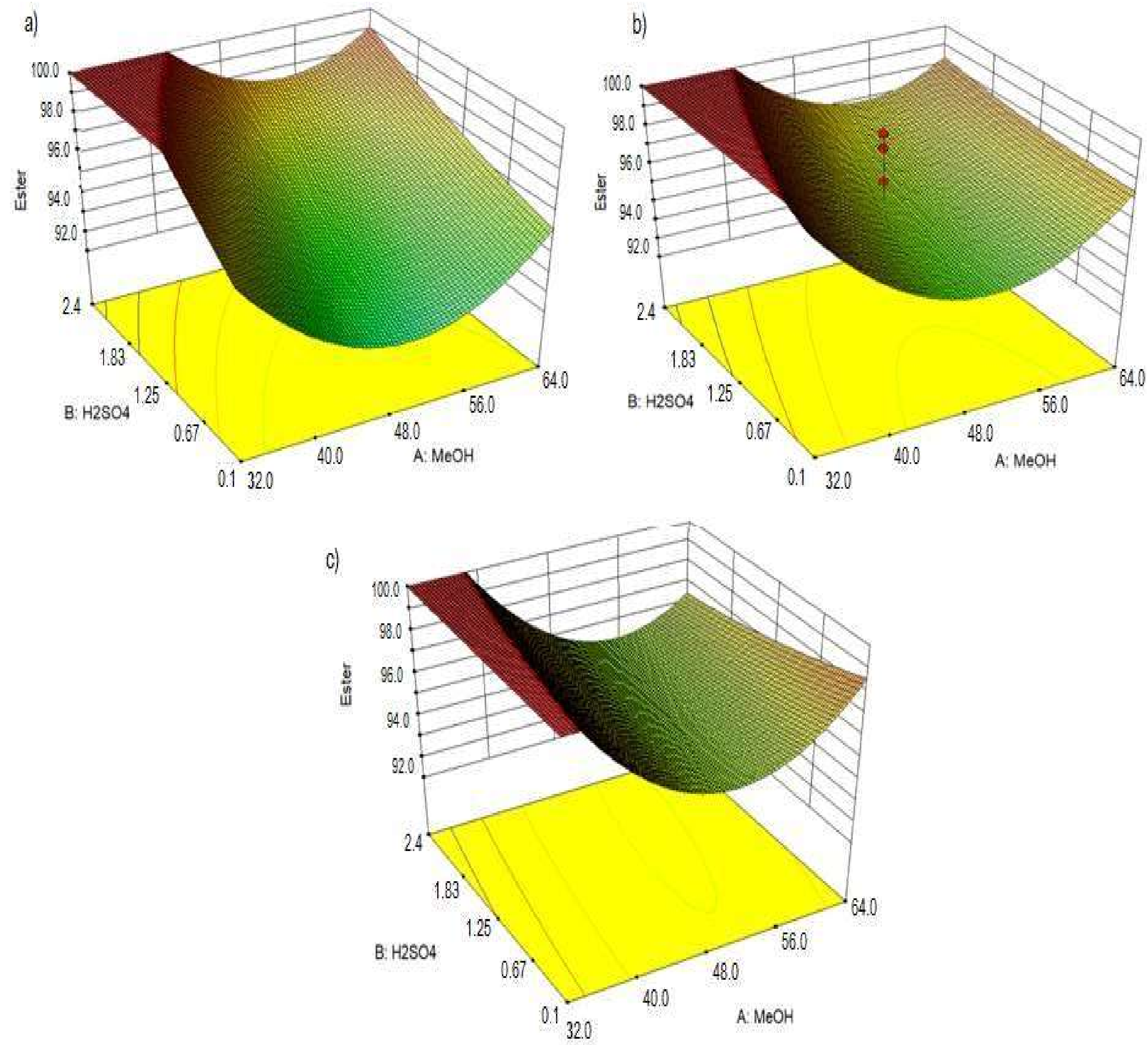


Figure 2: The effect of acid sulfuric and methanol used on ester yield (%) at (a) 0g, (b) 0.6 g and (c) 1.2 g $Fe_2(SO_4)_3$.

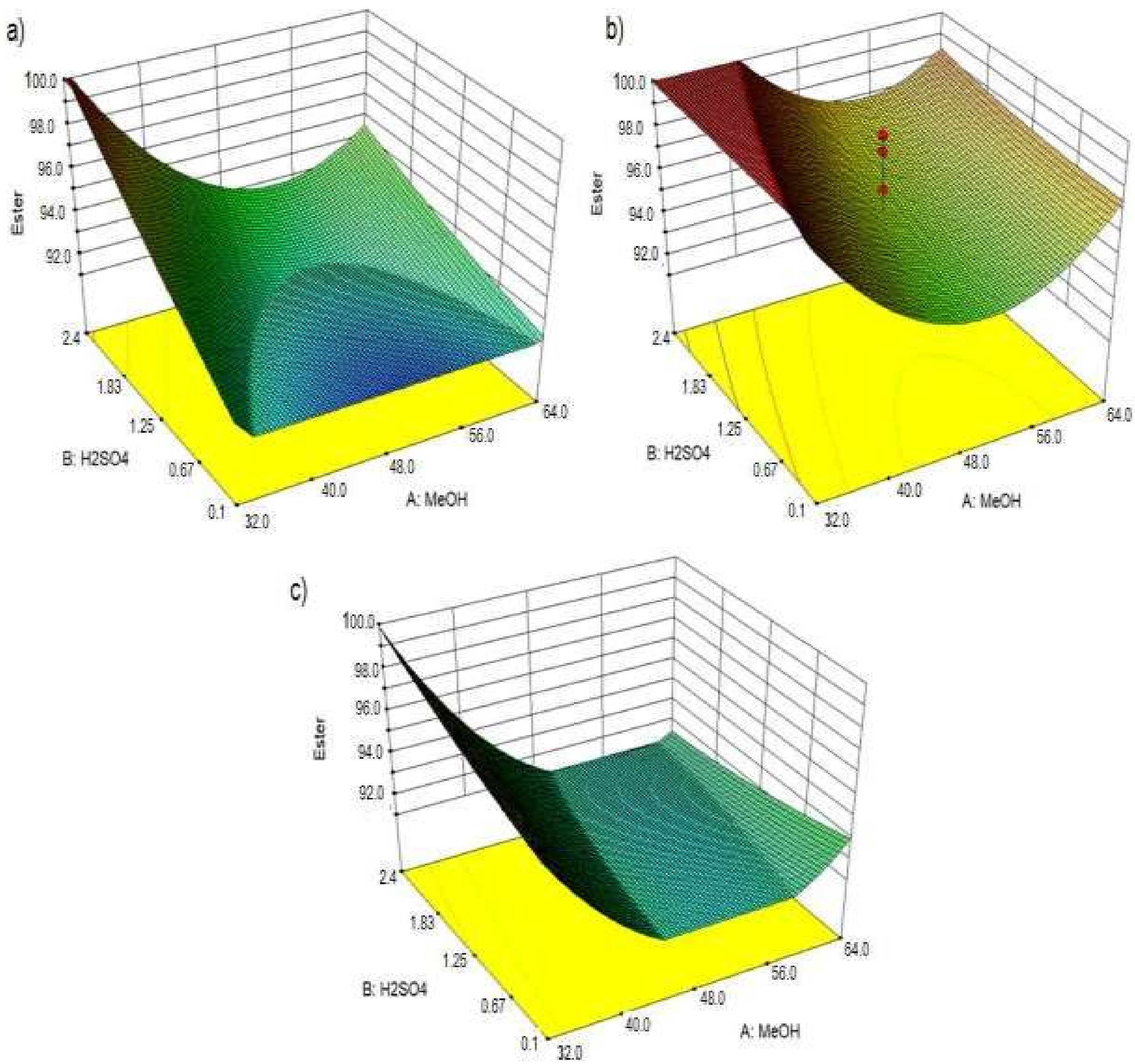


Figure 3: The effect of acid sulfuric and methanol used on ester yield (%) at (a) contact time 60 min, (b) 120 min and (c) 180 min.

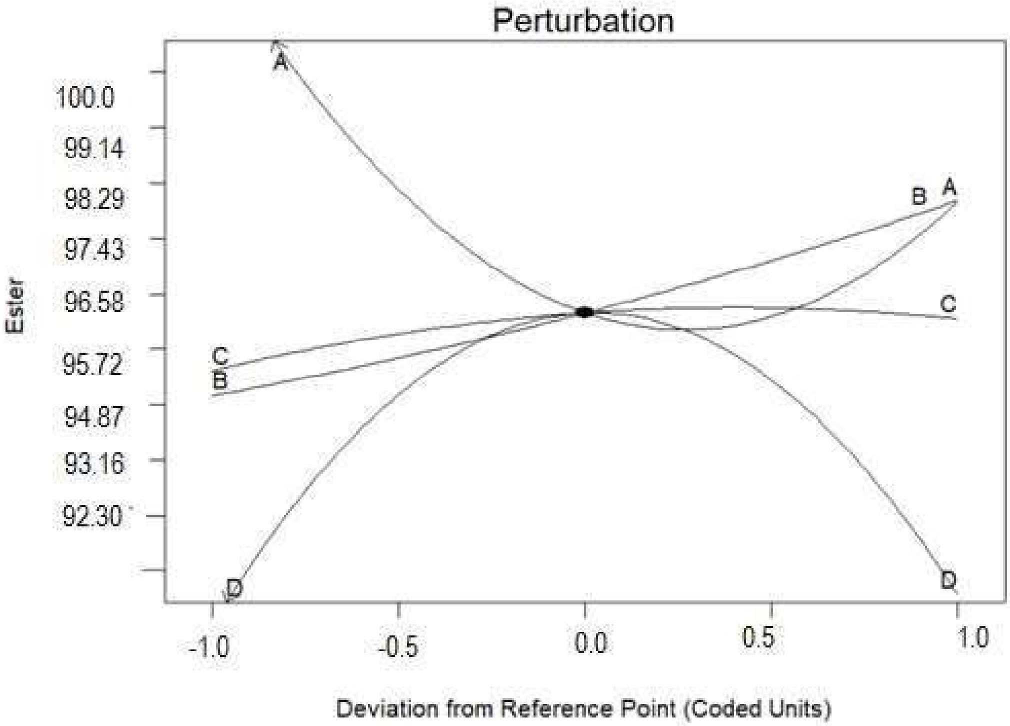


Figure 4: Pertubation plot for ester yield

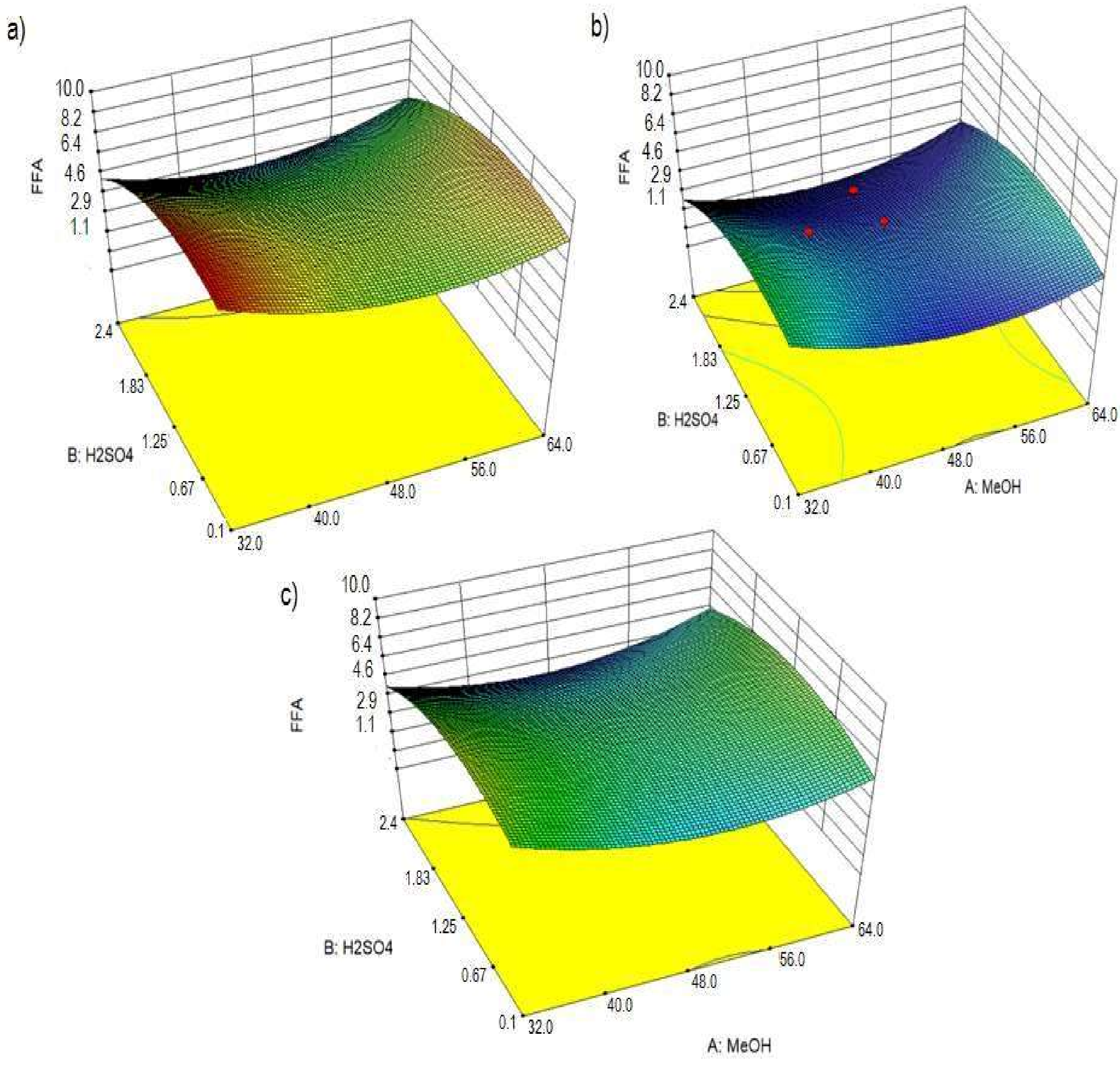


Figure 5: The effect of acid sulfuric and methanol used on FFA yield (%) at (a) contact time 60 min, (b) 120 min and (c) 180 min.

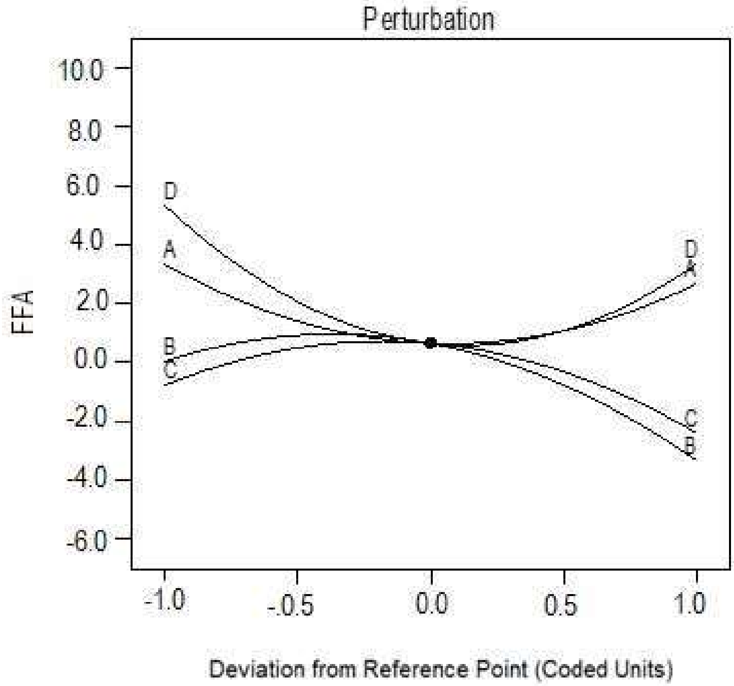


Figure 6: Pertubation plot for FFA yield

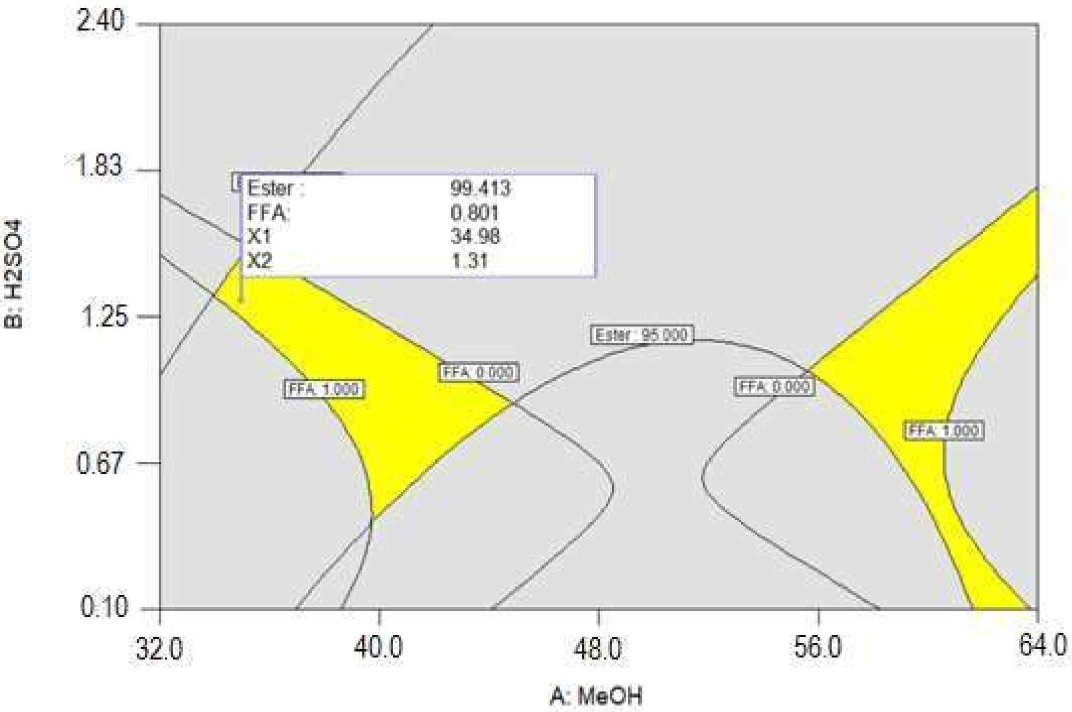


Fig. 7. Overlay plot for optimum conditions (34.98 ml MeOH, 1.31 ml H_2SO_4, 0 g $Fe_2(SO_4)_3$ and reaction time 120 min)


Wastewater Treatment Plant
Brown Grease Collection
BioDiesel