Optimisation Of The Production Parameters Of Delonix Regia Methyl Ester Using Box- Behnken Design

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Abstract: The optimisation of the production parameters of *Delonix regia* ester was carried out with the view to establish the parameters for the production of optimum methyl ester yield from *Delonix regia* seed oil. The effects of reaction temperature, reaction time, alcohol: oil molar ratio and catalyst concentration as well as it interaction effects on the yield of methyl ester was investigated using the response surface methodology Box-behnken design. Data obtained were analyzed statistically using Design expect 9.0 statistical package to determine the response model, surface respond analysis of variance (ANOVA). The data collected from optimization of the reaction process was fitted to model. The results showed that the percentage yield in term of reaction temperature, time, molar ratio, concentration and interaction terms of reaction temperature and reaction time were significant (p ≤ 0.05) while the lack of fit F-value for the *Delonix regia* methyl ester yield response showed that it was not significant ($p \leq 0.05$) relative to the pure error. This indicates that all the models predicted for methyl ester yield response were adequate. Regression models for data on response methyl ester yield were significant ($p \leq 0.05$) with satisfactory R^2 value of 0.829. The boundaries of the design intergalactic of methyl ester yield have the lowest value at 72 % within the process range of 40 ^{0}C to 56 ^{0}C for Temperature, 30 to 53 minutes for Reaction time, for all production processes while the highest of 90.21 % with the process boundary range of 55 to 60 ^{0}C for A: Temperature, 40 to 60 minutes reaction time. The optimization solution gave the process conditions for each process factors at the highest desirability prediction of 0.642 as best reaction temperature of 53.20^{0}C and the reaction time of 60 minutes, alcohol: oil molar ratio of 2:1 and catalyst concentration of 0.69% when the set goal is based on the physic-thermal properties of produced methyl ester.

Keywords: Alcohol, Catalyst, Delonix regia, methyl ester, temperature, time

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1.0 INTRODUCTION

The problem of continuous fossil fuel depletion and environmental pollution is of great concern all over the world [1], [2], [3], [4]. The excessive use of fossil fuel globally has resulted in environmental degradation such as the green house effect, ozone layer depletion, climate change, acid rain among others [5], [6], [1]. The possible solution to this worldwide petroleum problem is the use of biodegradable product. A lot of research has been carried out to produce environmentally friendly alternative sources of energy to replace the fossil fuel [7], [8], [9], [10]. Biofuels produced from food crops and seed oil that can be used as an alternative to fossil fuel has been reported. Biofuels are solid, liquid or gaseous fuel produced from biorenewable feedstock [8], [11]. Liquid biofuels are potential and important replacement for the fossil fuel; the major biofuels are bioethanol and biodiesel [12]. Biofuel are none polluting, environmentally friendly, locally available sustainable and security of continuous supply and many benefits for the economy and consumers [12], [13], [9], [14], [15].

Biodiesel is considered as relevant technology for developing and industrialised countries [16], [17]. It has been reported that biodiesel is far more soluble than petroleum diesel enabling marine animal to survive higher concentration than petroleum fuel if spill occurs [18], [19]. Biodiesel results in lower emission of most pollutants relative to diesel [20]. The various products of vegetable oil and its mixtures with diesel have been used as alternative for fossil fuel [15], [16]. It has been reported that for vegetable oils or its mixture used, there is the need to modify the engine due to its unsuitable properties such as the ignition qualities and viscosity [16], [17] or to process the oil so as to modify its undesirable properties [18], [19]. The process by which these undesirable characteristics of vegetable oil can be modified to make it suitable for use in existing diesel engines is called

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esterification [19]. Esterification process is carried out when oil has high FFA; the process is done by the use of acid catalyst and alcohol with the aid of vacuum distillation and stirring over a period of time in a reactor [20]. Transesterification process is the process of producing ester, by using alkaline catalyst and alcohol for the reaction process. Production of ester requires good separation techniques during production process in order to prevent chemical bond chain brake, the process separate glycerol and ester. Ester separation can simply be done by the use of separating funnel [21], [22]. However, the use of vegetable oil for the production of biodiesel has not economical due to the high competition for its use for human consumption and cost of production, hence the need to use non edible oil. In an attempt to reduce the cost of biodiesel, various researches has been carried out using seed oil such as jatropha, coconut, bitter almond, palm oil, soybean, citrus seed, peanut, *Delonix regia* etc [16], [18], [20], [22], [23], [24], [25], [26], [27], [28], [29], [30]. The factors that influence the yield of biodiesel are the catalyst concentration, alcohol: oil molar ratio, reaction temperature and time. Hence the aim of this work is to optimise the reaction process in the production of biodiesel from *Delonix regia* seed oil with a view to increase desirable quality biodiesel yield.

2.0 MATERIALS AND METHODS

The *Delonix regia* seed oil was filtered using a cartilage filter to remove debris and the oil was heated at 100^{o}C for 1hour in order to remove any water molecules. The oil was then cooled and stored in sealed plastic bottles until required. The esterification process was carried out using two litre (2L) of *Delonix regia* oil which was measured and transfer into a beaker. Five hundred millimetre of (500 ml) methanol and ten millilitre (10ml) (5 % v/v) sulphuric acid were measured and mixed in a beaker. The temperature of the oil was raised to 55°C via hot plate after which the methanol-acid mixture was added. Mechanical stirrer set at 300 rpm was inserted into the beaker containing the mixture and the reaction temperature was maintained at 50°C. After 30 minutes of reaction time, the product was poured into a separating funnel and allowed to settle for 12 hours after which two separate layers were obtained [19], [20], [28]. Separation and washing of the top layer was done with warm water. The process was repeated for all the oil samples. Transesterification of esterified *Delonix regia* seed oil was conceded with methanol in the presence of catalyst (KOH) [24], [25], [29], [22]. Reactions were conducted in batches at different Temperature, Time, Alcohol: Oil molar ratio and Catalyst Concentration based on the experimental design matrix (Table 1).

Table 1. Experimental design for the optimization of the Transesterification reaction process for biodiesel production

Runs	A	B	C	D
1	60	45	5	1.00
2	60	45	8	0.75
3	60	45	5	0.50
4	50	45	2	0.50
5	50	45	5	0.75
6	40	60	5	0.75
7	50	60	2	0.75
8	40	45	8	0.75
9	60	30	5	0.75
10	50	45	5	0.75
11	50	45	5	0.75
12	50	45	8	0.50
13	50	45	5	0.75
14	40	45	5	1.00
15	50	45	5	0.75
16	50	60	5	0.50
17	50	30	8	0.75
18	40	30	5	0.75
19	50	30	2	0.75
20	50	30	5	1.00
21	50	60	8	0.75
22	40	45	5	0.50
23	50	45	2	1.00
24	50	30	5	0.50
25	60	60	5	0.75
26	40	45	2	0.75
27	50	60	5	1.00
28	60	45	2	0.75
29	50	45	8	1.00

Where:

A= Factor 1: Temperature (^oC)

B = Factor 2: Time (Minutes)

C = Factor 3: Alcohol:oil (Molar ratio)

F = Factor 4: catalyst concentraion (%)

This mixture was poured into the reactor and placed on an electric mixer and mechanical stirrer. The stirring speed was maintained at 300rpm. After the reaction process the contents were allowed to cool at ambient air condition. This reactant was then poured into a separating funnel and separation was allowed to take place under gravity for 12hours. The *Delonix regia* methyl ester which is the biodiesel was found floating on top while the denser glycerine, excess alcohol, catalyst, impurities and traces of un-reacted oils settled at the bottom of the funnel. All experiments were carried out using the response surface methodology, Box-behnken experimental design. Data obtained were analyzed statistically using Design expect 9.0 statistical package to determine the response model, surface respond analysis of variance (ANOVA). The data collected from optimization of the reaction process was fitted to model. Developed model from the factor interaction and model validation was analysed. In establishing a model for a particular process, $Y = \beta_0+\beta x_1+ \beta x_2 + \beta x_1 x + \beta x_1^2+ \beta x_2^2 + \beta x_1^2 x_2 + \beta x_1 x_2^2 + \beta x_1^3 + \beta x_2^3+ £$. The validity of that model in predicting the output of a process is essential as its relevance depends to a large extent on its accuracy. In this study, the validity of Response Surface Methodology (RSM) as a modelling and optimization tool is determined by developing linear, two factor interactions, quadratic, cubic models to show a model that best fit the experimental result by conducting robustness test using R-square value (R^2), Adjustable R-square, Root Mean Square Error, Predicted R-square value, Adequate Precision, Predicted Residual Sum Square (PRESS) and Coefficient of Variation %.

3.0 RESULTS AND DISCUSSION

The results of the percentage methyl ester yield from *Delonix regia* seed oil as influenced by the processing parameters of temperature, time, alcohol:oil molar ratio and catalyst concentration are as presened in Table 2. The highest yield of methyl ester yield of 90.21% was obtained when produced at 50^{o}C, 60minutes, 8:1 alcohol:oil molar ratio and 0.75% catalyst concentration while the lowest yield of 72.30% was obtained at 50^{o}C, 45 minutes, 2:1 alcohol:oil molar ratio and 1.00% catalyst concentration.

Table 2: Delonnix regia Methyl ester yield as influenced by production parameters

Runs	A	B	C	D	%yield
1	60	45	5 : 1	1.00	73.80
2	60	45	8 : 1	0.75	82.00
3	60	45	5 : 1	0.50	78.00
4	50	45	2 : 1	0.50	76.91
5	50	45	5 : 1	0.75	78.54
6	40	60	5 : 1	0.75	82.00
7	50	60	2 : 1	0.75	80.40
8	40	45	8 : 1	0.75	74.31
9	60	30	5 : 1	0.75	84.00
10	50	45	5 : 1	0.75	78.00
11	50	45	5 : 1	0.75	83.40
12	50	45	8 : 1	0.5	81.00
13	50	45	5 : 1	0.75	78.80
14	40	45	5 : 1	1.00	72.00
15	50	45	5 : 1	0.75	77.90
16	50	60	5 : 1	0.50	86.30
17	50	30	8 : 1	0.75	78.00
18	40	30	5 : 1	0.75	72.81
19	50	30	2 : 1	0.75	74.00
20	50	30	5 : 1	1.00	76.90
21	50	60	8 : 1	0.75	90.21
22	40	45	5 : 1	0.50	74.80
23	50	45	2 : 1	1.00	72.30
24	50	30	5 : 1	0.50	75.00
25	60	60	5 : 1	0.75	89.20
26	40	45	2 : 1	0.75	72.50
27	50	60	5 : 1	1.00	87.20
28	60	45	2 : 1	0.75	84.13
29	50	45	8 : 1	1.00	79.38

Where:

A= Factor 1: Temperature (^oC)

B = Factor 2: Time (Minutes)

C = Factor 3: Alcohol:oil (Molar ratio)

F = Factor 4: catalyst concentraion (%)

The quadratic regression coefficient was obtained by engaging a least squares method technique to predict quadratic polynomial models for the *Delonix regia* methyl ester percentage yield (%). The yield% process term of reaction temperature, time, molar ratio, concentration and interaction terms of reaction temperature and reaction time were significant ($p \leq 0.05$) while the lack of fit F-value for the *Delonix regia* methyl ester yield response showed that it was not significant ($p \leq 0.05$) relative to the pure error. This indicates that all the models predicted for the Y response were adequate. Regression models for data on response methyl ester yield were significant ($p \leq 0.05$) with satisfactory R^2 value of 0.829, however, the model was significant. The Response Surface Methodology (RSM) was carried out using the Box-behnken design. The Box-behnken design is one of the best ways of evaluating the relationships between responses, variables and interactions that exist by duplicating for every combination of categorical factor levels. The relationships between independent and dependent variables are shown in the three-dimensional-representation as response surfaces Figure 1 and in a contour plot Figure 2, curves of equal response values are drawn on a plane whose coordinates represent the levels of the independent factors. Each contour represents a specific value for the height of the surface above the plane defined for combination of the levels of the factors. Therefore, different surface height values enable one to focus attention on the levels of the factors at which changes in the surface height occur in the experiment. The variable response based on the Response Surface Quadratic Model terms that are statistically significant are as plotted in Figure 1. The plot shows interaction A: Temperature, B: Reaction time, while holding Oil-Alcohol molar ratio at 5:1 and Catalyst concentration at a constant level of 0.75%. The boundaries of the design intergalactic of methyl ester yield have the lowest value at 72 % within the process range of 40 ^0C to 56 ^0C for A: Temperature, 30 to 53 minutes for B: Reaction time, for all production processes while the highest *Delonix regia* methyl ester produced at 90.21 % with the process boundary range of 55 to 60 ^0C for A: Temperature, 40 to 60 minutes reaction time (Figure 2). The other factors of interaction showed lower *Delonix regia* methyl ester yield responds boundary plots Figures 3 to Figure7 except the factor interaction of time and alcohol:oil (molar ratio) (Figure 5) which showed the boundary to achieve high yield of *Delonix ragia* methyl ester yield at 52.50 to 60 minutes reaction time with molar ratio of 5:1 to 6:1 which is similar to previous studies carried out on some non-edible seed oil [19], [22], [28], [29].

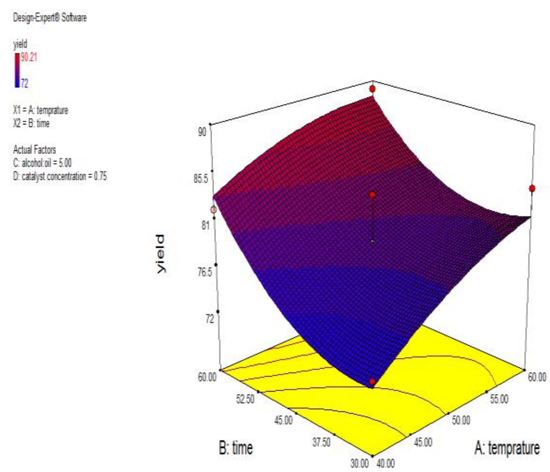

Figure 1: 3-D response surface plot of temperature and time effect on Delonix regia methyl ester yield.

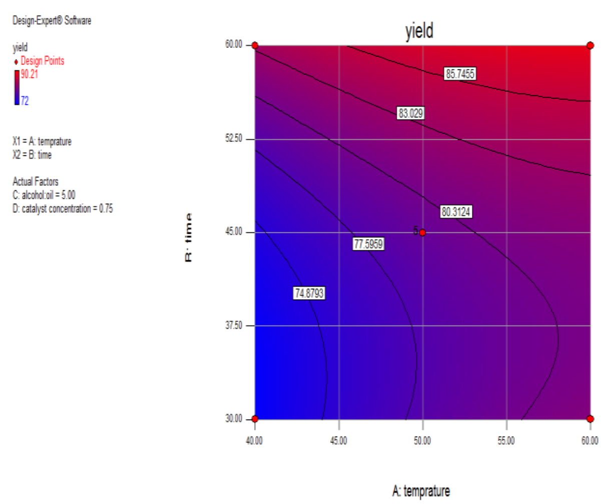

Figure 2: Contour plot of temperature and time effect on Delonix regia methyl ester yield.

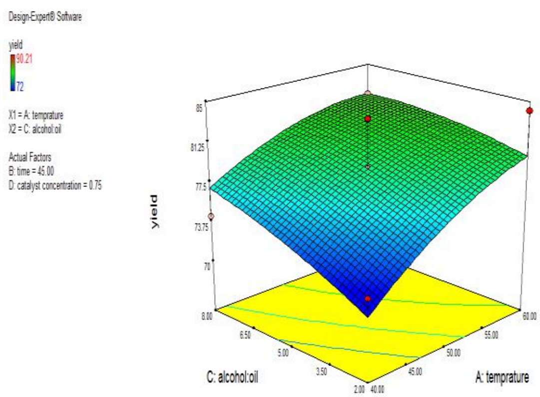

Figure 3: 3-D response surface plot of temperature and alcohol: oil (molar ratio) effect on Delonix regia methyl ester yield.

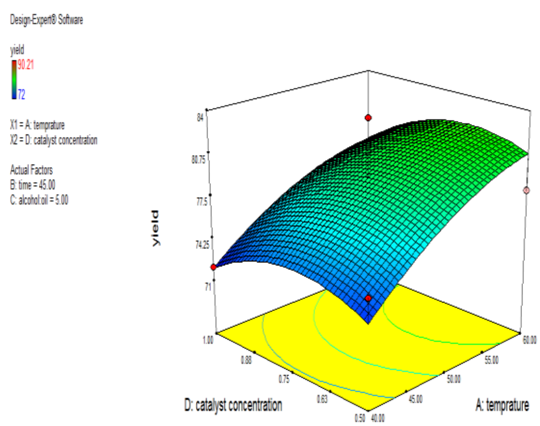

Figure 4: 3-D response surface plot of temperature and catalyst concentration effect on Delonix regia methyl ester yield.

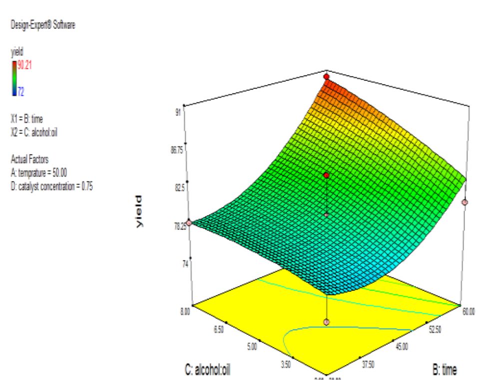

Figure 5: 3-D response surface plot of time and alcohol: oil (molar ratio) effect on Delonix regia methyl ester yield.

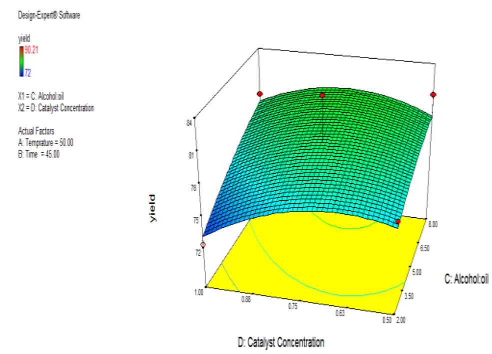

Figure 6: 3-D response surface plot of alcohol: oil (molar ratio) and catalyst concentration effect on Delonix regia methyl ester yield.

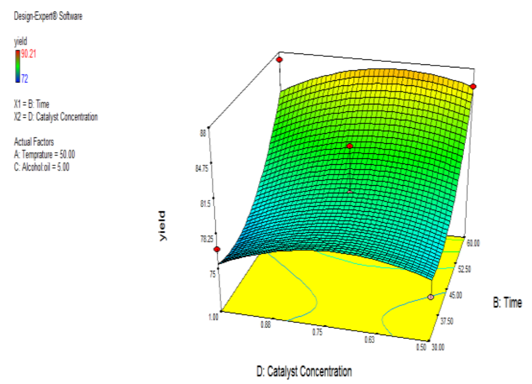

Figure 7: 3-D response surface plot of time and catalyst concentration alcohol: oil (molar ratio) effect on Delonix regia methyl ester yield.

Optimization process

Numerical Optimization analysis carried out on the produced *Delonix regia* biodiesel by setting goals on the investigated physic-thermal properties of the produced based on the experimental design matrix of the *Delonix regia* methyl ester. The desirable qualities of biodiesel include minimum value of moisture content, pour point, cloud point and viscosity (kinematic and dynamic) with maximum values of methyl ester yield, density, smoke and flash point; hence the best set objectives of each these parameters (maximum, minimum and within range) of *Delonix regia* methyl ester was investigated and the responses are as presented in the overlay plot in Figure 8. The optimization best four solution give the process conditions for each process factors at the desirability prediction values, the selected condition with reference to the highest desirability prediction of 0.642, (Table 3) revealed the best reaction temperature of 53.20^{0}C and the reaction time of 60 minutes, alcohol: oil molar ratio of 2:1 and catalyst concentration of 0.69%.

Table 3: Numerical Optimization Desirability solution for Delonix regia biodiesel

S/No	A	B	C	D	Desirability
1.	53.20	60.00	2.00	0.69	0.642
2.	53.74	59.96	2.00	0.70	0.641
3.	52.17	60.00	2.00	0.68	0.641
4.	52.20	60.00	2.00	0.67	0.640

Where:

A= Factor 1: Temperature (oC)

B = Factor 2: Time (Minutes)

C = Factor 3: Alcohol:oil (Molar ratio)

F = Factor 4: catalyst concentraion (%)

The boundary for maximum yield of *Delonix regia* biodiesel when considering two interaction molar ratios 5:1 to 6:1 and set goal based on the physicochemical properties of produced methyl ester. This study gives more realistic conditions for the production of methyl ester from *Delonix regia* seed oil not only in terms of yield but also terms of desirable physic-thermal qualities.

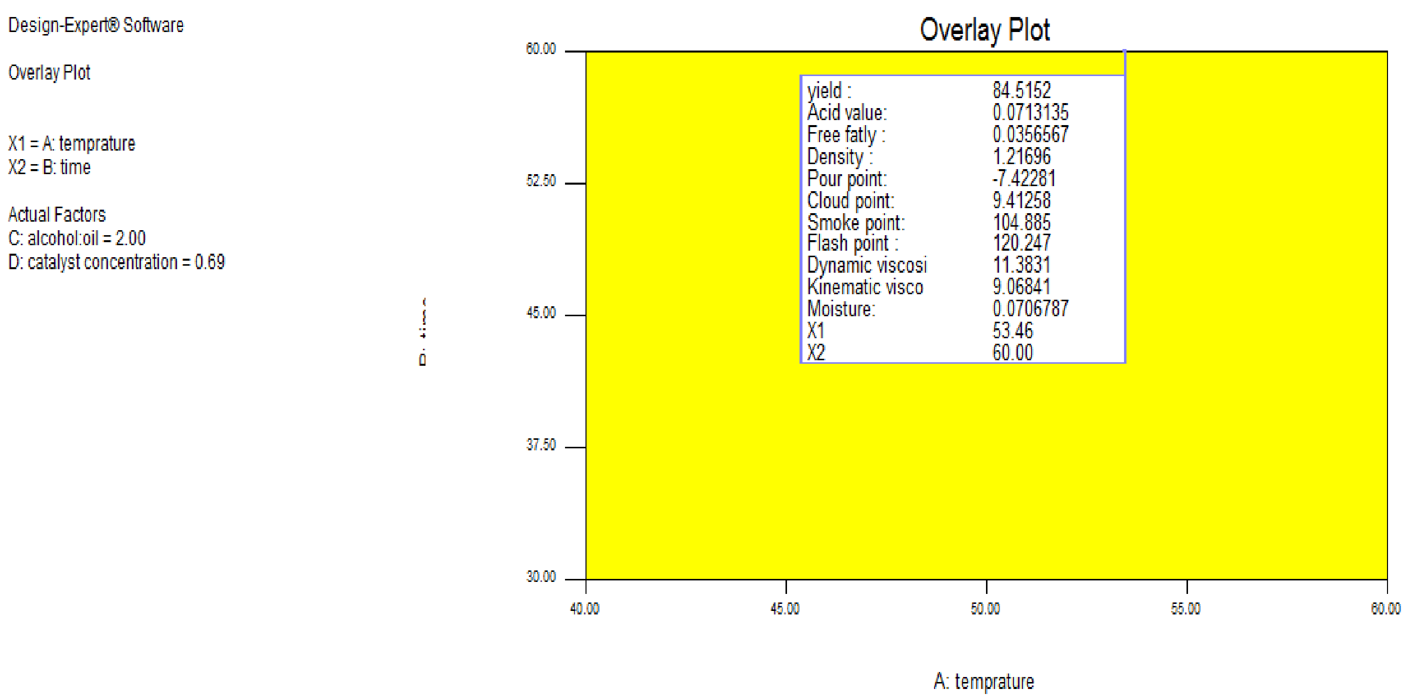

Figure 8: Graphical ovelay plot of set goal for optimization process.

Conclusion

It is concluded that *Delonix regia* methyl ester with the highest desirability prediction of 0.642 in terms of minimum moisture content, cloud point, pour point and viscosity with maximum yield of 84.50% can be produced at 53.20^{0}C reaction temperature, 60 minutes 2:1 alcohol: oil molar ratio and 0.69% catalyst concentration.

Acknowledgements

This work was funded by the Directorate for Research, Innovation and Development (DRID), Federal University Technology, Minna, Niger State, Nigeria under the Award of Tetfund Institution-Based Research Intervention (IBRI) Fund for research, code number: TETFUND/FUTMINNA/2017/B/06.

References

[1] Kesse D G (2000) Global warming – facts, assessment, countermeasures. *J. Petrol Sci Eng* 26: 141 – 149. Doi: 10, 1016/S0920 – 4105(00)00030 – 9

[2] Cao X (2003) Climate change and energy development: implications for developing countries. Resource Policy 29:61 – 67,

doi:10.1016/j.resourpol.2004.05.001

[3] Johansson, Y. McCarthy S (1999) Global warming post Kyoto: continuing impasse or prospects for progress? *Energy Dev Rep Energy*, pp 69 – 71.

[4] Demiras A, (2007) Gasoline and diesel fuel blends with alcohols, *Energy Edu Sci Technol* 19:87 – 92

[5] Reijnders L, (2006) Conditions for the sustainability of biomass based fuel use. *Energy Policy* 34:863 – 876.

[6] Murphy J D, McCarthy K (2005). The optimal production of biogas for use as a transport fuel in Ireland. Renew Energy 30:2111 – 2127, doi:10.1016/j.renene.2005.02.004

[7] Mann, M. And P. Spath (1997) Life cycle assessment of a biomass Gasification Combined cycle Gasification System, Golden, CO, National Renewable Energy Laboratory

[8] Demirbas A, (2006) Global biofuel strategies, *Energy Edu Sci Technol*, 17:27 – 63

[9] Demiras, M F, Balat M, (2006) Recent advances on the production and utilization trends of biofuels: A global perspective, *Energy Convers Mgmt* 47:2371 – 2381.

[10] Puppan, D., (2002). Environmental evaluation of biofuels, Periodica Polytechnica Ser Soc Man Sci, 2002; 10: 95 – 116.

[11] Kojima, M and T Johson (2005) Potential for Biofuels for Transport in Developing countries, Washington. DC , World Bank.

[12] Fulton, L., Howes, T. and Hardy, J. (2004) Biofuel for transport: An International Perspective, Paris, France, International Energy Agency

[13] Cook J and J Beyea (2005). An analysis of environmental impacts of energy crops in the USA: methodologies, conclusions & recommendations, Washington DC, (2005) www.panix.com/~jimcook/data/ec.workshop.html

[14] Earley J., T. Earley and M Straub (2005), Specific Environmental effects of trade liberalization: oil seeds, Washington, DC, International Policy council for food & Agriculture

[15] Kim, S. and Dale, B. E. (2005). Life cycle assessment of various cropping systems utilized for producing biofuels: Bioethanol and biodiesel, *Biomass Bioenergy* 29:426 – 439.

[16] Altin, R, Cetinkaya, S. and Yucesu, H.S. (2001). The potential of using vegetable oil fuels as fuel for diesel engines. Energy Conversation and Management 42, pp 529-38, 2001.

[17] Oghenejoboh, K. M., Akhihiero, E.T. and Adiotomre, K.O. (2010). Viability of biofuel as alternative fuel in Nigeria's transport system. *International journal of engineering* 4(3), pp 445-453.

[18] Becker, K. and G. Francis (2005). Biodiesel from Jatropha Plantations on Degraded Land, Stuttgart, University of Hohenheim cited in TERI (2005) Liquid Biofuels for Transportation: India Country Study on Potential and Implications for Sustainable Agriculture and Energy, Report prepared for the Deutsche Gesellschaft fur Technische Zusammenarbeit (GTZ) GmbH, New Delhi, October www.gtz.de/de/dokumente/en-biofuels-for-transpotation-in-india-2005.pdf

[19] Aransiola, E. F., Betiku, E., Ikhuomoregbe D.I.O. and. Ojumu, T.V. (2012). Production of biodiesel from crude neem oil feedstock and its emissions from internal combustion engines. *African Journal of Biotechnology,* Vol. 11, No. 2, pp. 6178 – 6186, 2012.

[20] Perdersen, J. R., A. Ingemarsson and J. O. Olsson (1999). Oxidation of rapeseed oil, rapeseed methyl ester (RME) and diesel fuel studied with GC/MS. *Chemosphere*, vol 38, no 11, pp 2467-2474

[21] Reddy, P.N. and Raju, A.V. (2009). Experimental investigation on jatropha biodiesel and additive in diesel engine. *Indian Journal of Science and Technology*, 20, pp25-31, 2009.

[22] Tariq, Z., Ullah, K., and Sharma, V. K. (2012). Bitter Almond oil as non-edible feedstock for biodiesel production. Abstract of the 3rd international workshop on renewable energy for sustainable

development in Africa, Enugu pp31.

[23] He, H., Wang T., and Zhu, S. (2007). Continuous production of biodiesel fuel from vegetable oil using supercritical methanol process. The State Key Lab of Chemical Energy, Tsinghua University, Beinjing, China, pp 30.

[24] Tiwari, A.K., Kumar, A. and Raheman, H. (2007). Biodiesel production from jatropha oil with high free fatty acid: An optimized process. *Biomass Bioenergy* 31(8), pp569-575.

[25] Agarry, S.E., Ajani, A.O., Aworanti, A.O., and Solomon, B.O., (2010) Alkali- catalyzed production of biodiesel fuel from Nigerian citrus seed oil. Proceeding of the Nigerian society OF Chemical Engineers, 40, pp 145-154.

[26] Dorado, M.P., Ballesteros, E., Lopez, F.J. and Mittelbach, M. (2004). Optimization of alkali-catalyzed trans-esterification of brassica oil for biodiesel production. *Energy Fuel*, 18 (1) pp77-83.

[27] Oloefule, A.U., Ibeto, C.N. and Ugwuamake, I.E. (2012). Determination of Optimal catalyst concentration for biodiesel yield from coconut oil, Abstract of the 3rd international workshop on renewable energy for sustainable development In Africa, Enugu, pp20.

[28] Okey, E. N and Okey, P. A. (2013). Optimization of biodiesel production from non edible seeds of *Delonix regia* (Gul Mohr*) International Journal of Bioresource Technology* Vol. 1, No. 1, February 2013, PP: 01 – 08, ISSN: 2327-7734 (online)Available online www.acascipub.com

[29] Abdullah, B. M. and Salimon, J. (2011).Optimization of Process Parameters for Diesters Biolubricant using D-optimal Design. *World Academy of Science, Engineering and Technology International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering* Volume 5, Issue 8.

[30] Ahmad, M., Rashid, S., Khan, M.A., Zafar, M., Sultan, S., and Gulzar, S. (2009). Optimization of base catalysed transesterification of peanut oil biodiesel, *African Jounal of Biotechnology*, 8 (3), pp 441-443, 2009.