

Optimization of the Biodiesel Production via Heterogenous Catalyzed Transesterification of Neem Seed Oil using Response Surface Methodology (RSM)

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ABSTRACT

Biodiesel production from neem seed oil and performance evaluation of three selected catalyst was investigated. Neem seed oil was used for its suitability as feedstock for biodiesel production. The oil was extracted using soxhlet extraction method using n- hexane as a solvent and yielded 42.1%. Biodiesel was produced according to box behnken design in response surface methodology, to study the effect of experimental variables such as methanol to oil ratio, catalyst concentration, temperature and reaction time. Three (3) catalysts were used during the process namely CaO, MgO and ZnO. The model shows the highest of biodiesel yield of 89% w/w using MgO at 9:1 methanol to oil ratio, catalyst concentration of 1.1% w/w, reaction time was 120 minutes, and temperature was kept constant at 600C. ZnO performance on the transesterification of neem seed oil to biodiesel yielded 88% w/w at 6:1methanol to oil ratio, 0.8% w/w catalyst concentration and 90 minutes was the reaction time. Similarly CaO performance on the trasesterification of neem seed oil to biodiesel yielded percentage of 84 % at 6:1, catalyst concentration of 0.8% w/w and reaction time was 90 minutes. Methanol to oil ratio and catalyst concentration has significant effect on trasensterification of neem seed oil to biodesel than reaction time among others studied. The physiochemical properties of produced biodiesel was analyzed and characterized for its Fatty Acid Methyl Ester (FAME) profile using GCMS. Fuel properties of the biodiesel obtained are within the recommended standard of ASTM and suitable to be an alternative source of fuel.

INTRODUCTION

According to Intergovernmental Panel on Climate Change (2008), 10.2% of the world's total output of primary energy (energy that has not undergone any conversion or transformation) comes from biomass. The International Energy Agency (IEA) projects that biodiesel will be the fastest-growing renewable energy source between now and 2030, providing as much as 30% of the power consumed worldwide by 2050 (Renewable Energy Option, 2016). Biodiesel is considered as a substitute for conventional diesel and is gaining ground as a biodegradable, environmentally friendly, readily available energy source. Biodiesel is one of the candidates that will serve to supplement petrol diesel and provide needed energy because of its abundance and potential source all over the world (Khan et al., 2010). The use of homogeneous catalyst in biodiesel production leads to soap formation, consumption of catalyst, reduction of process efficiency and cannot be reused. This causes an increase in viscosity and formation of gels. However, there is difficulty in separation of catalyst from the product and wastage of large amount of water during purification of biodiesel produced. The use of heterogeneous catalysts will provide a cheaper and efficient way to overcome the problems stated.

LITERATURE REVIEW

Vegetable oils are chemically complex esters of fatty acids. These are the fats naturally present in oil seeds, and known as tri-glycerides of fatty acids (Ramadhas et al., 2005). The molecular weight of these tri-glycerides would be of order of 800 kg/m³ or more. Because of their high molecular weights these fats have high viscosity causing major problems in their use as fuels in CI engines (Gafar et al., 2012). These molecules have to be split into simpler molecules so that they have viscosity and other properties comparable to standard diesel oils. Modifying the vegetable oils (to make them lighter) can be achieved in many ways, including; Pyrolysis, Micro emulsification, Dilution and transesterification. Among these, transesterification is the most commonly used commercial process to produce clean and environmentally friendly light vegetable oil fuel i.e. biodiesel (Gafar et al., 2012; Sandra et al., 2013).

The fatty acid triglycerides themselves are esters of fatty acids and the chemical splitting up of the heavy molecules, giving rise to simpler esters, is known as transesterification. The triglycerides are reacted with a suitable alcohol (Methyl, Ethyl, or others) in the presence of a catalyst under a controlled temperature for a given length of time. The final products are Alkyl esters and Glycerin. The Alkyl esters, having favorable properties as fuels for use in CI engines, are the main product and the Glycerin, is a by-product (Farage et al., 2011).

METHODOLOGY

Materials

Neem seeds were collected from Usmanu Danfodiyo University Sokoto premises. Conventional laboratory apparatus and reagents were used in conduct of this research. All of the reagents used were ($\geq 99\%$, grade: analytical reagent).

Method

The neem seeds dehulled using pestle and mortar to obtain the soft seeds which were then cleaned by removing fibers, hay, leaves and other dirt. The dried seeds were then mechanically grinded using pestle and mortar in to powder. The powder was then used to extract oil using soxhlet extraction method.

Catalyst Preparation

The catalyst was prepared by measuring methanol (10cm³) then poured into a measuring flask after which the Zinc Oxide powder was carefully measured according to the design and added to the measuring flask. A cork was placed tightly on the measuring flask, the flask was swirled round thoroughly for about five minutes repeatedly about six times to obtain a heterogenous mixture of metal oxide catalysts in methanol to produce the methoxide. The same procedure was applied for the preparation of Magnesium oxide and Calcium Oxide calcium. (Asri *et al.*, 2012; Win and Ekasith 2012; Dalibar *et al.*, 2015)

Experimental design

A 3-level-3-factor box benkhen design (BBD) was employed in transesterification of the *Azadirachta indica* oil to biodiesel. Twenty (20) experimental runs were carried out for each of the three (3) catalyst, the independent variables are Molar ratio of alcohol: oil, temperature, catalyst concentration, and reaction time.

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

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^n \sum_{j=1}^{i-1} \beta_{ij} x_i x_j + e \quad 1$$

Where Y is the predicted response, x_i and x_j are uncoded independent variables, β_i and β_{ij} are coefficients estimated from regression, they represent the linear, quadratic and cubical effect of A, B, C, and D on response. Design Expert 6.0 package was used for regression analysis of variance (ANOVA) and response surface methodology was performed using the Design Expert 6.0 software. Response surface plots was developed using the fitted quadratic polynomial equation obtained from regression analysis (Sukjit and Punsuvon, 2013).

Table 1. Reaction condition variables and levels for Box Behnken Design

Independent Variables	Units	Code Levels		
		-1	0	+1
Methanol to oil	Ratio	3:1	6:1	9:1
Catalyst loading	%wt	0.5	0.8	1.1
Reaction Time	min	60	90	120

RESEARCH RESULT

Table 2. Experimental design with observed values from transesterification of Neem seed oil using CaO

Runs	MeOH to oil	cat.conc	time(min)	yield%
1	9:1	0.5	120	56
2	6:1	0.8	90	76
3	6:1	1.1	90	64
4	3:1	1.1	120	44.69
5	9:1	1.1	90	82
6	6:1	1.1	90	80
7	3:1	1.1	120	72.57
8	6:1	0.8	90	84
9	6:1	0.8	120	76
10	6:1	0.8	90	84
11	9:1	1.1	90	80
12	6:1	0.8	120	56
13	6:1	1.1	90	82
14	3:1	0.8	90	35
15	3:1	1.1	60	71
16	6:1	0.8	90	83
17	3:1	0.5	60	50.07
18	9:1	1.1	60	78
19	9:1	0.5	60	76
20	6:1	0.8	90	80

Table 3. Experimental design with observed values from transesterification of Neem seed oil using MgO

Runs	MeOH to oil	cat.conc	time	yield%
1	9:1	0.5	120	45
2	6:1	0.8	90	70
3	6:1	0.5	90	68
4	3:1	0.5	120	43
5	9:1	0.5	90	89
6	6:1	0.8	90	75
7	3:1	1.1	120	77
8	6:1	0.8	90	80
9	6:1	0.8	90	73
10	6:1	0.8	120	76
11	9:1	1.1	120	89
12	6:1	0.8	90	59
13	6:1	1.1	90	82
14	3:1	0.8	90	35
15	3:1	1.1	60	80
16	6:1	0.8	90	76
17	3:1	0.5	60	50.07
18	9:1	1.1	60	78
19	9:1	0.5	60	76
20	6:1	0.8	90	80

Table 4. Experimental design with observed values from transesterification of Neem seed oil using ZnO

Runs	MeOH to oil	cat.conc	time (min)	yield%
1	9: 1	0.5	120	57
2	6: 1	0.8	90	76
3	6: 1	0.5	90	68
4	3: 1	0.5	120	47
5	9: 1	0.8	90	88
6	6: 1	0.8	90	83
7	3: 1	1.1	120	73
8	6; 1	0.8	90	78
9	6; 1	0.8	90	80
10	6: 1	0.8	120	85
11	9: 1	1.1	120	80
12	6: 1	0.8	60	56
13	6: 1	1.1	90	78
14	3: 1	0.8	90	35
15	3: 1	1.1	60	61
16	6: 1	0.8	90	76
17	3: 1	0.5	60	50.07
18	9: 1	1.1	60	78
19	9: 1	0.5	60	75
20	6: 1	0.8	90	88

DISCUSSION

Effect of Process Variables on the Transesterification of Neem Oil

The percentage yield of biodiesel during transesterification is known to be affected by different process parameters. In this study performance of three (3) selected catalysts were investigated and compared by varying the levels of process parameters (namely, methanol to oil ratio, catalyst concentration and reaction time) while keeping temperature and agitation speed constant.

Catalyst and Molar Ratio

CaO catalyzed transesterification was firstly examined. The effects of variables as was tested for significance, with ANOVA values of "Prob>F" less than 0.0500 indicating model terms are significant. In this case A (methanol to oil ratio), B (Catalyst) and A2 were the significant model terms. The highest yield was observed when the methanol to oil ratio was 6:1, catalysts concentration 0.8% w/w and reaction time of 90 min to obtain yield of 84%.

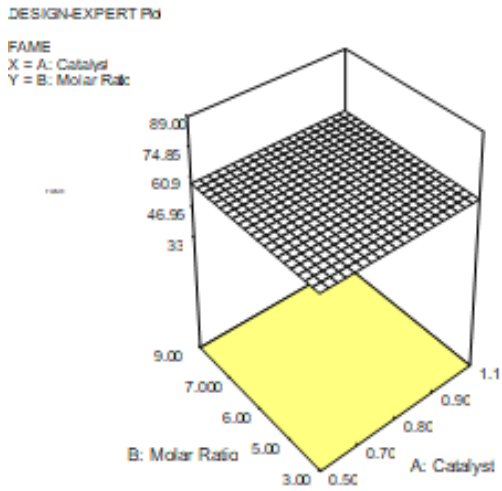


Fig 1. CaO/ Methanol

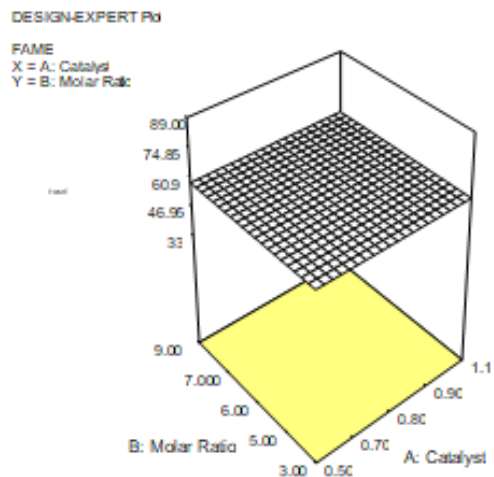


Fig 2. MgO/ Methanol

The performance of MgO catalysts on the transesterification was also investigated. The effect of the variables as linear products was tested for significance using ANOVA. Values of “Prob>F” less than 0.0500 indicated model terms are significant. In this case A (methanol to oil ratio) and B (catalyst) were the significant model terms. The highest yield was observed when methanol was 9:1, catalyst concentration 0.8 w/w and reaction time of 90 minutes which gave 89%w/w of biodiesel. Similarly when methanol to oil ratio was at 9:1, Catalyst concentration was 1.1 % w/w and reaction time was 120 minutes, biodiesel yield of 89%w/w was obtained.

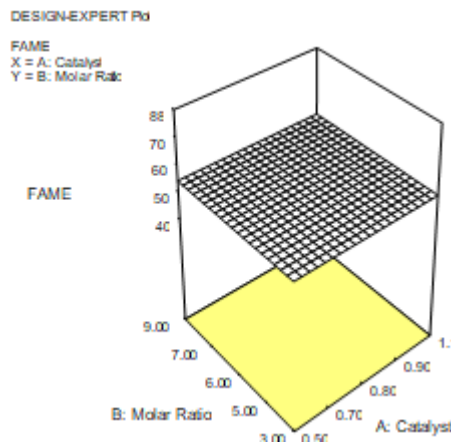


Fig 3. ZnO/Methanol

Validation of the Model

Validation experiment was conducted to determine the optimum *azadirachta indica* biodiesel yield when the process variables were set at the favourable predicted maximum levels established by the model, through Box Bhenken and RSM. The per cent error was investigated for validation of experiments. Errors between predicted and actual values were calculated

$$\text{Error} = \frac{(\text{Actual Value} - \text{Predicted Value}) \times 100}{\text{Actual Value}}$$

In the optimized condition for conversion of *azadirachta indica* oil to biodiesel using CaO, MgO and ZnO were, 70.63%, 71.58% and 75.76% biodiesel (FAME) yield was obtained from the validation experiment. The percentage error between the predicted and actual values was found to be 0.63, 1.08, and 0.77 respectively. The results clearly indicated that no significant difference was observed. In the un-optimized condition the highest *azadirachta indica* for the biodiesel yield was 70.63%, 71.58, and 75.76 for Cao, MgO and ZnO respectively, while in the optimized condition the highest biodiesel yield is 70.00%, 70.50% and 74.99% respectively. The results clearly indicated the effectiveness of process variables.

Table 5. Fatty Acid Methyl Ester Percentage Composition Identified in Biodiesel Produced from Neem Seed Oil.

Methyl Ester formula ZnO	CaO	CaO	CaO	MgO	MgO	MgO	ZnO	ZnO
	0.5	0.8	1.1	0.5	0.8	1.1	0.5	0.8
1.1								
Palmitic 14.87	C ₁₆ H ₃₂ O ₂ 12.89	14.73	8.84	10.02	10.25	1.82	9.22	12.43
Oleic 53.06	C ₁₈ H ₃₄ O ₂ 42.36	46.79	69.97	39.78	40.38	38.64	34.04	42.07
Stearic 14.61	C ₁₈ H ₃₆ O ₂ 18.21	17.33	9.0	15.43	10.61	15.71	14.75	14.88
Eicosanoic 2.5	C ₁₈ H ₃₀ O ₂ 1.76	2.3	2.0	2.38	2.3	2.81	1.06	2.33
Palmitoleic 5.7	C ₁₆ H ₃₀ O ₂ 5.32	4.9	5.3	0.22	1.2	0.11	5.2	5.6
Others 9.26	19.46	13.95	3.69	32.17	35.0	40.91	35.0	22.69
Total 100	100	100	100	100	100	100	100	100

Table 6. Biodiesel properties.

Parameters	Testing Method	Specification	NSME
Kinematic Viscosity @ 40°C (mm ² /S)	ASTM D 445	1.9–6.0	4.9 ±0.391
Acid Value (mgKOH/g)	ASTM D 664	0.80 max	79.0 ±0.005
Cetane Number	ASTM D613	47min	54.9 ±0.074
Cloud point (°C)	ASTM D2500	No limit	9 ±0.432
Flash point (°C)	ASTM D 93	130	157 ±0.056

CONCLUSIONS AND RECOMMENDATIONS

Conclusion

The study demonstrated the possibility of producing biodiesel from Neem seed oil using response surface methodology. The response surface technique was used to determine the optimal conditions for the transesterification process. The model shows the highest of biodiesel yield of 89% w/w using MgO at 9:1 methanol to oil ratio, catalyst concentration of 1.1% w/w, reaction time was 120 minutes, and temperature was kept constant at 600C. ZnO performance on the transesterification of neem seed oil to biodiesel yielded 88% w/w at 6:1 methanol to oil ratio, 0.8% w/w catalyst concentration and 90 minutes was the reaction time. Similarly CaO performance on the transesterification of neem seed oil to biodiesel yielded percentage of 84 % at 6:1, catalyst concentration of 0.8% w/w and reaction time was 90 minutes. Methanol to oil ratio and catalyst concentration has significant effect on transesterification of neem seed oil to biodiesel than reaction time among others studied.

Recommendations

Based on the findings from the results obtained, the followings are recommended

1. Engine test of Neem Seed Methyl Ester (NSME) should be carried out so as to compare its efficiency with petroleum diesel
2. Catalyst characterization should be carried to examine the surface area
3. The government, policy makers and private sectors should be made to recognize the benefit to be gained from biofuels, particularly biodiesel fuels.

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