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Optimization of Process Parameters of Alkali Based Clay Catalyst for the Production of Biodiesel

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A B S T R A C T

Utilization of locally sourced materials promote raw materials Biodiesel was produced by transesterification of palm kernel oil (PKO) with ethanol in the presence of non-synthetic heterogeneous catalyst (combination of KOH/meta Kaolin). The process parameters investigated are catalyst (1-6 g), ethanol (10-25 wt% ethanol/%wt PKO), reaction temperature (30-120 °C) and reaction time, (60-100 min). These parameters were considered for optimization using Response Surface Methodology (RSM) with Central Composite Design (CCD) for yield of biodiesel produced. The optimum yield of biodiesel of 96% was obtained using the optimized numerical values of 17.5% ethanol (by mass of PKO) and 3.5 g catalyst at 75°C for 80 min. The viscosity (4.84 mm^2/s), specific gravity (0.86), pour point (+5 °C), flash point (178 °C), and cloud point (+8 °C) of the biodiesel obtained at optimum condition compared favorably with ASTM standards. It was inferred from the research that biodiesel with suitable fuel properties can be produced from PKO using non-synthetic KOH impregnated on Kaolin with ethanol extracted from agricultural based raw materials.

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INTRODUCTION

Biodiesel is a renewable fuel consisting of fatty acid alkyl esters (FAAE) derived through transesterification of vegetable oils, animal fat and recycled oil from the food industry with alcohol [1]. Biodiesel is recognized as "green fuel" with several advantages over fossil fuel. Some of the advantages are non-toxic and biodegradable [1]. It is free of sulfur and aromatics, making it a cleaner burning fuel with reduced emission of SOx, CO, unburnt hydrocarbons and particulate matter [2]. Despite the promises recorded in the production of biodiesel, the cost of production is still relatively high when compared to the cost of production of petroleum-based diesel fuel. Production sequence that will reduce cost of production will enhance attraction towards the use of this energy source [3].

The choice of the catalysts used for production of biodiesel affected the yield of biodiesel and rate of the reaction [4]. Conventionally, potassium hydroxide or sodium hydroxide and strong acid in form of homogeneous based-catalyst have demonstrated increase in yield of biodiesel due to its fast rate of reaction. One of the shortcomings of using of homogenous based catalyst is selection of the most suitable reaction path that will minimize the production of ester hydrolysis that transformed to Free Fathy Acid (FFA). These FFAs can form emulsion of soap through saponification process and separation of these extra products is difficult which tends to increase the production cost of biodiesel. [2, 5]. On the other hand, heterogenous catalysts are gaining research attention because it addressed some of the challenges that homogenous based catalysts posed on the production of biodiesel. Some of which are regeneration of catalysts, ease of separation, free of corrosion and system not considerably affected by FFA [3]. It is important to highlight the fact that heterogeneous reaction is slower than homogenous based reaction for biodiesel production [6].

Several solid based synthetic and non-synthetic heterogenous catalysts used for biodiesel production are highlighted in the literature [5, 7]. Kaolin clays are inexpensive and are readily available. Kaolin clay has proved useful in many industrial processes especially heterogenous catalyst, due to its wide surface area and high porosity [8]. Impregnation of such clay with any of the commonly used alkalis and the development of mesoporous Kaolin impregnated with these alkalis may provide greater opportunity to avoid the diffusion limitation and improvement of transesterification of vegetable oils [8].

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The significance of operating conditions of biodiesel condition have been established regardless on the choice of catalyst type adopted and researchers have been trying to study the influence of these operating conditions on the yield of biodiesel. In the previous studies, process parameters such as reaction temperature, reaction time, ethanol to oil ratio and catalyst were manipulated by Center Composite Design (CCD) to optimize biodiesel yield using one variable at a time. This method has been described to be tedious and time consuming [9]. Furthermore, the one variable at a time technique does not show interactive effects of variables with respect to the yield [10]. Two variables Time and catalyst concentration were identified as key factors by Vafakish and Barari [3] and conducted sensitivity studies on their effects on yield of biodiesel. Therefore, where multi-parameters are studied simultaneously, CCD is a suitable alternative to simplify interactive effects among the reaction variables. By establishing three-dimensional plot from the experimental data, the overall behavior of the reaction variables can be easily understood and the interactions between the variables would be more visible [11].

This study therefore investigated the potential of extracted KOH deposited on Kaolin (KOH/meta Kaolin) in the production of biodiesel from Palm Kernel Oil (PKO). Biodiesel properties (viscosity, specific gravity, pour point, flash point, and cloud point) at the optimum condition were determined and the results compared with American Society for Testing and Material (ASTM) standards for biodiesel.

MATERIAL AND METHOD

Material

The caustic potash (KOH) used for this investigation was extracted from locally sourced plantain peels. Kaolin clay used was mined from Asa river valley, Kulende area, Ilorin (Latitude 8º 33' N, and Longitude 4º 34' 46 E). The local gin (Ogogoro) used was obtained at a local market in Erin, Oyun local government area of Kwara state and palm kernel oil (PKO) was obtained from Gbagina oil manufacturing company, Offa, Kwara state, Nigeria. All materials used were therefore non-synthetic.

Catalyst preparation

The mined Kaolin was wet beneficiated using an experimentally determined optimum mixing ratio of 0.1kg: 1litre (clay to water), and optimum settling time of 24 hours [12]. Fine kaolin slurry collected was sun dried and calcined at 750 °C for 2 hours in a muffle furnace for processing into meta Kaolin. A series of KOH/meta Kaolin supported catalyst with mass ratio ranging between 0.5 and 1/2.5 and 6 was prepared via incipient wetness impregnation. Each mixture was made with addition of distilled water to induce plasticity. After impregnation, the slurry was dried in an oven operated at 110 °C for 4 hours to remove moisture and the dried catalyst was calcined in a muffle furnace at a temperature of 400 °C for 5 hours according to Hilary [13].

Transesterification Process

100 g of palm kernel oil was measured and poured in a three neck round bottom flask equipped with stirrer, thermometer and condenser. The oil was pre-heated to 75 ºC and put in a water bath maintained at the same temperature. 1 g of KOH/meta Kaolin catalyst and 20 g ethanol were simultaneously weighed and poured into the flask. The entire mixtures were allowed to mix for 100 minutes at a predetermined speed. The product from the flask was poured into a separating funnel and allowed to stand overnight to enhance phase separation. The lower part which contains glycerol, un-reacted catalyst, and impurities was drained into a beaker; the weight of glycerol collected was measured and recorded. The remaining ester layer was washed with warm distilled water to remove residual alcohol, catalyst, and unreacted tri, di-, and monoglycerides. After washing and phase settling, water was drained off from the bottom of the separating bottle and the weight of biodiesel obtained was measured and recorded. This procedure was used to carry out the transesterification of palm kernel oil (PKO) following experimental design.

Experimental design for biodiesel production

Central composite design (CCD) was applied for both analysis and optimization study of the biodiesel production from palm kernel oil. The selected independent parameters evaluated were reaction temperature, reaction time, amount of catalysts and ethanol to oil ratio whilst the dependent variable was FAEE yield. The range and levels of the independent variables for transesterification process listed in Table 1. Each response obtained from the transesterification process was used to develop a mathematical model that correlates the biodiesel yield to the independent reaction variables via second-order polynomial equation as given in Equation 1 [14]:

$$Y = \mu_0 + \sum_{i=1}^{n} \mu_i x_i + \sum_{i=1}^{n} \mu_{ii} x^2{}_i + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \mu_{ij} x_i x_j \quad (1)$$

where, Y is the predicted FAEE yield, μ_o is the constant coefficient, μ_i is the linear coefficients, μ_{ij} is the interaction coefficients, μ_{ii} is the quadratic coefficients and xi, xj are the coded values of the experimental variables.

Design Expert software version 6.0.8 was used for regression analysis of the experimental data to fit the equations. The quality of the developed model was determined from the value of correlation coefficient (R^2) while evaluation of the statistical significance of the equations developed was determined by using the analysis of variance (ANOVA).

Analysis of biodiesel produced

The properties of the biodiesel produced at optimal conditions were measured using the ASTM standards. Properties such as kinematic viscosity, specific gravity, pour point, flash point, and cloud point of the biodiesel were ascertained following ASTM D445, ASTM D1298, ASTM D97, ASTM D93, and ASTM D25100-8, respectively.

TABLE 1. Ranges of values used to generate data for PKO transesterification reaction using Design-Expert software 6.0.8 version

Factors	Unit	Level	
		Low	High
Reaction temperature	ºC	30.00	120.00
Reaction time	Minute	60.00	100.00
Ethanol to oil ratio	%	10.00	25.00
Catalyst	g	1.00	6.00

RESULTS AND DISCUSSION

Development of regression model of the process

Table 2 showed a full experimental design for biodiesel production with the experimental and predicted yield as responses. It was observed from the table that the biodiesel yield ranges between 25.5 and 96%. According to the sequential model sum of square, the best model that fitted the responses was quadratic due to its highest order polynomial with significance of additional terms; the model was not aliased. The final equation in terms of coded factor for the biodiesel production is as shown in Equation 2:

$$Yield = +130.25 - 171.63A + 3.16B - 7.57C + 206.04D - 112.49A^2 - 82.21D^2 - 168.88AD - 2.24BC + 149.39A^3 + 11.94C^3 - 233.14D^3 - 243.80A^2D \quad (2)$$

where; The coded terms A, B, C and D represented reaction temperature, reaction time, ethanol to oil ratio, and amount of catalyst, respectively.

Positive sign in front of the terms indicated synergic effect while negative sign indicated antagonistic effect [15]. The experimental data was further subjected to Analysis of variance (ANOVA) to verify the significance and fitness of the process parameters as shown in Table 3.

From the ANOVA, A, B, C, A^2, and C^2 are significant model terms. The lack of fit F-value of 0.74 and p-value of 0.6827 implied that lack of fit is not significant relative to the pure error and the model is satisfactorily fitted to experimental data. The R^2 value for the model was 0.8436 which means 84.36% of the total variation in the biodiesel yield was attributed to the experimental variables under study. The closer the R^2 value to the unity, the better the model will be as the predicted yield and the actual yield were in reasonable agreement [11]. The importance of the individual factors on the biodiesel yield generated from the software was presented in Figure 1. The figure showed that time and ethanol to oil ratio show increase in yield with increase in the two factors while temperature and catalyst showed a sinusoidal behavior with increase in their values.

The 3D surface plots generated for the combination of variables used in the model generated were presented in Figure 2 (a and b). The response surfaces in the figures show positive effect of reaction temperature, reaction time and ethanol to oil molar ratio on PKO biodiesel yield. This implies that biodiesel yield increases when any of these factors increase. However, catalyst concentration has a negative effect on the yield. This is because high catalyst concentration can trigger the triglyceride saponification (soap formation) side-reaction [16]. From this figure, it was observed that the reaction temperature, reaction time and ethanol to oil molar ratio interaction are significant because biodiesel yield increases only on increasing these parameters. Therefore, yield is high when these parameters are high.

TABLE 2. Results showing biodiesel yield

Run	Temperature (ºC)	Time (min)	EOR (%)	Catalyst (g)	Actual Yield (%)	Predicted Value
1	120	60	25	1	88.7	88.43
2	30	60	25	6	65	65.77
3	30	100	25	6	88	86.59
4	75	80	17.5	3.5	96	88.4
5	120	100	10	6	92.5	80.76
6	75	80	17.5	3.5	95	88.4
7	120	60	10	6	68	76.58
8	120	100	25	1	90	95.4
9	30	60	10	6	56	45.64
10	120	100	10	1	89	86.43
11	30	100	10	1	54.6	54.19
12	75	40	17.5	3.5	78.9	80.43
13	30	100	10	6	59	57.47
14	30	100	25	1	87	77.41
15	75	80	17.5	8.5	90	95.46
16	75	80	17.5	3.5	95.7	88.4
17	75	80	32.5	3.5	90	85.73
18	30	60	10	1	55	48.56
19	120	80	17.5	3.5	25.5	35.79
20	30	60	25	1	56	62.79
21	75	80	17.5	3.5	95	88.4
22	120	100	25	6	91	95.63
23	120	60	25	6	87	82.46
24	75	80	2.5	3.5	45.6	56.63
25	75	80	17.5	3.5	67.3	88.4
26	165	80	17.5	3.5	65	64.8
27	75	80	17.5	3.5	89.3	88.4
28	75	80	17.5	1	86	91.17
29	75	120	17.5	3.5	94	99.23
30	120	60	10	1	92	88.45

TABLE 3. ANOVA for PKO biodiesel

Source	Sum of Square	Degree of Freedom	Mean Square	F Value	Prob > F	Comments
Model	9161.719	12	763.4766	22.95376	< 0.0001	significant
A	3764.485	1	3764.485	113.1784	< 0.0001	
B	54.31341	1	54.31341	1.632921	0.2221	
C	145.6638	1	145.6638	4.379352	0.0551	
D	3445.892	1	3445.892	103.6	< 0.0001	
A^2	3283.318	1	3283.318	98.71223	< 0.0001	
D^2	1943.102	1	1943.102	58.41895	< 0.0001	
AD	2307.331	1	2307.331	69.36939	< 0.0001	
BC	12.36833	1	12.36833	0.371851	0.5518	
A^3	3807.195	1	3807.195	114.4625	< 0.0001	
C^3	1246.69	1	1246.69	37.48146	< 0.0001	
D^3	3564.262	1	3564.262	107.1588	< 0.0001	
A^2D	2201.666	1	2201.666	66.19261	< 0.0001	
Residual	465.6611	14	33.26151			
Lack of Fit	434.8811	10	43.48811	5.651477	0.0548	not significant
Cor Total	9627.38	26				

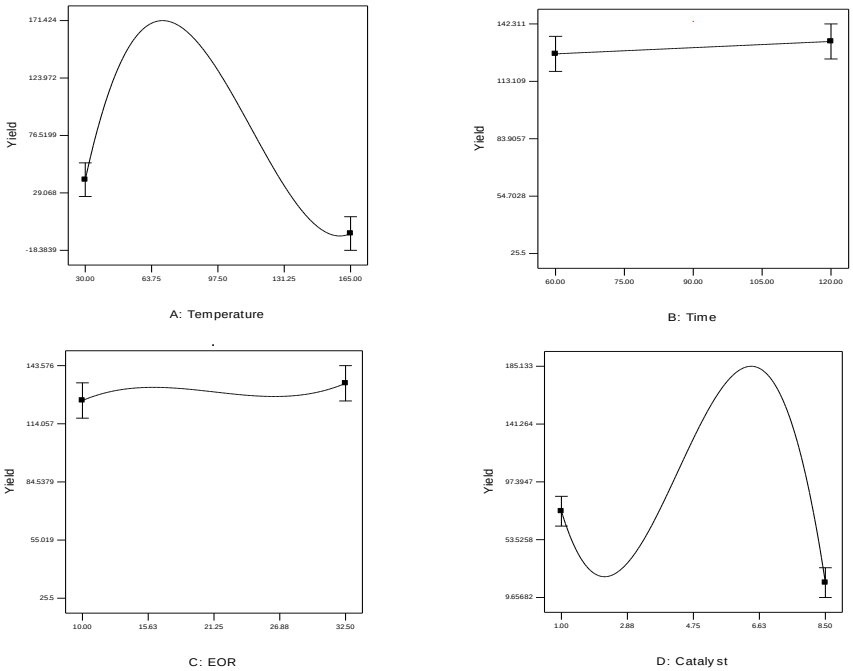

Figure 1. Individual response of factor to yield of biodiesel produced

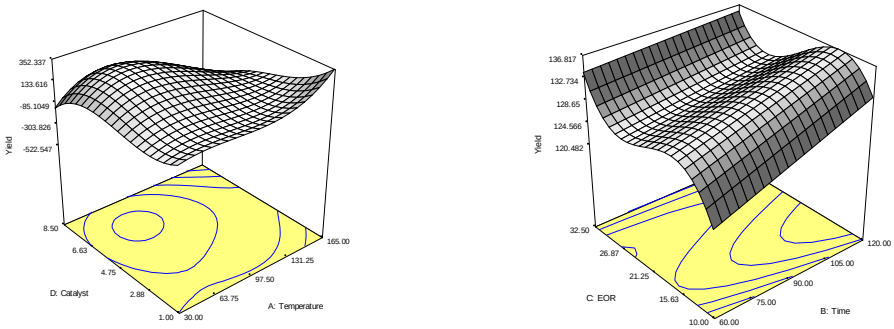

Figure 2. 3D plots of interaction of factors on Biodiesel yield

Optimization of PKO biodiesel produced

High product yields are always desired for large scale production in the biodiesel industry [11]. Thus, optimization study was carried out to study the interactive effect of operating parameters on the yield of biodiesel. Biodiesel yield was set to maximum value, while the other reaction parameters used for model development (Table 2) are ranged between and low. The optimum biodiesel yield of 98.87% was obtained by trans-esterifying PKO with 23.2 wt. % of ethanol to oil molar ratio and 5.09 g catalyst at 90.79 ºC for 94.13 min. The experimental yield was in good agreement with the predicted yield, with relatively small percentage error (2.87%). This indicated that the proposed statistical model was suitable for prediction of optimized biodiesel yield and for optimization of the transesterification process [11].

Fuel characterization results

Table 4 shows the results of the analysis of optimum PKO biodiesel produced. The viscosity (4.842 mm^2/s), specific gravity (0.856), pour point (+5 ºC), flash point (178 ºC), and cloud point (+8 ºC) of the biodiesel obtained at optimum condition compared favorably with ASTM standards.

TABLE 4. Results of measured fuel properties

Fuel characteristics	PKO biodiesel	Biodiesel Standard (ASTM D6751)	Petroleum diesel (Alamu, 2007)	Units
Specific gravity @ 15 ºC	0.886		0.854	kg/l
Specific gravity @ 40 ºC	0.868		0.838	kg/l
Specific gravity @ 60 ºC	0.856	0.88	0.825	kg/l
Viscosity @ 40 ºC	4.842	1.9 – 6.0	2.847	mm^2/s
Pour point	5	-15 to 10	-16	ºC
Flash point	178	> 130	74	ºC
Cloud point	8	-3 to 12	-12	ºC

CONCLUSION

Response surface methodology with central composite design was employed in studying the effects of reaction temperature, reaction time, ethanol to oil molar ratio, and catalyst on biodiesel production, and the optimization of biodiesel produced. The high biodiesel yield can be correlated to the basicity of the catalyst. Optimum biodiesel yield of 96 % was obtained using 17.5% ethanol (by mass of PKO) and 3.5 g catalyst at 75 ºC for 80 min. The viscosity (4.842 mm^2/s), specific gravity (0.856), pour point (+5 ºC), flash point (178 ºC), and cloud point (+8 ºC) of the biodiesel obtained at optimum condition compared favorably with ASTM standards. The study showed that biodiesel with suitable fuel properties can be produced from PKO using non-synthetic KOH impregnated on Kaolin with ethanol extracted from agricultural based raw materials. It can therefore be concluded that non-synthetic materials can replaced successfully the conventional synthetic KOH and ethanol and hence making the fuel less expensive.

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Persian Abstract

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چکیده

استفاده از ترکیبات محلی، جهت بهبود تولید بیودیزل از طریق ترنس‌استریفیکاسیون روغن دانه پالم (PKO) با استفاده از اتانول و در حضور کاتالیست ناهمگن غیر سنتزی (ترکیب KOH/ متاکائولین) بررسی شد. پارامترهای ارزیابی‌شده در فرایند عبارتند از: کاتالیست (۶-۱ گرم)، اتانول (۲۵-۱۰ درصد وزنی به درصد وزنی PKO)، دمای واکنش (°C ۱۲۰-۳۰) و مدت زمان واکنش (۱۰۰-۶۰ دقیقه). این پارامترها برای بهینه‌سازی بازده بیودیزل تولیدی، با استفاده از روش سطح پاسخ (RSM) با طراحی ترکیبی مرکزی (CCD) در نظر گرفته شدند. بازده بهینه بیودیزل به میزان ۹۶٪، با استفاده از مقدار ۱۷/۵٪ اتانول (نسبت به جرم) و ۳/۵ گرم کاتالیست در دمای ºC ۷۵ به مدت ۸۰ دقیقه به دست آمد. ویسکوزیته (mm^2/s ۴/۸۴)، وزن مخصوص (۰/۸۶)، نقطه ریزش (ºC ۵+)، نقطه فلش (ºC ۱۷۸)، و نقطه ابری شدن (ºC ۸+) بیودیزل در شرایط بهینه با استانداردهای ASTM به طور مطلوبی مقایسه شد. نتایج حاصل از این پژوهش نشان می‌دهد که بیودیزل به عنوان یک سوخت مناسب می‌تواند از PKO، با استفاده از کاتالیست KOH غیر سنتزی ترکیب‌شده با کائولین و اتانول استخراج شده از مواد اولیه حاصل از ضایعات کشاورزی، تولید گردد.

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