HCME: An environment-friendly I.C. engine fuel

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Abstract

*The study revealed that Hura crepitans oil is a good candidate for Hura crepitans methyl ester (HCME) production. Two steps (esterification and transesterification) production stages influenced the high yield of HCME. Three possible experimental runs were performed in each step, the best of the three conditions were 1.45 (% v/v) for H_2SO_4 conc., 5:1 for methanol/oil molar ratio, 40 min for reaction time which gave 1.06 % for FFA in the first step, in the second step, 92.70 %(w/w) of HCME was obtained at 0.55% KOH, 5:1 methanol/oil molar ratio, 60 ^{o}C temperature and 30 min reaction time. The produced HCME had fuel properties which satisfied both ASTME D6751 and EN 1424 standards. The fatty acid profile of the HCME revealed the dominant fatty acids were linoleic (64.50%), oleic (17.54%) and palmitic (12.70%). Exhaust emissions from an internal combustion (I.C.) engine revealed that there is 60% decreased in CO, 58% decreased in NOx, 60% decreased in HC, 39% decrease in smoke opacity and 42% decreased in BSFC at B20, respectively. Flue gas temperature increased by 12% at B20, 45% increased in BTE at B50 when compared to pure diesel (AGO). Hence, it can be concluded that
B20 (20% HCME + 80% AGO) will provides the best emission reduction at the lowest cost.*

1.   Introduction

Few people realize that vegetable oilseeds can be used for more than frying fast food. Indeed, Rudolph Diesel's first public exhibition of the internal combustion technology that was to later bear his name featured an engine running on peanut oil. He envisioned freeing small businesses from the monopolistic coal and steam power of the day by using organic fuels in his engine. Unfortunately, it turned out that his engine also lent itself to burning low-grade fractions of petroleum, and the rest is history. Diesel engine manufacturers optimized the design for lighter oils, and the use of vegetable oil never really got a chance. But, experimenters throughout the world have been reviving Diesel's vision, and vegetable oilseeds is finding increasing use, particularly in the US, UK, Germany, and Australia.

Because of this heritage, the fuel injection pump and the fuel injectors in modern diesel engines won't work on room temperature vegetable oilseeds because of its thickness. However, there are three common ways to thin vegetable oilseeds so it can be used in diesel engines, this includes; blend the vegetable oil with a lighter fuel, heat the vegetable oil until it becomes thin enough and changing the chemical composition of the vegetable oil.

Blending is fraught with problems, and although some enthusiasts swear by it, others end up

swearing at it, as they damage expensive injection pumps with the heavier fluid. Some have suffered explosions when trying to mix extremely lighter fuels, like gasoline, with vegetable oil. Those reporting success seem to be limited to a mix no more than 50/50 with petro-diesel at no colder than "shirt sleeve" temperatures, on a few engines that have very robust injection pumps. Meanwhile, heating vegetable oil to about 80°C (or about 180°F), it's viscosity is only a bit above that of normal diesel fuel, and so can make its way through pumps and injectors, cools down and gels, thereby causing damage to the engine. It can also results in a lot of heat wastage, presence of impurities in the oil and water in the fuel which can cause expensive engine damage, this method is not preferable. But, the act of changing the chemical composition, also known as transesterification process (biodiesel), is safe, reliable, and cost effective, reduces pollution, and will work in almost any diesel engine without modification.

Internal combustion (I.C.) engines play a major role in transportation, industrial power generation and in the agricultural sector. There is a need to search and find ways of using alternative fuels, which are preferably renewable and also emit low levels of gaseous and particulate pollutants in internal combustion engines. As per the literature survey, fuels like vegetable oils, biodiesel (transistorized vegetable oils to methyl esters), alcohols, natural gas, biogas, hydrogen, liquefied petroleum gas (LPG), etc. are being investigated by researchers for engine applications. In the case of agricultural applications, fuels that can be produced in rural areas in a decentralized manner, near the consumption points will be favoured. The permissible emission levels can also be different in rural areas as compared to urban areas on account of the large differences in the number density of engines. Many researchers have done work on conversion of edible and non-edible vegetable oilseeds such as beniseed (*Sesamum indicum*), sorrel oil (*Hibiscus sabdariffa*), coconut oil, linseed, Jatropha, Karanja (*Pongamia glabra*), kusum (*Schlerlchera trijuga*), pongamia, etc, to biodiesel, separately to study the performance and emission characteristics of I.C. engine [1,2,3,4,5,6]. However, competitions for commercial edible vegetable oilseeds which are obtainable from just about a dozen species of plant have necessitated the search for oils from underutilized tropical plants such as *Hura crepitans* (Sandbox). Despite the potential of this under-utilized species as a source of less consumed food and medicine, to authors' best knowledge, sparse information is available on the suitability of it biodiesel in I.C. engine and whose emission characteristics hitherto remains untapped. Therefore, the study is aimed at investigating the emission characteristics of *Hura crepitans* (Sandbox) methyl ester (HCME) biodiesel in I.C. engine.

2. Materials and Methods

2.1 Materials

The *Hura crepitans* oil used for this study was collected from the Department of Agricultural Engineering, University of Markudi, Nigeria. The convectional fuel (AGO) was purchased from Obafemi Awolowo University's petrol station in Ile-Ife. All chemicals such as Methanol (CH_3OH), potassium hydroxide (KOH), anhydrous calcium

chloride (CaCl$_2$), sulphuric acid (H$_2$SO$_4$), sodium hydroxide pellet (NaOH) etc, were all of analytical grade.

2.2 Experimental procedure

2.2.1 Pretreatment – Acid catalyzed esterification

The crude unrefined *Hura crepitans* oil was golden yellow in colour. The FFA was determined through the standard titrimetric method. The initial acid value of the oil was obtained to be 4.22 ± 0.01 mg KOH/g oil (FFA level of 2.11 ± 0.01 %), which is far above the < 1.50 specification limit for satisfactorily alkaline catalyst transesterification reaction. Hence, the FFAs were first esterified with catalyst (H$_2$SO$_4$). Using the standard AOAC method, the acid value of separated product at the bottom was determined. This process was repeated in triplicate and the product having acid value < 2.11 ± 0.01 mg KOH/g (FFA = 1.06) oil was used for the alkalis transesterification stage (step 2). Table 1 shows the reaction time, concentration of acid (H$_2$SO$_4$) and methanol/oil molar ratio used with the acid value and FFAs computed.

2.2.2 Alkalis catalyzed transesterification

According to the method of [7], the reaction was carried out with 5:1 methanol/oil molar ratio using 0.55% KOH as an alkaline base catalyst. The amount of KOH (5.5 g/l of preheated *Hura crepitans* oil) was reached based on the amount needed to neutralize the unreacted acids (2.11 mg KOH/g oil) in this stage. The reaction was carried out at 60 ^{o}C for 30 min in a reactor. At the completion of the reaction, the product was transferred to a separating funnel for glycerol and HCME separation. Glycerol was tapped off and the HCME left was washed with ionized water to remove residual catalyst, glycerol, methanol and soap. The washed HCME was further dried over heated CaCl$_2$ powder. The HCME yield was determined gravimetrically as described in Eq.1. The experiment was carried out in triplicate in order to select the best optimum condition with highest yield (Table 2).

$$HCME\ Yield\ \%(w/w) = \frac{Weight\ of\ Hura\ crepitans\ \text{oil used (g)}}{Weight\ of\ HCME\ obtained\ (g)} \quad 1$$

2.3 Physicochemical analysis of the Hura crepitans (Sandbox) oil and HCME

The evaluation of physicochemical and other properties of the oil and HCME were determined by [8], method, Wijs method and the methods reported by [9]. The quality of biodiesel is very important for the performance and emission characteristics of a diesel engine. Thus, the HCME produced was sent to the Nigeria National Petroleum Company (NNPC) Laboratory for chromatography analysis of fatty acids present in the HCME quality testing using standard methods.

2.4 Emission Characterization of HCME on I.C. engine

The blend of HCME and AGO were mixed in different proportions such as B10, B20, B30, B40 and B50. The same procedure was repeated for 100% AGO (B0) and 100% HCME (B100).The emissions (CO, NOx, HC, Smoke

opacity and Flue gas temperature) were recorded using EGA4 palm top flue gas analyzer having Ni-MH rechargeable battery, opacity of smoke was measure using smoke meter. Brake specific fuel consumption (BSFC) and brake thermal efficiency were computed.

3.   Results and Discussion
3.1   Oil production characteristics

3.1.1   Pretreatment process - Acid catalyzed esterification
This section describes a series of tests that were conducted to develop the acid–catalyzed pretreatment process. Since Hura crepitans oil tends to have variable properties that could influence the repeatability of the tests, the pretreatment step was repeated in triplicate and the mean value of yield (acid values) was titrimetrically obtained. % FFA was computed (Table 1). The results obtained shows that the FFA of 1.06 mg KOH/g oil at the following working variable, reaction time, 40 min, methanol/oil molar ratio, 5:1 and 1.45 (% v/v) H_2SO_4 conc. were suitable for the best yield in the second step alkalis transesterification process.

3.1.2   Alkalis catalyzed transesterification process
The yield of HCME obtained during the alkalis catalyzed transesterification process was 92.70% (w/w) at the following variable conditions, 0.55% KOH, 5:1 Methanol/oil molar ratio, 60 ^{o}C reaction temperature and 30 min reaction time. The validity of the HCME was confirmed by carrying out three independent replicates experiments (Table 2).

3.2   Physicochemical analysis and other properties of Hura crepitans oil and HCME

3.2.1   Physical properties of the Hura crepitans oil and HCME
In order to evaluate the quality of the crude Hura crepitans oil and HCME, the content and compositions of the oil and HCME was subjected to physicochemical analysis and the results obtained were shown in Table 3. At room temperature, the oil was golden yellow in colour and the HCME was light yellow. The refractive index increases but the moisture content decreases after conversion of oil to HCME, indicating a good shelf life characteristic of oil. Observations on the colour, moisture content and refractive index of the oil and HCME agreed with previously published report [10]. The specific gravity of the oil was determined as 0.93 which was reduced to 0.86 after conversion, indicates that the oil and HCME are less dense than water with refractive index of 1.480 and 1.490, respectively. Although, [11], reported mean value of 0.98 on specific gravity for the same oil, [12] reported a range between 0.874-8.2312 for most of the vegetable seed oils. The viscosity, which is a measure of the resistance of material to shear, was determined to be 6.32 mm^2/s and 2.78 mm^2/s, respectively. The higher value obtained for the oil in this study indicates the oil could be used as lubricant in engine parts in the tropics if left overnight as solidification temperature of the oil is below 10 ^{o}C at any season [13]. The densities obtained in this present work were in line with what was obtained by [10].

3.2.2   Chemical properties of the Hura crepitans oil and HCME
Table 3 contains results obtained for the chemical properties of crude Hura crepitans oil and HCME. The high acid

value of the seed oil and HCME showed that it is non-edible and is a good candidate for biodiesel production. This can be used to check the level of oxidative deterioration of the oil and biodiesel by enzymatic or chemical oxidation. The acid value is expected to range from 0.00 - 3.00 mg KOH/g material, before it can find application in industries but the value is high for oil under study. That is why acid value was made fit by subjecting the oil to biodiesel and this may also improve its quality for industrial purposes [11]. A high Saponification value obtained for the seed oil, suggesting high concentration of triglycerides suitable for biodiesel production. The iodine value of the seed oil was high (125.90 g of I_2/100 g of oil), which signified the oil contained a substantial level of unsaturation and could be used to quantify the amount of double bonds present in the oil which reflects the susceptibility of oil to oxidation before conversion to biodiesel. Peroxide value measures the content of hydro-peroxides in the oil and its low value indicates high resistance to oxidation. The value obtained for the seed oil and HCME in this work were well within the limit stipulated for vegetable oils and biodiesel. This shows that the oil is not rancid and considered stable [14]. The HHV determined for the oil was 39.28 MJ/kg and it is within the range earlier reported [15] for vegetable oils (37.47 – 40.62 MJ/kg). The rise in the HHV after conversion of oil to HCME is a proved that the oil is not only good for biodiesel production, but can be suitably used as fuel in I.C. engine.

3.2.3 Other properties of the Hura crepitans oil and HCME
Additional fuel properties such as cetane number, API, diesel index,

means molecular mass and aniline point of the seed oil and HCME were determined (Table 3). Cetane number is a measure of the fuel's ignition delay and combustion quality. Standard specification for cetane number biodiesel is 40 minimum [16]. The cetane number of the seed oil (45.05) showed that it have high fuel potential before being converted to HCME (cetane number- 50.40). The cetane number reported for most vegetable oils range from 27.6 to 52.9 [15,17]. The API, diesel index and aniline point of the oil and HCME were comparable with other reported work [9]. The two steps transesterification of the oil improved its fuel properties.

3.3 Fatty acid profile of the Hura crepitans oil and HCME
Gas chromatography analysis of fatty acids present in the seed oil and HCME was showed in Table 4. The results indicated that the oil is highly unsaturated. The dominant fatty acids were linoleic (58.52%), oleic (20.31%), palmitic (16.01%), stearic (3.10%), linolenic acid (C18:3) (1.60%) and others (0.46%). Whereas, the dominant fatty acids found in HCME were linoleic (64.50%), oleic (17.54%), palmitic (12.70%), stearic (1.74%), linolenic acid (3.50%) and others (0.02%) The values observed in this work are within the ranges previously reported [18,19]. This indicates that fatty acid composition will play a dominant role in establishing the cetane number [19,20].

3.4 Emission characterization
The test were conducted on a four stroke, air cooled, single cylinder direct injection diesel engine, developing a power output of 3.23 kW at a constant of

2600 rpm. Table 5 shows the specifications of the engine. The characterization of fuel behavior with respect to emissions and performance was carried out by determined the CO, NOx, HC, Smoke opacity, Flue gas temperature, BSFC and BTE.

3.4.1   Carbon monoxide (CO) emission (ppm)

CO is only a very weak direct greenhouse gas, but has important indirect effects on global warming. CO is an ozone precursor, but to a lesser extent than unburned hydrocarbons or nitrogen oxides. Biomass burning and fossil fuel use are the main sources of man-made CO emission. The most potential control is through direct reduction in fossil fuel use. Since the emission of CO depended on rotational speed, it decreased with increased in concentration of biodiesel.

Figure 1 shows the variation of CO with blends at different speed of revolution of I.C. engine. At the speed range of 800-1000 rpm, the CO emission was found to be highest at B0, followed by B10, B50 and B100. The CO decreases with increases in concentration of biodiesel blends as fuel [21]. At speed range of 1000-1200 rpm, the emission of B0 and B10 was found to be the highest compared with blends of B20 and B100. B50 has the lowest emission at this speed range. It was also observed that at highest speed range (1200-1400 rpm), the CO emission concentration was lowest at B50 while B0 has the highest emission concentration. Therefore, the CO emission concentration at B20 is the lowest with 60% emission reduction when compare with B0 (100% AGO).

3.4.2   NOx emission

NOx should not be confused with N_2O, which is a greenhouse gas. It is the total concentration of NO and NO_2. When NOx and volatile organic compounds (VOCs) react in the presence of sunlight, they form photochemical smog, a significant form of air pollution, especially in the summer. It adverse effect is damage to the lung tissue and reduction in lung function [22]. It can also forms nitric acid which contributes to acid rain if the combustion emission is not regulated in the environmental. NOx also increase in proportion to ignition advance, regardless of variations in the air/fuel ratio.

Figure 2 shows the variation of NOx emission concentration with the blends at different speed ranges. B20 at the highest speed range (1200-1400 rpm) has the lowest NOx concentration, followed by B10, B50, B0 and B100. At 1000-1200 rpm, B10 and B20 were found to have the same NOx concentration been the lowest, followed by B0, B50 and B100. Similarly, the highest NOx concentration was observed at B100 within the range of 800-1000 rpm, followed by B0, B50, B10 and B20. Hence, B20 at highest speed range has the lowest NOx emission concentration with 58% reduction compared to B0.

3.4.3   HC (Hydrocarbon) emission

The exhaust gases emitted by 4-cycle spark I.C. engine does not operate at 100% efficiency, and the air/flue mixture when burned produces exhaust gases containing various pollutants. Among these are the HC made up of principally of minute particles of unburned gasoline; these particle react photo-chemically with sunlight to produce smog; and NOx which combines with water to produce so-called acid rain.

HCs are measured in ppm (parts per million). Their presence in the exhaust stream is a result of unburned or partly burned fuel, and engine oil. HC emissions increase in proportion to ignition advance, except at very lean air/fuel ratios. Factors such as poor mixture distribution, ignition misfires and low engine temperatures, will all cause significant increases in HC.

Figure 3 shows the variation of HC emission with the blends at different speed ranges. The figure showed that at all speed ranges, the HC emission was found to be the highest at B0; this is followed by B100, B50, B10 and B20. B20 at a speed range of 1000-1200 rpm has the lowest HC emission with 60% reduction when compare with B0.

3.4.4 Smoke opacity emission (%)

Smoke opacity is a measurement of smoke density from 0% – clean and 100%– dirty. Smoke opacity can be in many shades including grey/black (unburnt fuel), blue (burnt oil – worn engine) or white (water condensation). It is the level of peak smoke opacity for diesel-powered motor vehicles. The level of opacity measurement remains the core of federal, state and local air pollution control effort as more visible emission observers verify now than ever before.

Figure 4 shows the variation of smoke opacity with the blends ratio at various speed ranges. B0 at the speed range of 1200-1400 rpm has the highest smoke opacity, followed by B100, B50, B10 and B20. B20 has the lowest smoke opacity at speed range 1000-1200 rpm. Whereas, B0 at the lowest speed (800-1000 rpm) range has the lowest emission of smoke opacity with 64% reduction.

3.4.5 Brake specific fuel consumption (BSFC) emission

The BSFC is the amount of fuel which an engine consumed for each unit of break powers per hour. It indicates the efficiency with which the engine develops the power from fuel. Majorly used to compare the performance of different engine but always tends to be the same for similar engine.

Figure 5 shows the graph of variation of BSFC with the blends at various speed ranges. B50 at all speed ranges has the highest BSFC with 36% increase when compared with B0. Although, the BSFC is the same at all speed ranges for B0. B20 at the speed range of 800-1000 rpm has the lowest BSFC with 42% reduction when compared with B0.

3.4.6 Flue gas temperature (deg. C)

In the low temperature combustion region the exhaust temperature is critical even for diesel fuel due to its negative effects on turbocharger performance, so the lower exhaust temperature observed for neat biodiesel could be an important drawback for its applicability in future diesel engines.

Figure 6 shows the flue gas temperature variation with the blends ratio. B20 has the lowest at the speed range of 800-1000 rpm. B10 at the speed ranges of 1000-1200 rpm and 1200-1400 rpm has the highest flue gas temperature as well as B20 at 1000-1200 rpm and B100 at 1200-1400 rpm, respectively. This is due to lower cetane number and higher ignition delay of the blend [23]. Hence, the highest flue gas temperature was found at 1000-1200 rpm for B10, B20 and B100 with 12% increase.

3.4.7 Brake thermal efficiency (BTE)

BTE is the ratio of output to that of input energy in the form of fuel. It gives the efficiency with which the chemical energy of fuel is converted into mechanical work. It shows that all chemical energy of fuel is not converted to heat energy. The fuel efficiency tend to peak at higher engine speeds [24].

Figure 7 therefore shows the BTE variation with the blends at various speed ranges. The BTE decreases as the blend ratio increases at all speed ranges. However, B100 at speed range of 800-1000 rpm has the lowest BTE with 23% reduction when compared with B0 at the same speed range. B50 has the highest BTE at the speed range 1200-1400 rpm, these shows 45% increased in the BTE when compared with B0.

4. Conclusion

The results obtained in this study revealed that *Hura crepitans* oil is a good candidate for HCME production. Two steps production processes influenced the high yield of HCME. Three possible experimental runs were performed in each step, the best of the operating conditions were 1.45 (% v/v) for H_2SO_4 conc., 5:1 for Methanol/oil molar ratio, 40 min Reaction time which gave 1.06 % for FFA in the first step, in the second step, 92.70 %(w/w) of HCME at 0.55% KOH, 5:1 methanol/oil molar ratio, 60 ^{o}C temperature and 30 min reaction time was achieved.

The produced HCME had fuel properties which satisfied both ASTME D6751 and EN 1424 standards. Emission assessment revealed 60% decreased in CO, 58% decreased in NOx, 60% decreased in HC, 39% decrease in smoke opacity and 42% decreased in BSFC at B20, respectively. Flue gas temperature increased by 12% at B20. Meanwhile, there is 45% increased in BTE at B50.

Table 1: Pretreatment process - Acid catalyzed esterification

Variables	Values		
H_2SO_4 conc. (% v/v)	1.30	1.45	1.60
Methanol/oil molar ratio	4	5	6
Reaction time (min)	30	40	50
Titrimetric acid values (mg KOH/ g oil)	3.20	2.11	2.54
% FFA	1.60	1.06	1.27

Table 2: Alkalis catalyzed transesterification process

KOH (%)	Methanol/oil molar ratio	Reaction temp. (^{o}C)	Reaction time (min)	HCME yield % (w/w)
0.55	5:1	60	30	92.40
0.55	5: 1	60	30	92.50
0.55	5:1	60	30	92.70

Table 3: Properties of *Hura crepitans* (Sandbox) oil and HCME Comparison to Biodiesel Specification

Parameters	Hura crepitans oil (sandbox)	HCME	ASTM D6751	EN 14214
Physical properties				

	Golden yellow	Light yellow		
Colour	Golden yellow	Light yellow		
Moisture content %	0.40 ± 0.001	0.001 ± 0.001	0.05 max	0.02
Specific gravity	0.930 ± 0.01	0.860 ± 0.015	0.86-0.90	0.85
Viscosity (mm^2/s) at 40°C	6.32 ± 0.01	2.78 ± 0.02	1.9-6.0	3.5-5.0
Density (g/cm^3) at 25°C	1.42 ± 0.01	0.92 ± 0.02	0.84	0.86-0.90
Chemical properties				
Iodine value (g I$_2$/100g)	125.90 ± 0.10	116.40 ± 1.40	-	120 max
Acid value (mg KOH/g oil)	4.22 ± 0.10	2.34 ± 0.15	< 0.80	0.5 max
%FFA (as oleic acid)	2.11 ± 0.01	1.17 ± 0.02	-	-
Saponification value (Mg KOH/g oil)	201.60 ± 0.50	180.20 ± 0.10	-	-
Peroxide value	3.04 ± 0.10	2.48 ± 0.10	-	-
Other properties				
Cloud point ^{o}C	-	8.00	6	12 max
Flash point ^{o}C	-	112.00	100 min	>120
Pour point ^{o}C	-	-14.00	- 15	-
Diesel index	48.68 ± 0.20	56.11 ± 0.11	50.40	-
API	20.65 ± 0.14	33. 03 ± 0.40	36.95	-
Mean molecular mass	277.78 ± 1.60	310.77 ± 1.45		
Cetane number	45.05 ± 4.80	50.40 ± 1.20	47 min	51 min
HHV (MJ/kg)	39.28 ± 0.30	40.30 ± 010	-	-
Aniline point	235.74 ± 0.13	169.88 ± 0.50	331.00	-

values are means of triplicate determination ± standard deviation of mean

Table 4: Fatty Acids Compositions of the *Hura crepitans* (Sandbox) oil and HCME Produced

Parameters	Compositions %	
	Oil	HCME
Palmitic acid (C16:0)	16.01	12.70
Stearic acids (C18:0)	3.10	1.74
Oleic acids (C18:1)	20.31	17.54
Linoleic acids (C18:2)	58.52	64.50
Linolenic acid (C18:3)	1.60	3.50
Other	0.46	0.02
Total	100	100

Table 5: Engine specifications

| Parameter	Specification
Type of engine	Single cylinder
Engine brand name	165F, Direct injection, four-stroke, Internal Combustion Engine.
Stroke length	0.11 m
Bore and stroke	87.5 mm x 110 mm
Cooling method	Air
Injector operating pressure	200 bar/ 23 ^{o}C BTDC
Dynamometer current	Eddy current
Compression ratio	16.5:1
Response time	4 micro seconds
Rated speed	2600 rpm
Resolution in 1 degree	360 degree encoder with a resolution of 1
Rated power	3.2 kW
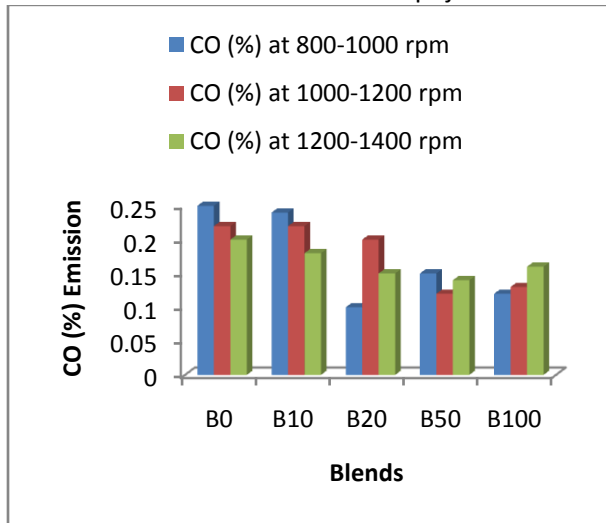
Figure 1: CO emission vs. blends
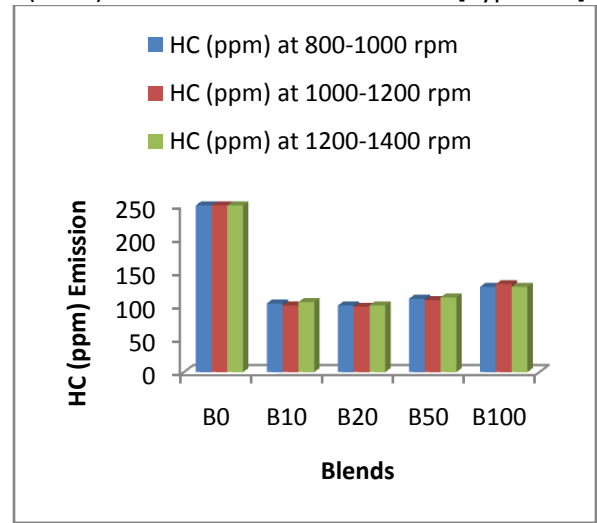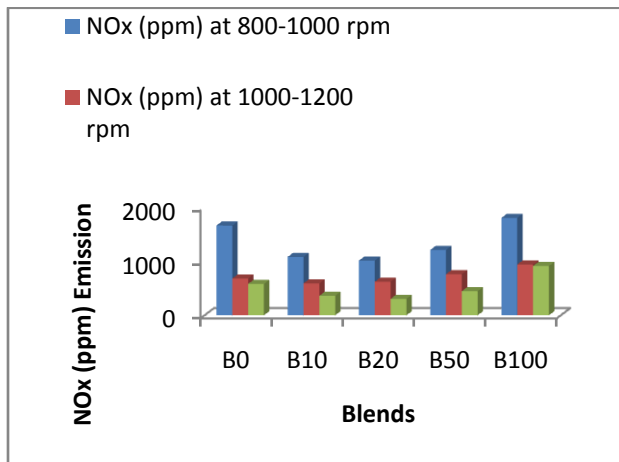

Figure 3: HC emission vs. blends

Figure 2: NOx emission vs. blends
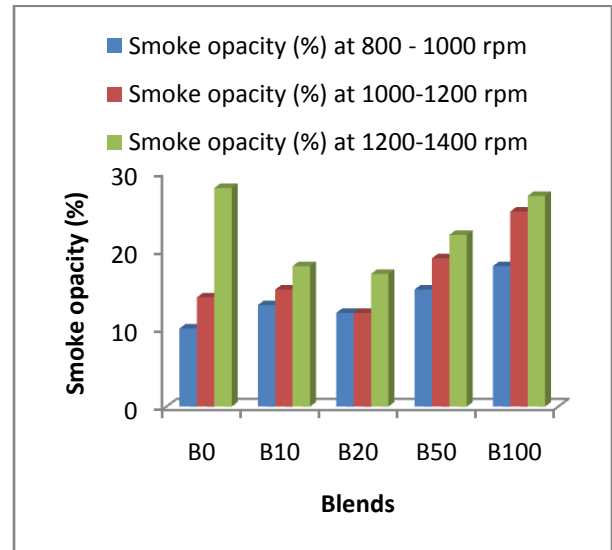
Figure 4: Smoke opacity vs. blends
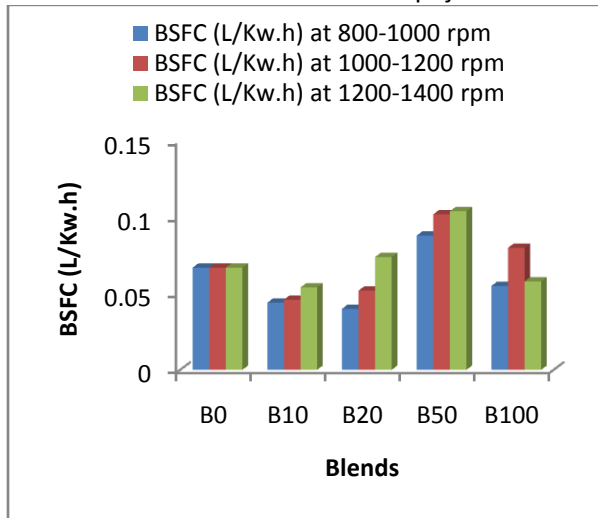
Figure 5: BSFC vs. blends
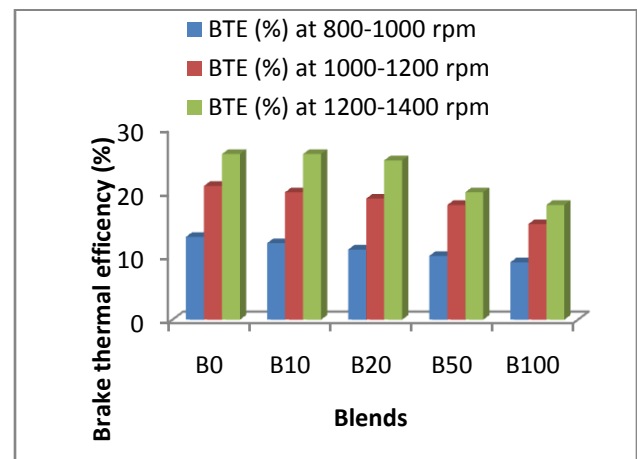

Figure 7: Brake thermal efficiency vs. blends

Figure 6: Flue gas temperature vs. blends

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