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FOUR-FACTOR RESPONSE SURFACE OPTIMIZATION AND ENGINE EMISSION ANALYSIS OF RUBBER SEED OIL BIODIESEL

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ABSTRACT

Fossil fuel, the major sources of world energy needs is beset with the problems of rapid depletion and negative environmental impact. Among the various alternatives investigated for diesel replacement, biodiesel has emerged the most suitable. This research work focused on response surface optimization and engine emission analysis of rubber seed oil (RSO) biodiesel. The oil from rubber seed was solvent extracted and characterized based on American Society for Testing and Materials (ASTM) method. The fatty acid profile and the oil functional groups were determined using gas chromatography mass spectroscopy and Fourier transform infrared spectroscopy respectively. The effect of process parameters on the yield of rubber seed oil biodiesel or rubber seed oil fatty acid methyl ester (RSOFAME) was investigated using one factor at a time method. The process parameters and RSOFAME yield were optimized using response surface methodology (RSM). The engine emission analysis of RSOFAME, diesel and their blends was carried out using Perkin 4:108 diesel engine. The oil content of RSO was determined as 40.02%. The RSO physiochemical properties were determined as, acid value, free fatty acid, saponification value, iodine value, peroxide value, kinematic viscosity, fire point, flash point, cloud point, pour point, refractive index specific gravity, moisture content, and density, 28.72mgKOHg⁻¹, 14.36%, 185.66mgKOHg⁻¹ 120.4gI₂100g⁻¹, 14.62meqkg⁻¹, 38.5mm²s⁻¹ @ 400C, 1800C, 1320C, 60C, 20C 1.428, 0.92, 7%, 920Kgm⁻³, respectively. The RSOFAME fuel properties were determined as, density, kinematic viscosity, cetane number, flash point, cloud point, water content, acid value, calorific value, iodine value, and pour point, 880kgm⁻³ 4.25mm²s⁻¹ 58.2, 1640C, 40C. 0.44%, 0.32mgKOHg⁻¹, 38.5MJkg⁻¹, 72gI₂100g⁻¹, 20C, respectively. The optimum conditions suggested by the result analysis for maximum RSOFAME yield of 93% within the ranges studied were: methanol to oil molar ratio 7:1, catalyst concentration 0.75%wt, reaction temperature 500C, reaction time 45 minutes. Actual experiment based on the optimum conditions produced 91.79% yield of RSOFAME. The engine emission analysis revealed that carbon monoxide (CO), hydrocarbon (HC) and nitrogen oxides (NO_x) emission increased with increase in engine load. At a specific engine load, CO and HC emission decreased with increase in biodiesel fraction while NO_x increased with increase of biodiesel fraction.

KEYWORDS: Characterization, engine load, optimization, rubber seed oil, transesterification.

1. INTRODUCTION

The world energy demand is increasing by day as a result of population explosion and spate of industrialization. The major energy sources of the world, petroleum, coal and natural gas, known as fossil fuels as they are derived from the plants and animal remains from the earth crust, is fast depleting as a result of high energy demand by the rapidly increasing population and industrial development. It has been reported by [1] that 75 million barrels of crude oil is consumed daily worldwide. It is therefore envisaged that a time is coming when the fossil fuel will eventually be exhausted. The use of fossil fuels in automobiles and various engines impact negatively on the environment as it results in emission of green house gases that cause climatic change and harmful substances like sulphur oxides (SO_x), nitrogen oxides (NO_x) and methane [2]. The growing concern due to fast depletion and environmental pollution caused by the conventional fossil fuels has led to the search for environmentally friendly and renewable fuels. Out of the various options investigated for replacement of fossil fuel, biodiesel has proved the foremost for reduction of exhaust emission (3).

A proper selection of feedstock for production of biodiesel is critical for viable alternative fuel to petrodiesel. Although, biodiesel is gaining popularity, more than 95% of the renewable resources used for its production are edible oils [4], which will in a long term have serious implications on food availability and the cost of biodiesel as it may be more expensive than petro-diesel. Worldwide, biodiesel production is mainly from edible oils such as soya bean, sunflower, canola, palm oils etc. Therefore, concerted research efforts are geared towards identifying and evaluating non-edible seed oils as suitable feed stock. The non-edible oils that are being studied and are promising as suitable feedstock for biodiesel production are: neem (*A. indica*), jatropha tree (*J. curcas*), karanja (*P.pinnata*), tobacco seed (*N. tabacum L.*), rice bran, mahua (*M. indica*), rubber plant (*H. brasiliensis*), castor, linseed, and microalgae. *Jatropha curcas* oil plants have been widely studied with respect to biodiesel production from non-edible oils ([5-7] but the use of most of other non-edible oil plants such as rubber, neem, castor etc have not been intensely studied as *Jatropha curcas*. Akin to proper selection of feedstock for biodiesel production, the quest for optimal production of biodiesel from the feed stock is also of paramount importance for viable alternative to fossil fuel. This research work therefore focused on the optimization and engine emission analysis of biodiesel produced using relatively low-cost materials, none-edible rubber seed oil feedstock, homogeneous sodium hydroxide catalyst and methanol solvent. The rubber tree (*Hevea brasiliensis*) is a perennial plantation crop, and it's indigenous to South America. Since its introduction to the orient around 1876, it has been cultivated as an industrial crop. The rubber tree grows in hot, humid climates, native of the tropical rain forests of the Amazon valley, is a tall tree that attain the height of about 20m [8]. Rubber seed oil yield from rubber plantations varies from 100 to 150 kilogram per hectare depending on soil fertility and crop

density. Rubber Seed Oil is a semi-drying substance. The uses of RSO include, synthesis of alkyd resin and paint coatings, production of biodiesel [9, 10]. The rubber seed consist of about 40% kernel with 20-25% moisture. Approximately 40-50% of oil is found in the dried kernel which contributes to 20 million liters of oil yearly [11]. Up till now the rubber seeds has not been considered much useful and are therefore not converted into useful products. The oil consists of high percentage of free fatty acid (17%) and is therefore unsuitable for biodiesel production by direct transesterification. The oil was rather esterified by pretreatment with acid catalyst and then transesterified with alkali catalyst using methanol solvent. The engine emission analysis is another factor that is very important for viable alternative fuel for petro-diesel. Therefore, the engine emission analysis of the RSOFAME was carried out to ascertain its suitability and emission characteristics in compression ignition engines.

2 MATERIALS AND METHOD

2.1 Materials

Rubber seeds, reagents, glassware, equipment including gas chromatography mass spectrometer, (GC-MS), Fourier transform infrared spectroscopy (FTIR), viscometer, magnetic hot plate, soxhlet extractor.

2.2 Experimental Methods

2.2.1 Extraction of oil from rubber seeds

The rubber seeds was purchased from Sapele in Delta state, Nigeria where rubber plantation abound. The seeds were de-shelled and the inner seed coat was removed by winnowing. The kernel was then dried in an oven at 500C for five hours to reduce the water content. It was then grind with mechanical grinder in order to expose more surface area of the seed for faster and maximum oil extraction. Solvent extraction using soxhlet extractor was used for determination of oil content of the seed. The bulk of oil used in this research work was obtained by solvent extraction. 3kg of the dried, ground seed was introduced into a plastic container containing 3 liters of n-hexane. The mixed content of the container were vigorously shaken after covering the container. The container was made air tight to prevent evaporation of the methanol and then kept for a day for maceration of the ground seed. Then the dissolved oil in hexane was decanted and the slurry filtered. The filtrate was then distilled to recover the methanol at 650C [12]. The percentage oil yield was calculated as:

$$\% \text{ oil yield} = \text{weight of oil obtained} \div \text{weight of seed sample} \times 100 \quad (1)$$

2.2.2 Characterization of rubber seed oil

The physiochemical properties of the oil extracted from rubber seeds was characterized based on American Society for Testing Materials, ASTM 6751 (1973) method. Analytical equipment's, GC MS (QP2010 plus Shimadzu, Japan) and FTIR (M530 Bulk scientific FTIR) were used to determine the fatty acid profile and the functional groups of the oil respectively.

2.2.3 Effect of process parameters on biodiesel yield

The effects of process parameter on biodiesel yield from rubber seed oil were investigated based on one factor at a time method, involving keeping a factor constant at a time and varying the others in turn. The four factors investigated were, molar ratio of methanol to oil, catalyst concentration, reaction time and reaction temperature.

2.3 Synthesis of RSOFAME

Synthesis of biodiesel from the oil involves two-steps, esterification by pretreatment of the oil using methanol and acid catalyst and then synthesis of the biodiesel by transesterification using methanol and sodium hydroxide catalyst. Esterification involves heating the oil to a temperature of 1100C for 10 minutes to remove most of the water present in the oil. The oil was cooled and then introduced into a 500ml three-necked round bottomed flask fitted with a condenser and a thermometer at the middle and side arms respectively. Then methanol of 60%w/w of oil mixed with concentrated sulphuric acid of 7% w/w of oil was added. The set up was heated to 600C for 60 minutes with a magnetic heating mantle and the agitation speed set at 400rpm. The reaction mixture after cooling was transferred into 250ml separating funnels where it settles and separate into water, pre-treated oil and methanol layers. The pre-treated oil after being tapped off was wet-washed and oven dried at 1050C for complete evaporation of water. The pre-treated oil was then transesterified using methanol and sodium hydroxide catalyst. A specified quantity of the pre-treated oil was run into a 500ml three- necked round bottomed flask fitted with a condenser, a thermometer and a receiver on the middle and the side arms respectively. Then a known amount of mixture of sodium hydroxide catalyst in methanol was added into the flask. The stirrer was switched on to a specified speed and the reaction mixture was heated and refluxed for the required reaction time The reaction mixture was made to stand for a day in separating funnels where it separated into the upper biodiesel layer and the lower glycerol layer. The remnants of sodium hydroxide, methanol and glycerol in the biodiesel were removed by wet-washing. The washed biodiesel was then oven dried at 1050C until all the residual water was removed. The percentage biodiesel yield is given by the expression of equation (1).

$$\% \text{ biodiesel yield} = \text{Volume of biodiesel produced} \div \text{volume of oil used} \times 100 \quad (2)$$

2.4 Determination of fuel properties of RSOFAME

The fuel properties of the rubber seed oil biodiesel were characterized based on ASTM standards. The properties determined include density, viscosity, iodine value, cetane number, acid value, free fatty acid, calorific value, flash point etc.

2.5 Design of Experiment for Optimization of Transesterification of RSO

Design of experiment and optimization of the reaction conditions were carried out using design expert software version 12.0. The experimental design employed is two-level four factor fractional factorial design including 30 experiments. The independent factors involved are methanol to oil molar ratio, catalyst concentration, reaction temperature and reaction time while the dependent factor or response was percentage biodiesel yield obtained by transesterification of the rubber seed oil. The choice of level of factors of independent variables were based on the earlier experiments performed on the effects of process variables on RSOFAME yield, and the factor levels are given in table 1. The experimental design matrix for transesterification of rubber seed oil in coded and uncoded forms are given in tables 2. Alpha (α) is defined as a distance from the center point which can be either inside or outside the range, with the maximum value of $2n/4$, where n is the number of factors [13]. It is noteworthy to point out that the software uses the concept of the coded values for investigation of the significant.

Table 1: Experimental range and levels of independent process variables for biodiesel production

Independent variable	Units	+ α	High level	Mid-range	Low level	- α
Temperature (A)	$^{\circ}\text{C}$	65	60	50	40	35
Catalyst conc. (B)	Wt%	1.125	1	0.75	0.5	0.375
Reaction time (C)	Minute	67.5	60	45	30	22.5
Methanol to oil molar ratio (D)	mol/mol	11.5	10	7	4	2.5

Table2: Experimental design matrix for transesterification studies of RSOFAME

Std	Run	Temperature (°C) A		Catalyst concentration (wt %) B		Reaction time (Minutes) C		Methanol to oil molar ratio (ml/mol) D		RSOFAM E Yield (%)
		Code d	Uncode d	Code d	Uncode d	Code d	Uncode d	Code d	Uncode d	
1	12	-1	40	-1	0.5	-1	30	1	4	
2	16	1	60	-1	0.5	-1	30	1	4	
3	4	-1	40	1	1	-1	30	-1	4	
4	11	-1	60	1	1	-1	30	-1	4	
5	23	-1	40	-1	0.5	1	60	-1	4	
6	13	1	60	-1	0.5	1	60	-1	4	
7	25	-1	40	1	1	1	60	-1	4	
8	18	1	60	1	1	1	60	-1	4	
9	22	-1	40	-1	0.5	-1	30	1	10	
10	7	1	60	-1	0.5	-1	30	1	10	
11	29	-1	40	1	1	-1	30	1	10	
12	28	1	60	1	1	-1	30	1	10	
13	20	-1	40	-1	0.5	1	60	1	10	
14	15	1	60	-1	0.5	1	60	1	10	
15	21	-1	40	1	1	1	60	1	10	
16	17	1	60	1	1	1	60	1	10	
17	26	-α	35	0	0.75	0	45	0	7	
18	30	+α	65	0	0.75	0	45	0	7	
19	6	0	50	-α	0.375	0	45	0	7	
20	8	0	50	+α	1.125	0	45	0	7	
21	1	0	50	0	0.75	-α	22.5	0	7	
22	19	0	50	0	0.75	+α	67.5	0	7	
23	2	0	50	0	0.75	0	45	-α	2.5	
24	9	0	50	0	0.75	0	45	+α	11.5	
25	10	0	50	0	0.75	0	45	0	7	
26	27	0	50	0	0.75	0	45	0	7	
27	3	0	50	0	0.75	0	45	0	7	
28	24	0	50	0	0.75	0	45	0	7	
29	14	0	50	0	0.75	0	45	0	7	
30	5	0	50	0	0.75	0	45	0	7	

terms, thus equation in coded values is used to study the effect of the variables on the response. The empirical equation is represented by equation 3.

$$Y = \beta_0 + \sum_{i=1}^4 \beta_i X_i + \sum_{i=1}^4 \sum_{j=i+1}^4 \beta_{ij} X_i X_j + \sum_{i=1}^4 \beta_{ii} X_i^2 \quad (3)$$

Where Y is the predicted percentage yield of biodiesel, X_i and X_j are the transesterification process variables, β_0 is the offset term, β_i is the coefficient of linear (single) effect, β_{ij} is the coefficient of interaction effect and β_{ii} is the coefficient of quadratic effect.

2.6 Engine emission test for RSOFAME

The engine emission test of the RSOFAME was carried out on a Perkins 4:108 diesel engines mounted on a steady state engine test bed as shown in plate1. The engine is a four cylinder, water-cooled, naturally aspirated, 4-stroke CI engine. The engine specification is as given in Table 3. The experiment was conducted with no. 2 diesel fuel, biodiesel and their blends. The blends consist of percentage by volume of biodiesel 0, 20, 40, 60, 80, 100% denoted as B0, B20, B40, B60, B80, and B100 respectively. B0 and B100 are neat diesel and biodiesel respectively. 100cm³ of the biodiesel blend under test was run into the fuel chamber of the engine. The engine was started and kept at constant speed of 1900rpm, and loaded 20kg. The exhaust gases, nitrogen oxides, NO_x, carbon monoxide, CO, and hydrocarbon, HC were measured with a portable digital gas analyzer (Testo XL 450). The data of exhaust emissions were taken from the end of exhaust pipe of the engine. After taking the necessary readings at the specified speed, the load on the engine was adjusted using the dynamometer loading wheel. The procedure was repeated for higher load values of 40kg, 60kg, 80kg and 100kg.



Plate 4: Perkin 4:108 diesel engine mounted on Steady state engine test bed at UNN Nsuka

Table 3: Engine specifications

Components	Values
ENGINE	
Type	Perkins 4:108
Bore	79.735mm
Stroke	88.9mm
Swept volume	1.76litres/cycle
Compression ratio	22:1
Maximum BHP	38
Maximum speed	3000rpm
Number of cylinder head	4
Diameter of exhaust	1 ¹ / ₂ "
Length of exhaust pipe	36"31'
DYNAMOMETER	
Capacity	112kw/150hp
Maximum speed	7500rpm
KW	($N_m \times \text{rev/min}$)/9549.305
FUEL GUAGE	
Capacity	50-100 cc
AIR BOX	
Orifice size	58.86mm
Coefficient of discharge	0.6

Source: Department of Mechanical Engineering, University of Nigeria Nsuka

3 Results and Discussion

3.1 Extraction of rubber seed oil

The rubber seeds oil was extracted with n-hexane solvent, the choice of which was based on a comparative study by [14] who obtained highest oil yield from rubber seeds using n-hexane solvent compared with other notable solvents for extraction. The result from the extraction process showed rubber seed to contain 30.02%.

3.2 The physiochemical properties of rubber seed oil

The physicochemical properties of the extracted rubber seed oil are as summarized in Table 4.

Rubber seed oil has relatively high acid value of 28.72mgKOH/g. The high acid value of the feedstock react with excess alkali to yield soap which retards the separation of the biodiesel from the glycerol [15] and thereby reduce the amount of biodiesel produced. The saponification value of the oil 185.66mgKOH/g

is not sufficiently high to be suitable for soap production and therefore probably a good choice for biodiesel production. The iodine value of the oil, 120mgI₂/100g, shows the oil to be a semidrying type. Peroxide value which indicate the degree of saturation and the rancidity of the oil was obtained as 14.62meq/kg in this work. The high peroxide value is indicative of the susceptibility of the oil to peroxidation during storage and handling [15]. The high kinematic viscosity and density of the oil 60.08mm²/s and 920kg/m³ respectively make its atomization in internal combustion engine difficult as this has been associated with increase in engine deposits [16] and hence cannot be used directly as biodiesel. The flash point of rubber seed oil, 132°C is moderately high. . Oils of high flash point are safe for handling and storage.

Table 4: Physiochemical properties of RSO

Properties	Unit	RSO
Acid value	mgKOH/g	28.72
Free fatty acid	%	14.36
Saponification value	mgKOH/g	185.66
Iodine value	(gI ₂ /100g oil)	120.4
Peroxide value	meq/kg	14.62
Kinematic viscosity	mm ² s ⁻¹ @ 40°C	60.08
Fire point	°C	180
Flash point	°C	132
Cloud point	°C	6
Pour point	°C	2
Refractive index		1.428
Specific gravity		0.92
Moisture content	%	7
Density	Kg/m ³	920

Table 5: Fatty Acid Profile of Rubber Seed oil

Components Common Name	Systematic Name	Structural Formula	Concentration (%)
Oleic Acid C18:1	Cis-9-	C ₉ H ₁₈ =C ₈ H ₁₅ COOH	19.6
Lauric Acid C12	Octadecanoic	CH ₃ (CH ₂) ₁₀ COOH	3.983
Myristic Acid C14	Dodecanoic	CH ₃ (CH ₂) ₁₂ COOH	7.750
Palmitic Acid C16	Tetradecanoic	CH ₃ (CH ₂) ₁₄ COOH	16.698
Stearic acid C18	Hexadecanoic acid	CH ₃ (CH ₂) ₁₆ COOH	29.058
linoleic Acid C18:2	Octadeca-9, 12-Dienoic	C ₆ H ₁₂ =C ₃ H ₄ =C ₇ H ₁₄ COOH	22.588

3.3 Fatty Acid Profile of RSO

The results of the gas chromatographic analysis of the fatty acid composition of the rubber seed oil is shown in Table 5. The individual peaks of the gas chromatogram are as identified in figure 1. From the figure, the seven peaks that represent the major fatty acids present in the rubber seed oil can be identified. For rubber seed oil, the following fatty acids were identified, 19.6 % oleic acid C18:1, 3.98% lauric acid C12, 7.75% myristic cid C14, 16.69% palmitic acid C16, 29.058% Stearic acid C18 which is the most abundant saturated fatty acid in the oil, 22.5% linoleic Acid C18, which is the most abundant unsaturated fatty acid present in the oil.

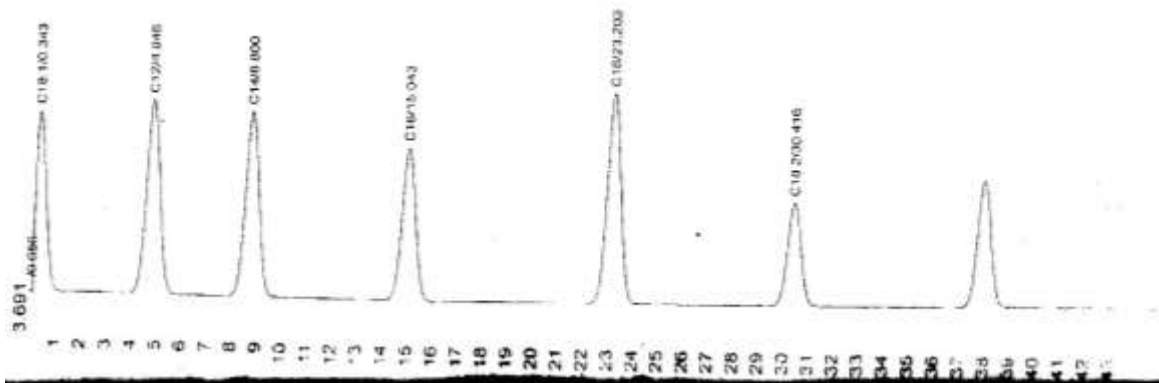


Figure 1: GC-MS plot of RSO

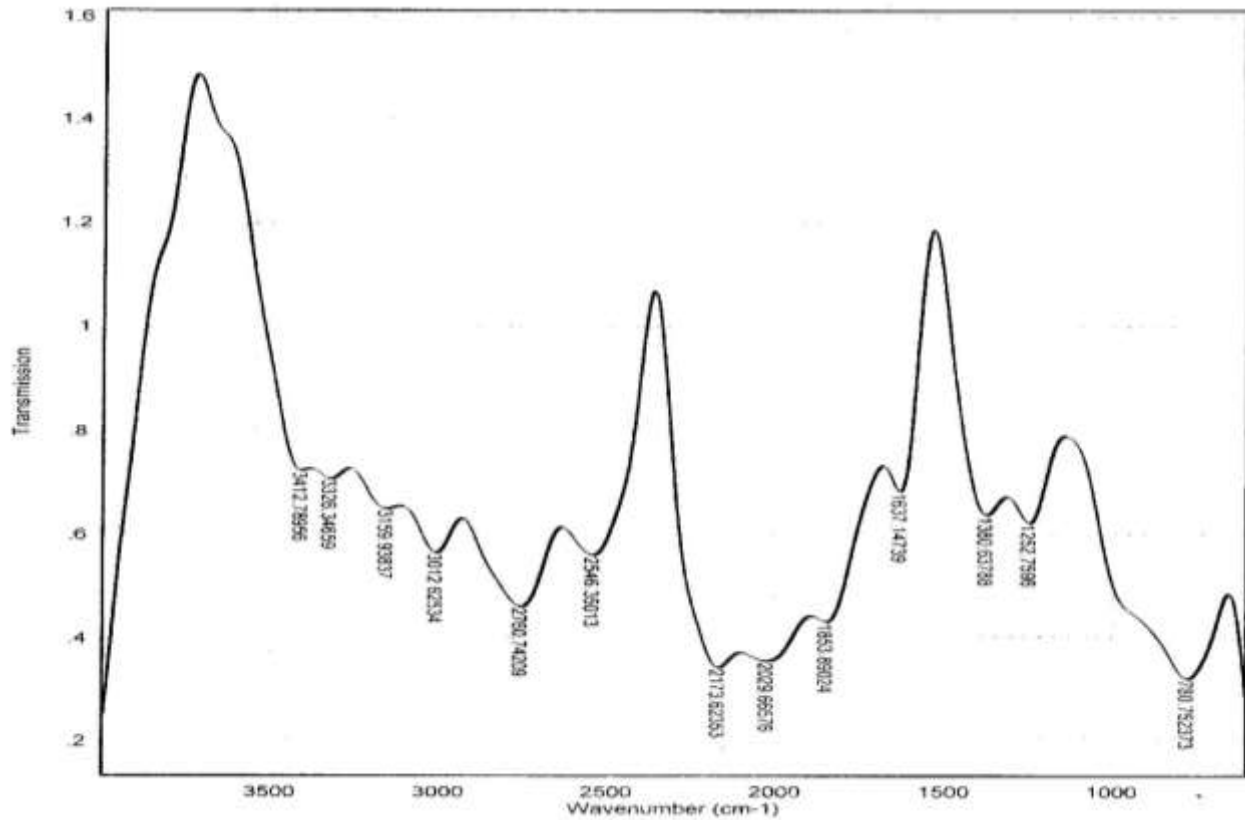


Figure 2: FTIR spectra of RSO

3.4 FTIR Analysis of Oil Samples

The Fourier Transform Infrared Spectroscopy (FTIR) is an important analysis technique which detects various characteristic functional group present in the oil. The FTIR plot for rubber seed oil is shown in figure 2. The various vibrations and functional groups are presented in Table 6. For the rubber seed oil, the presence of alcohol was detected at 3412.79, 3159.938, and 2760.742 with O-H stretching. O-H and C-H bending vibrations at 1380.638 and 1853.89 depicts the presence of phenol and aromatic compounds. Alkene's presence was detected at 1637.147 with C=C vibration.

Table 6: FTIR functional group frequencies of rubber seed oil

Frequency wave number (cm⁻¹)	Types of Vibration	Functional Group
780.7524	C-H bending	
1252.76	C-O stretching	alkyl aryl ether
1380.638	O-H bending	Phenol
1637.147	C=C stretching	Alkene
1853.89	C-H bending	Aromatic compound
2173.624	S-C=N stretching	Thiocyanate
2546.35	S-H stretching	Thiol
2760.742	O-H stretching	Alcohol
3012.625	C-H stretching	Alkene
3159.938	O-H stretching	Alcohol
3326.347	N-H stretching	Secondary amine
3412.79	O-H stretching	Alcohol

3.5 Effect of process parameters on the yield of biodiesel

3.5.1 Effect of methanol to oil molar ratio on biodiesel yield

The effect of methanol to oil molar ratio on the yield of biodiesel is represented in Figure 3. Methanol to oil molar ratio in the range of 2:1 to 12:1 were used to determine its effect on biodiesel yield. RSOFAME yield increased with increase in methanol to oil molar ratio up to 8:1. Further increase in methanol to oil molar ratio was not favorable to biodiesel production. This is resulted as very high methanol content decreased the catalytic activity of the catalyst resulting in the reduction of biodiesel produced. Theoretically, the stoichiometric molar ratio of methanol to oil in order to produce a mole of biodiesel is 3:1, but in reality, excess of methanol is required for the reaction to go to completion but not in such an excess that is detrimental to the reaction. It has been reported by the researchers [17,18] that when too much of alcohol is used in transesterification, the polarity of reaction mixture is increased, thus increasing the solubility of glycerol and promote the reverse reaction between glycerol and biodiesel, thereby reducing biodiesel yield.

3.5.2 Effect of reaction temperature on biodiesel yield

The reaction temperature was varied from 500C to 750C and the other parameters were kept constant in order to investigate its effect on the yield of biodiesel from RSO. The result as depicted in figure 4 which shows that biodiesel yield increases with increase in temperature until a maximum yield was obtained at 650C when the yield started decreasing. The decrease in biodiesel yield beyond the optimum temperature of 650C resulted because above the optimum temperature of 650C most of the methanol is lost by evaporation, leaving a reaction mixture with higher concentration of alkali catalyst that favor soap formation [19]. The formation of soap retards proper dispersion and mixing of the reaction mixture and

hinders separation of glycerol from biodiesel and thus reduced the ester yield. This trend conforms with the findings of [7].

3.5.3 Effect of catalyst Concentration on biodiesel yield

The effect of catalyst concentration on biodiesel yield was studied between 0.25 to 1.5%, while the other variables were kept constant as shown in figure 5. Breaking of bonds is required for a chemical reaction to commence and the minimum energy to achieve this is known as activation energy. Catalyst tends to provide alternative reaction pathways for breaking and remaking of bonds. Figure 5 shows the effect of catalyst concentration on biodiesel yield. From the figure, it could be seen that the biodiesel yield increased with increase in catalyst concentration and peaked at the optimum catalyst concentration of 1% when it started decreasing with increase in catalyst concentration. The decrease in biodiesel yield beyond the optimal catalyst concentration of 1% resulted from the fact that the resulting excess catalyst react with the oil to form soap which increases the viscosity of the reaction mixture, hindering effective dispersion and mixing of the reactants and also hinder the separation of glycerol from biodiesel which gives rise to reduction of biodiesel produced. This is in conformity with the findings of [20] and [21].

3.5.4 Effect of reaction time on biodiesel yield

The effect of reaction time on biodiesel yield was investigated from 15 to 90minutes while the other factors were kept constant. The yield of biodiesel was found to increase with increase in reaction time and peaked at 60 minutes when the yield started decreasing with increase in time as shown in figure 6. The decrease in biodiesel yield after optimal reaction time of 60 minutes may be due to reversible nature of transesterification reaction resulting in loss of esters [22]. Also, longer reaction time most times allows the fatty acids present to react with alkali and this results to soap formation. The presence of soap retards the formation of ester [15].

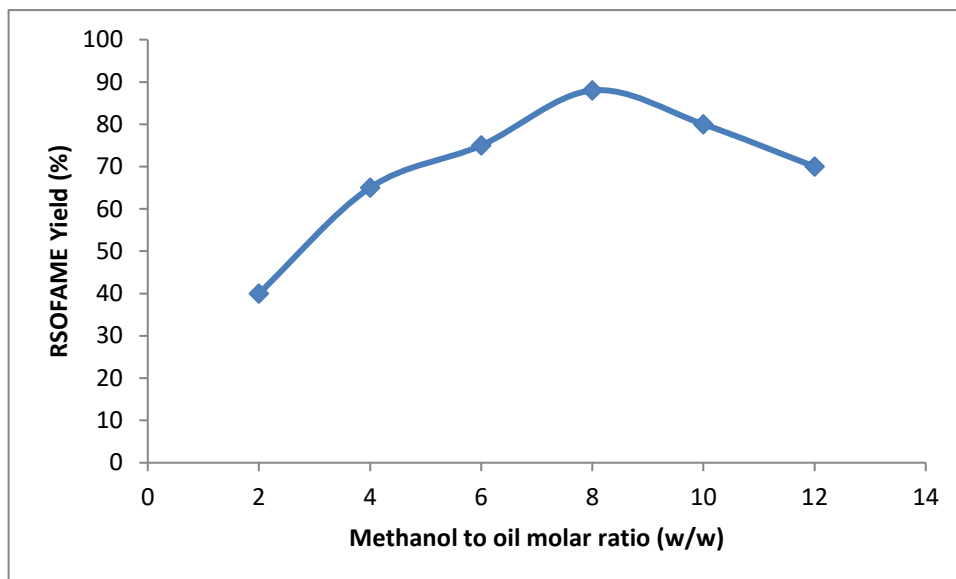


Figure 3: Effect of methanol to oil molar ratio on RSOFAME yield

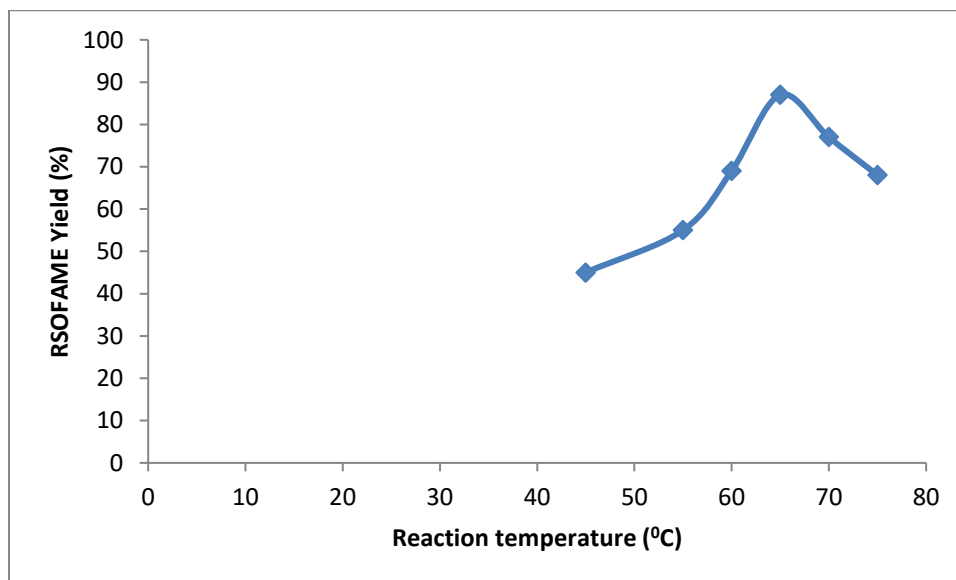


Figure: 4 Effect of reaction temperature on RSOFAME yield

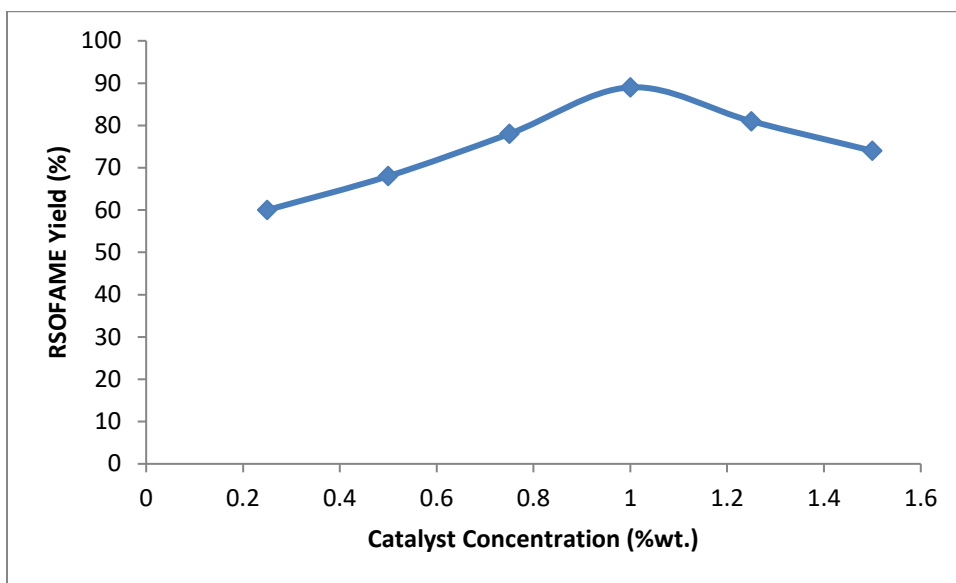


Figure 5: Effect of catalyst concentration on RSOFAME yield

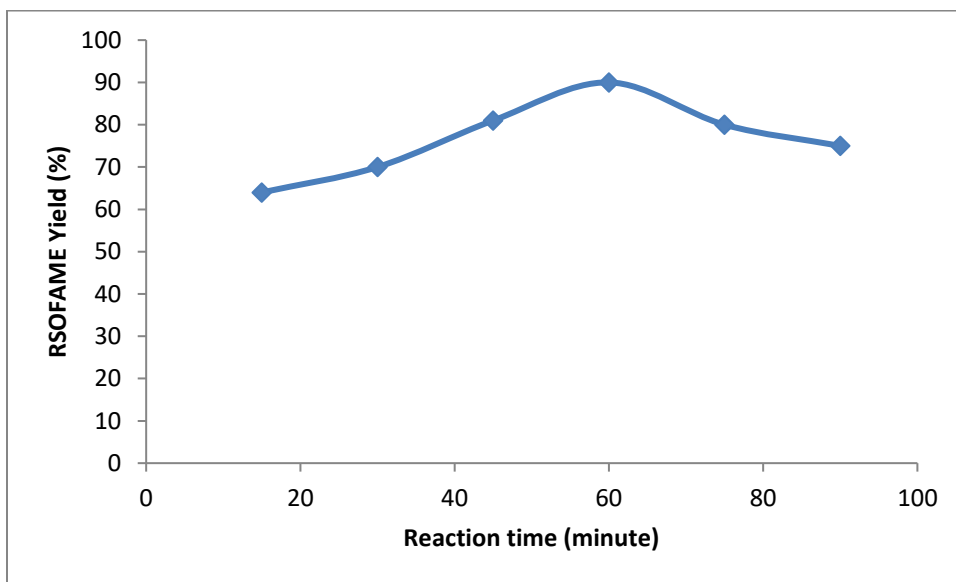


Figure 6: Effect of reaction time on RSOFAME yield

3.6 Fuel properties of the RSOFAME

The physicochemical characteristic of the produced RSOFAME are as given in table 7. The density and kinematic viscosity of the RSOFAME were determined as 0.88kg/m³ and 4.25mm²/s respectively. These values are within the ASTM limits and also in agreement with the findings of with literature values of [23] and [24]. High viscosity and density of fuel results in poor atomization in compression ignition engine which give rise to carbon deposits, plugging of fuel filter, and injector coking [25] and therefore reduction of the engine power output. Oils are transesterified in order to reduce the density and viscosity to avoid aforementioned problems. Cetane number indicates the ignition quality of the fuel. Biodiesel generally have higher cetane number than diesel [26]. Fuels of low cetane number show increase in emission due to incomplete combustion. The cetane number of the produced biodiesel is 58.2 which is within the ASTM standard limit and indicative of its good ignition response. Flash point indicates the degree of flammability of the material. Based on ASTM, a standard biodiesel should have flash point of ≥ 1300C for it to be classified as “nonflammable”. The determined flash point of the RSOFAME, 1640C is within the range of ASTM standard, indicative of the fact the rubber seed oil biodiesel is safe for handling and storage. Acid value indicates the degree of acidity of the biodiesel and therefore the corrosive tendency of the fuel to the machine parts. This was obtained as 0.32mgKOH/g. This is sufficiently low as not to have adverse effects on handling and on the machine parts. The cloud point and the pour point of RSOFAME was determined as 40C and 20C respectively.

Table 7: Fuel properties of RSOFAME

Properties	Unit	RSOFAME	ASTM Standards	Test method
Density	Kgm ⁻³	880	860-900	D93
Kinematic viscosity	mm ² s ⁻¹	4.25	1.9-6.0	D445
Cetane number		58.2	47min.	D613
Flash point	⁰ C	164	100-170	D93
Cloud point	⁰ C	4	-3-15	
Water & sediment	%	0.44	0.5	D2209
Acid value	mgKOHg ⁻¹	0.32		D664
Calorific value	MJKg ⁻¹	38.5	42.06	D35
Iodine value	gI ₂ /100g oil	72	42-166	
Pour point	⁰ C	2	+1 ⁰ Cmin	D97

The cloud point and the pour point of RSOFAME are not sufficiently low and might give rise to cold flow problems in cold seasons especially in the temperate and cold regions. However, these problems could be averted by addition of suitable cloud point and pour point depressants or by blending with diesel oil [27].

3.5: Statistical Analysis of Transesterification Using Central Composite Design (CCD)

To optimize transesterification of avocado pear oil, central composite design (CCD), a response surface methodology (RSM) was used to determine the optimum values of the process variables. Fractional factorial design was used to obtain a quadratic model, consisting of factorial trials to estimate quadratic effects. To examine the combined effect of the four different factors; catalyst concentration, methanol to oil molar ratio, reaction temperature, and reaction time on biodiesel yield and derive a model, a two-level-four-factor $(2^{(4-1)} + 2 \cdot 4 + 6)$ central composite response design = 30 experiments were performed. The factor levels are shown in Table 1. The matrix for the four variables was varied at two levels (-1 and +1). The lower level of variable was designated as “-1” and higher level as “+1”. The experiments were performed in random order to avoid systematic error. Equations 3 and 4 represent the mathematical model relating the transesterification reaction of rubber seed oil with the independent process variables obtained with the design Expert version 12.0. The design of experimental matrix of transesterification of rubber seed oil with the experimental values of the biodiesel yield are presented in Table 8. The coded and uncoded values of the test variables were used to optimize the variables namely catalyst concentration, methanol to oil molar ratio, reaction temperature and reaction time. The empirical relationship between yield (Y) and the four variables in coded values obtained by using the statistical package design-expert version 12.0 for determining the levels of factors which gives optimum percentage yield is given by equation 3, a quadratic regression equation that fitted the data:

$$\text{Biodiesel yield (RSO)} = +91.79 - 0.9024A + 3.37B + 2.59C + 2.05D - 7.25AB + 1.75AC + 1.63AD - 1.50BC + 2.38BD - 2.37CD - 9.43A^2 - 2.10B^2 - 10.10C^2 - 6.99D^2 \quad (3)$$

Equation 3 suggested that the yield of FAME has linear and quadratic effects on the four variables studied. Coefficients with one factor represent the single effect of that particular factor while coefficients with more than one factor represent the interaction effect between those factors. Positive sign in front of the terms indicates synergistic effect while negative sign indicates antagonistic effect of the factors. The adequacy of the above model was tested using design expert sequential model sum of squares and the model test statistics. From the statistical analysis, the coefficient of determination $R^2 = 0.9513$ is reasonable, and the predicted R^2 of 0.7151 is in a reasonable agreement with the adjusted R^2 of 0.9059. This test result is shown in the ANOVA Table 9.

3.5.1 Analysis of variance (ANOVA) for optimization of RSOFAME

The ANOVA results for the model terms are given in Table 9. ANOVA was applied to estimate the significance of the model at 5% significance level as shown in the Table. A model is considered significant if the p-value (significance probability value) is less than 0.05. From the ANOVA table 9, it can be stated that the linear, interactive and quadratic terms B, C, AB, BD, CD, A^2 , C^2 , D^2 are the significant terms for

RSO transesterification. Therefore, eliminating the insignificant terms the final model equation 4 below was obtained.

$$\text{Biodiesel yield (rubber)} = +91.79 + 3.37B + 2.59C - 7.25AB + 2.38BD - 2.37CD - 9.43A^2 - 10.10C^2 - 6.99D^2 \quad (5)$$

3.5.2 Optimization of process parameters of RSOFAME

The optimization of process variables in this study was carried out using design expert version 12.0. The optimum conditions suggested by the result analysis for maximum RSOFAME yield of 93% within the ranges studied were: methanol/oil molar ratio 7:1, catalyst concentration 0.75%wt, reaction temperature 500C, reaction time 45 minutes. Actual experiment based on the optimum conditions produced 91.79% yield of RSOFAME. The small percent error difference between the predicted and actual yield of 1.21% indicates that the regression model developed in this study was accurate in representing the overall data and reliable in predicting the yield at any given conditions within the range studied for RSOFAME produced.

Table 8: Experimental design matrix for factorial design of produced RSOFAME

Std	Run	Temperature (°C) A		Catalyst concentration (wt %) B		Reaction time (Minutes) C		Methanol to oil molar ratio (ml/mol) D		RSOFAM E Yield (%)
		Code d	Uncode d	Code d	Uncode d	Code d	Uncode d	Code d	Uncode d	
1	12	-1	40	-1	0.5	-1	30	1	4	50
2	16	1	60	-1	0.5	-1	30	1	4	51
3	4	-1	40	1	1	-1	30	-1	4	74
4	11	-1	60	1	1	-1	30	-1	4	52
5	23	-1	40	-1	0.5	1	60	-1	4	61
6	13	1	60	-1	0.5	1	60	-1	4	77
7	25	-1	40	1	1	1	60	-1	4	74
8	18	1	60	1	1	1	60	-1	4	56
9	22	-1	40	-1	0.5	-1	30	1	10	52
10	7	1	60	-1	0.5	-1	30	1	10	67
11	29	-1	40	1	1	-1	30	1	10	80
12	28	1	60	1	1	-1	30	1	10	62
13	20	-1	40	-1	0.5	1	60	1	10	50
14	15	1	60	-1	0.5	1	60	1	10	66
15	21	-1	40	1	1	1	60	1	10	79
16	17	1	60	1	1	1	60	1	10	69
17	26	- α	35	0	0.75	0	45	0	7	68
18	30	+ α	65	0	0.75	0	45	0	7	69
19	6	0	50	- α	0.375	0	45	0	7	86
20	8	0	50	+ α	1.125	0	45	0	7	84
21	1	0	50	0	0.75	- α	22.5	0	7	64
22	19	0	50	0	0.75	+ α	67.5	0	7	70
23	2	0	50	0	0.75	0	45	- α	2.5	70
24	9	0	50	0	0.75	0	45	+ α	11.5	78
25	10	0	50	0	0.75	0	45	0	7	93
26	27	0	50	0	0.75	0	45	0	7	93
27	3	0	50	0	0.75	0	45	0	7	93
28	24	0	50	0	0.75	0	45	0	7	93
29	14	0	50	0	0.75	0	45	0	7	93

30	5	0	50	0	0.75	0	45	0	7	93
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Table 9: ANOVA analysis for the optimization of biodiesel from Rubber Oil

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	5726.31	14	409.02	20.94	< 0.0001	significant
A-Temp	16.70	1	16.70	0.8545	0.3699	
B-Catalyst Conc.	232.24	1	232.24	11.89	0.0036	
C-Time	137.02	1	137.02	7.01	0.0183	
D-Methanol/oil ratio	86.05	1	86.05	4.40	0.0532	
AB	841.00	1	841.00	43.05	< 0.0001	
AC	49.00	1	49.00	2.51	0.1341	
AD	42.25	1	42.25	2.16	0.1621	
BC	36.00	1	36.00	1.84	0.1947	
BD	90.25	1	90.25	4.62	0.0483	
CD	90.25	1	90.25	4.62	0.0483	
A²	1012.64	1	1012.64	51.83	< 0.0001	
B²	50.21	1	50.21	2.57	0.1297	
C²	1160.81	1	1160.81	59.42	< 0.0001	
D²	555.86	1	555.86	28.45	< 0.0001	
Residual	293.06	15	19.54			
Lack of Fit	293.06	10	29.31			
Pure Error	0.0000	5	0.0000			
Cor Total	6019.37	29				

Fit Statistics for Rubber Oil

Std. Dev.	4.42	R²	0.9513
Mean	72.23	Adjusted R²	0.9059
C.V. %	6.12	Predicted R²	0.7151
		Adeq Precision	14.3956

3.6 Engine emission analysis of RSOFAME

3.6.1 Variation of CO and HC emissions with diesel, RSOFAME and their blends

The variation of CO and HC with engine load are shown in figures 8 and 9 respectively. From the figures, it could be observed that CO and HC emissions increase with increase in load. This is attributed to decrease in air-fuel ratio giving rise to incomplete burning and therefore more emission of CO and HC. Again, it is observed that at a specific load, CO and HC emission decreased with increase in biodiesel fraction in the blend. In their report on the impact of biodiesel emission in diesel engine, the researchers [28], [29]-[31] stated that the trend is reduction of CO and HC emission when diesel is replaced with biodiesel. Thus, CO

and HC reduce as the biodiesel content of the fuel increased, showing the fact that the use of biodiesel resulted in lower emissions of carbon monoxide (CO) and hydrocarbon (HC). This may be attributed to high oxygen content and lower carbon to hydrogen ratio in biodiesel. The oxygen content in biodiesel enhanced vaporization and atomization of biodiesel and blends leading to complete combustion and less presence of CO and HC compared to diesel fuel [32]. Lower carbon to hydrogen molecule in biodiesel presents less carbon to be burnt that will enhances the amount of CO and HC in the emission.

3.6.2 Variation of NO_x Emission with diesel, RSOFAME and their blends

Figures 7 show the variation of NO_x with load for diesel, RSOFAME and their blends. From the figure it could be seen that NO_x emission increased with increase in load. This can be explained from the fact that, increase in load results in decrease of air-fuel ratio giving rise to incomplete combustion with higher emission of NO_x. From the figure, it is also discerned that at specific load, NO_x emission increase with increase in biodiesel fraction. Again, the researchers, [33], [29]-[31] in their findings reported that the use of biodiesel increases the emission of NO_x. This may be attributed to the oxygen content of the biodiesel which enhances vaporization and atomization of the biodiesel and the blends leading to complete combustion of the nitrogen component of the biodiesel to its oxides.

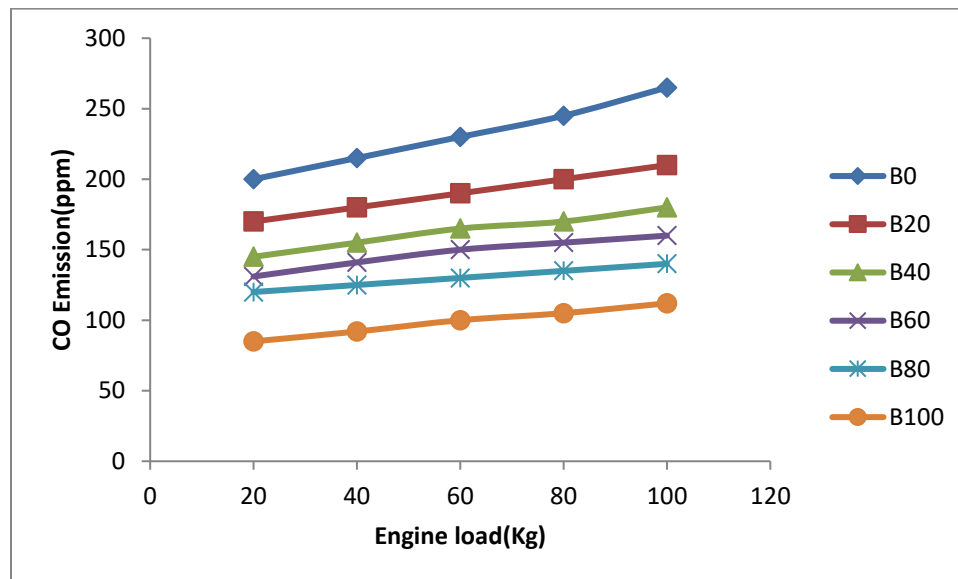


Figure 8: Variation of CO emission with engine load for varying biodiesel fraction

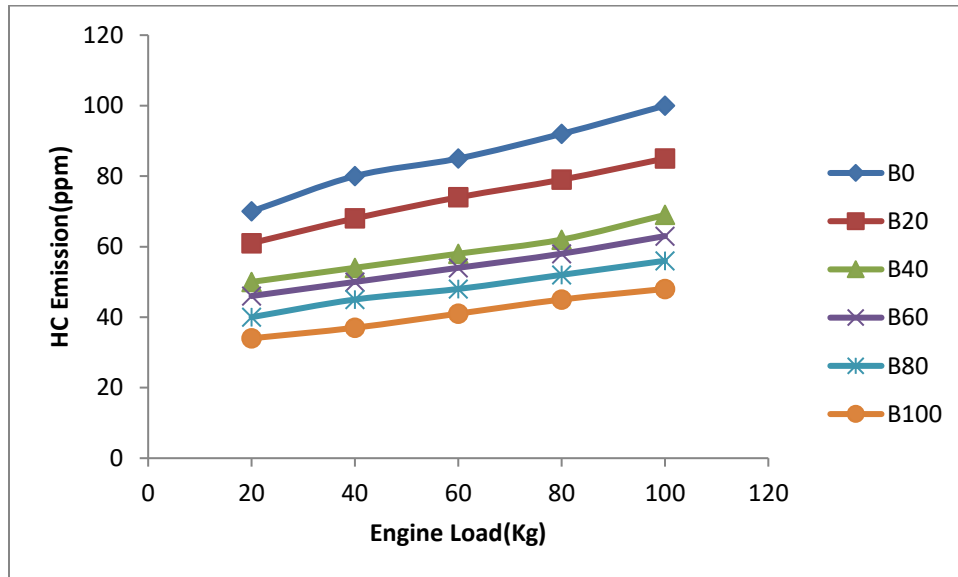


Figure 9: Variation of HC emission with engine load for varying biodiesel fraction

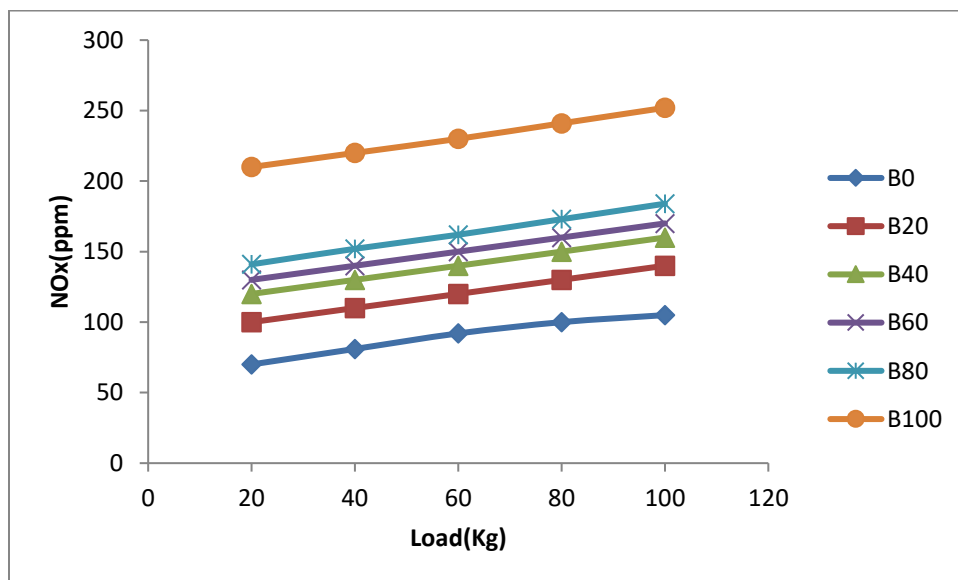


Figure 10: Variation of NOx emission with engine speed for varying biodiesel fraction

IV CONCLUSION

The optimum conditions suggested by the result analysis for maximum RSOFAME yield of 93% within the ranges studied were: methanol/oil molar ratio 7:1, catalyst concentration 0.75%wt, reaction temperature of 500C, reaction time of 45 minutes. Actual experiment based on the optimum conditions produced 91.79% yield of RSOFAME. The small percentage error difference between the predicted and actual yield of 1.21% indicates that the regression model developed in this study was accurate in representing the overall data and reliable in predicting the yield at any given conditions within the range studied for RSOFAME produced. The CO, HC and NO_x emission increased with increase in engine load. CO and HC emission decreased with increase in biodiesel fraction in the blend while NO_x emission increased with increase in biodiesel fraction.

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